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Assessment of human health and environmental risks for water resource recovery-based bio-composite materials

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Dissertation

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CONTENTS

LIST OF ABBREVIATIONS

AFS: Atomic Fluorescence Spectroscopy

AI: Accumulation Index

ASR: Automobile Shredder Residue

BMC: Bulk Moulding Compound

BOD: Biological Oxygen Demand

CCDF: Complementary Cumulative Distribution Function

CDF: Cumulative Density Function

CDI: Chronic Daily Intake

CECs: Contaminants of Emerging Concerns

CR: Cancer Risk

CRI: Cancer Risk Index

DALY: Disability Adjusted Life Years

DI: Deionized water

DSLT: Dynamic Surface Leaching Test

DWTPs: Drinking Water Treatment Plants

DWR: Wind Driven Rain

DWTL: Drinking Water Target Level

DWS: Drinking Water Safety

ECHA: European Chemical Agency

ERA: Environmental Risk Assessment

ETA: Event Tree Analysis

FMEA: Failure Mode Effects Analysis

FMECA: Failure Mode Effects Criticality Analysis

F-N: Frequency - Number

FTA: Fault Tree Analysis

GAC: Granular Activated Carbon

GC-MS: Gas chromatography - Mass spectrometry

GIABS: Gastro-Intestinal Absorption Factors

HAZOP: Hazard & Operability

HI: Hazard Index

HMPI: Heavy Metal Pollution Index

HPLC-UV: High-Performance Liquid Chromatography

HQ: Hazard Quotient

HRI: Health Risk Index

ICP-MS: Inductively Coupled Plasma Mass Spectrometry

IWSQUI: Irrigation Water Security Quality-based Index

KNMI: Koninklijk Nederlands Meteorologisch Instituut

PEC: Predicted Effects Concentration

PFAS: Per-and Polyfluoroalkyl Substances

PNEC: Predicted No-Effects Concentration

POP: Persistent Organic Pollution

PPE: Personal Protective Equipment

PDF: Probability Density Function

QMRA: Quantitative Microbial Risk Assessment

QCRA: Quantitative Chemical Risk Assessment

QMEA: Quantitative Microbial Environmental Assessment

RAC: Risk Assessment Code

RfC: Reference Allowed Concentration

RfD: Reference Allowed Dose

RH: Relative Humidity

RIVM: Dutch National Institute for Public Health and the Environment

RPN: Risk Priority Number

RQ: Risk Quotient

SDG: Sustainable Development Goal

SF: Slope Factor

SMRA: System Modelled Risk Analysis

TE: Top Event

USL: Current Process Control

USEPA: US Environmental Agency

VOCs: Volatile Organic Compounds

WHO: World Health Organization

WSP: Water Safety Plan

WWTPS: Wastewater Treatment Plants

SUMMARY

The necessity for sustainable industrial processes and solutions has been intensified by climate change, which has led to an increased focus on enhancing resource efficiency and reducing greenhouse gas emissions. In accordance with the principles of the circular economy, the implementation of improved water-smart solutions and enhanced water management processes, including the reuse and recycling of wastewater and the recovery of resources such as water, energy and nutrients, represents a pivotal strategy for addressing challenges such as climate change and water pollution.

This dissertation examines novel bio-composite materials derived from resources recovered from the water sector. These materials incorporate natural fibres derived from untreated wastewater (i.e., cellulose fibres) or surface water management (i.e., reed and grass fibres), as well as fillers such as calcite derived from drinking water softening processes or agricultural waste (i.e., coconut shells, olive powder, and food residue). Bio-based resins, such as polyester with a reduced styrene content or furan resin, containing furfuryl alcohol, serve as binders.

The presence of a wide range of pollutants has a significant impact on water resources as a result of human activities. It is therefore imperative that comprehensive testing is conducted to ensure that the utilisation of recovered resources does not result in any adverse effects on human health or the environment. It is crucial to emphasise that, because of their derivation from recycled raw materials, the utilisation of the novel bio-composite materials should not be assumed to be intrinsically risk-free. It is therefore imperative that a comprehensive risk assessment of the environmental and human health risks associated with the production and application of the new bio-composite materials is conducted.

The overall aim of this research project is to develop an approach for the evaluation of potential risks to human health and the environment that may result from the production and application of the new bio-composite materials. In line with this, four research questions have been formulated to conduct this study:

1. What are the main risks and related hazards associated with the production of new resource recovery-based bio-composite materials and their applications and how are these interlinked? What existing methods can be potentially used (and with what modifications) and which new ones need to be developed to assess these risks?

2. What is the best approach to define and quantify the human health risks involved in the production of bio-composite materials?

3. What is the environmental risk associated with the use of the new bio-composite materials in the aquatic environment? More specifically, what is the risk in case of canal bank protection elements made from these new materials?

4. What is the environmental risk associated with the use of new bio-composite materials based building façade elements and how does the weathering of these elements affect this risk?

Above research questions have been addressed and answered in Chapters 2 – 5 of this dissertation. Below, a summary of the work done in order to address the formulated research questions is provided.

A comprehensive literature review, detailed in Chapter 2, was conducted at the outset of this work to identify the principal hazards and associated risks involved in drinking water and wastewater treatment plants, water reuse, and water-based resources recovery. The literature study identified potential microbial and chemical contaminants of the raw materials used to produce the new water-based resource recovery bio-composite materials. These contaminants may pose a risk to human health and the environment. Nevertheless, it was found that no risk assessment methodologies have yet been used to assess the potential human health and environmental risks associated with the production and application of the new bio-composite materials.

The novel human health risk assessment framework, which is described in Chapter 3, employed a qualitative risk analysis as the initial step, followed by a quantitative risk analysis. The Hazard and Operability (HAZOP) method identified the principal hazards during the production, and the qualitative Event Tree Analysis (ETA) methodology created a corresponding risk map. The results of the qualitative risk assessment indicated that the main risks of new bio-composite materials are caused by chemical and microbial contamination, which can have a negative impact on human health and the environment. A quantitative human health risk assessment was conducted on four alternative new bio-composite materials, employing both Quantitative Chemical Risk Assessment (QCRA) and Quantitative Microbial Risk Assessment (QMRA) methodologies, with deterministic and stochastic approaches. The results of the chemical risk assessment indicated that the cancer risk from styrene and furfuryl alcohol exceeded the established safety threshold. Similarly, the microbial risk assessment identified significant concerns with *E. coli* in cellulose fibres, with the risk exceeding safety limit. The assessments were conducted under the most unfavourable circumstances, without the use of personal protective equipment (PPE) or safety protocols. Furthermore, the assumption of maximum exposure to contaminants was made due to the limited availability of input data, which resulted in an overestimation of the overall risk.

The presence of chemical contamination in raw materials used for the production of new bio-composite materials gave rise to concerns not only for human health but also for potential negative environmental impact. In order to assess the environmental risks involved, two applications of these new materials were considered in this study: (a) canal bank protection elements, which prevents soil from collapsing into the water and (b) façade building elements as decorations panels.

To assess the environmental risks of chemical release, from the bio-composite materials used as canal bank protection, laboratory column leaching tests were conducted. This preliminary step provided data for an approximate environmental risk assessment in real-world conditions. The environmental risk assessment framework, developed in accordance with European guidelines, as detailed in Chapter 4, showed that the concentration of chemicals leached into surface water was within safety threshold. However, styrene and furfuryl alcohol contained in the resins may still pose a concern to environmental risk. It is crucial to acknowledge that the interpretation of these results should be approached with caution, given the absence of on-site data and the numerous assumptions made, including instantaneous mixing of the leaching chemicals and the absence of Brownian motion. Furthermore, the background concentrations in freshwater and the fate and degradation of chemicals in surface water were not considered. Also, the leaching process was evaluated over time, with the observation of a plateau indicating a significant slowdown in the leaching process accompanied by a reduction in the driving force, thereby providing a better understanding of the leaching behaviour.

Bio-composite materials utilised as façade construction elements are more susceptible to adverse weather conditions than those used for canal bank protection. Chapter 5 presents an analysis of potential leaching from bio-composites on a real-world building of a pumping station in the Netherlands. Two bio-composite alternatives were tested, and two samples per material were used: one new sample (as the initial application) and one UV-treated sample (as the long-term application after weathering) per material, for a total of four samples. The samples were subjected to leaching tests simulating two rainfall events of a duration of one hour. The risk assessment demonstrated that no leached chemicals exceeded the safety threshold, with no detection of styrene or furfuryl alcohol in the leaching effluent samples. However, these findings should be interpreted with caution due to the limited input data and the assumptions made, including the lack of on-site data and the focus on a single rain event rather than analysing leaching over a longer time period. The weathering treatments affected the materials in different ways based on their resin composition. Material M3 (made of polyester resin) exhibited

aesthetic changes, while Material M4 (made of furan resin) demonstrated increased roughness, reduced water resistance and fibre detachment. Microscopic examination revealed significant wrinkling in M4, indicating that environmental exposure significantly affects these materials.

Overall, it can be concluded (Chapter 6) that both microbial and chemical risks are inherent in the production and applications of new bio-composite materials considered in this thesis. These risks originate from the utilization of specific raw materials, including calcite from drinking water, cellulose derived from wastewater, reed and grass sourced from surface water management conducted by water boards, as well as the resins and additives employed in new materials. The framework developed in this research, which includes laboratory testing, modelling and risk assessment methods, has been validated as applicable to the case studies used in this work. Being generic in nature, the framework also shows potential for human health and environmental risk assessments associated with different future applications of new bio-composite materials.

SAMENVATTING

De noodzaak voor duurzame industriële processen en oplossingen is versterkt door klimaatverandering, wat heeft geleid tot een grotere focus op het efficiënter gebruik van hulpbronnen en het terugdringen van de uitstoot van broeikasgassen. "Water smart" oplossingen en verbeterde waterbeheerprocessen, inclusief het hergebruik en recyclen van afvalwater en het terugwinnen van hulpbronnen zoals water, energie en voedingsstoffen, is een cruciale strategie voor het aanpakken van uitdagingen als klimaatverandering en watervervuiling.

In dit proefschrift worden nieuwe bio-composiet materialen onderzocht die zijn gemaakt van uit de watersector teruggewonnen grondstoffen. Deze materialen bevatten natuurlijke vezels afkomstig van onbehandeld afvalwater (cellulosevezels) of oppervlaktewaterbeheer (riet - en grasvezels), evenals vulstoffen zoals calciet afkomstig van onthardingsprocessen in de drinkwaterproductie, en agrarisch afval (kokosnootschalen, olijfpoeder, en voedselresten). Harsen met bio-based bestanddelen, zoals polyester met een verlaagd styreengehalte en furaanhars met furfurylalcoholgehalte, dienen als bindmiddel.

Menselijke activiteiten hebben een aanzienlijke impact op waterbronnen door de introductie van een breed scala aan verontreinigende stoffen. Het gebruik van teruggewonnen hulpbronnen vereist daarom uitgebreide testen om de kans op schadelijke effecten op de volksgezondheid en het milieu te minimaliseren. Belangrijk is om op te merken dat het gebruik van bio-composiet materialen, omdat ze zijn afgeleid van gerecyclede grondstoffen, niet als risicovrij mag worden beschouwd. Een uitgebreide beoordeling van de risico's voor het milieu en de menselijke gezondheid in relatie tot de productie en het gebruik van nieuwe bio-composiet materialen moet daarom gedaan worden.

Het algemene doel van dit onderzoeksproject is het ontwikkelen van een methodologie voor de evaluatie van potentiële risico's voor de menselijke gezondheid en het milieu die kunnen voortvloeien uit de productie en toepassing van de nieuwe bio-composiet materialen. In lijn hiermee zijn er vier onderzoeksvragen geformuleerd om dit onderzoek uit te voeren:

1. Wat zijn de belangrijkste risico's en gerelateerde gevaren samenhangend met de productie van nieuwe, op grondstoffenterugwinning gebaseerde bio-composiet materialen en hun toepassingen, en hoe hangen deze met elkaar samen? Welke bestaande methoden

kunnen worden gebruikt (en met welke aanpassingen), en welke moeten worden ontwikkeld om deze risico's te beoordelen?

2. Wat is de beste aanpak om de risico's voor de menselijke gezondheid bij de productie van bio-composiet materialen te definiëren en te kwantificeren?

3. Wat is het milieurisico van het gebruik van nieuwe bio-composiet materialen in het aquatisch milieu? Meer specifiek, wat is dit risico in het geval van oeverbeschermingselementen die met deze nieuwe materialen zijn gemaakt?

4. Wat is het milieurisico van het gebruik van gevelelementen op basis bio-composiet materialen en hoe beïnvloedt de verwering van deze elementen dit risico?

Bovenstaande onderzoeksvragen zijn behandeld en beantwoord in de hoofdstukken 2 – 5 van dit proefschrift. Hieronder volgt een samenvatting van het werk dat is gedaan om de geformuleerde onderzoeksvragen te beantwoorden.

Het werk is gestart met een literatuuronderzoek, beschreven in hoofdstuk 2 van dit proefschrift, om de belangrijkste gevaren en bijbehorende risico's van drinkwater- en afvalwaterzuivering, hergebruik van water en terugwinning van waterbronnen te identificeren. De literatuurstudie identificeerde mogelijke microbiële en chemische contaminanten in de grondstoffen die gebruikt worden om de nieuwe bio-composiet materialen te produceren. Deze contaminanten kunnen een risico vormen voor de menselijke gezondheid en het natuurlijke milieu. Desondanks bleek dat er nog geen risicobeoordelingsmethodologieën zijn gebruikt om de potentiële risico's voor de menselijke gezondheid en het milieu samenhangend met de productie en toepassing van de nieuwe bio-composiet materialen te kwantificeren.

Het nieuwe beoordelingskader voor risico's voor de menselijke gezondheid dat in hoofdstuk 3 van dit proefschrift wordt beschreven, gebruikte kwalitatieve risicoanalyse als eerste stap, gevolgd door kwantitatieve risicoanalyse. De Hazard and Operability (HAZOP)-method identificeerde de belangrijkste gevaren tijdens de productie en de kwalitatieve Event Tree Analysis (ETA)-method creëerde de bijbehorende risicokaart. De resultaten van de kwalitatieve risicobeoordeling gaven aan dat de belangrijkste risico's van nieuwe bio-composiet materialen veroorzaakt worden door chemische en microbiële verontreinigingen, die een negatieve invloed kunnen hebben op de menselijke gezondheid en het milieu. Er werd een kwantitatieve risicobeoordeling voor de menselijke gezondheid uitgevoerd voor vier alternatieven van nieuwe bio-composiet materialen waarbij gebruik werd gemaakt van zowel kwantitatieve chemische risicobeoordeling (quantitative chemical risk assessment, QCRA) als kwantitatieve microbiële risicobeoordeling (quantitative microbial risk assessment, QMRA) met deterministische en stochastische benaderingen.

De resultaten van de chemische risicobeoordeling toonden een verhoogd risico op kanker aan ten gevolge van overschrijding van de vastgestelde veiligheidsdrempels door styreen en furfurylalcohol . Ook de microbiële risicobeoordeling wees op een ernstig probleem als gevolg van E. coli in de cellulosevezels, waarbij de veiligheidsdrempel eveneens werd overschreden. Deze beoordelingen werden uitgevoerd op basis van worst-case scenario's, waarbij werd aangenomen dat er geen persoonlijke beschermingsmiddelen (PBM) of veiligheidsprotocollen werden gebruikt. Als gevolg van beperkte invoergegevens werd in de analyse uitgegaan van maximale blootstellingsniveaus aan chemische en microbiële verontreinigingen, wat leidde tot een overschatting van het algehele risico.

De aanwezigheid van chemische verontreiniging in grondstoffen die worden gebruikt voor de productie van nieuwe bio-composiet materialen leidde niet alleen tot zorgen over de menselijke gezondheid, maar ook over mogelijke negatieve milieueffecten. Om de milieurisico's te beoordelen werden in deze studie twee toepassingen van de nieuwe materialen onderzocht: (a) oeverbeschermingselementen voor kanalen, die voorkomen dat grond in het water stort, en (b) gevelelementen.

Om de milieurisico's van het vrijkomen van chemische stoffen uit het bio-composietmateriaal gebruikt als oeverbescherming te beoordelen, werden laboratorium kolomuitloogtesten uitgevoerd. Dit werd gedaan als een voorbereidende stap om de invoergegevens te verkrijgen die gebruikt kunnen worden voor een model-gebaseerde milieurisicobeoordeling in een echte situatie. Europese richtlijnen voor milieurisicobeoordeling werden gebruikt voor het ontwikkelen van het kader voor milieurisicobeoordeling, zoals beschreven in hoofdstuk 4. Uit de analyse van vier bio-composiet materialen die worden gebruikt voor oeverbescherming bleek dat de concentraties van alle uitgeloogde chemicaliën binnen de veiligheidsdrempels vielen. De aanwezigheid van styreen en furfurylalcohol in de harsen vormt echter een potentieel risico voor het milieu. Deze bevindingen moeten met de nodige voorzichtigheid geïnterpreteerd worden vanwege het ontbreken van velddata als invoergegevens, waardoor verschillende aannames nodig waren tijdens de beoordeling. Deze omvatten de aanname van instantane menging van uitgeloogde chemicaliën en de afwezigheid van Brownse beweging. Bovendien is er geen rekening gehouden met achtergrondconcentraties in het zoete water, het lot van chemische stoffen in oppervlaktewater, en mogelijke afbraak. Bovendien werd het uitloogproces in de loop van de tijd geëvalueerd, waarbij een plateau werd waargenomen dat duidt op een aanzienlijke vertraging van het uitloogproces, resulterend in een vermindering van de drijvende kracht.

Bio-composiet materialen die gebruikt worden als gevelelementen zijn gevoeliger voor slechte weersomstandigheden dan de materialen die gebruikt worden als oeverbescherming. De analyse van mogelijke uitloging van gevaarlijke stoffen uit deze elementen toegepast op een echt gebouw, een pompstation in Nederland, is beschreven in hoofdstuk 5. Gevelelementen van twee verschillende bio-composiet materialen werden getest in het laboratorium, en er werden twee monsters per materiaal gebruikt: één nieuw monster (als de initiële toepassing) en één met UV-straling behandeld monster (als de lange termijn toepassing na verwering) per materiaal, in totaal vier monsters. De monsters werden in het laboratorium getest door twee regenbuien van verschillende intensiteit en dezelfde duur van een uur te simuleren. De analyse van twee bio-composiet materialen die gebruikt worden in gevelelementen toonde aan dat de concentraties van alle uitgeloogde chemicaliën binnen aanvaardbare veiligheidsdrempels vielen, zonder detectie van styreen en furfurylalcohol in de uitgeloogde effluentmonsters. Toch moeten deze bevindingen met voorzichtigheid geïnterpreteerd worden vanwege de beperkte invoergegevens en de gemaakte aannames, waaronder het gebrek aan velddata en de focus op een enkele regenbui in plaats van een analyse van de uitloging over een langere periode. De verweringsbehandelingen hadden een verschillend effect op de materialen, afhankelijk van de gebruikte hars in het materiaal. Materiaal M3 (polyesterhars) vertoonde esthetische veranderingen, terwijl materiaal M4 (furaanhars) een verhoogde ruwheid, verminderde waterbestendigheid en vezelafscheiding vertoonde. Microscopisch onderzoek onthulde aanzienlijke rimpeling in M4, wat aangeeft dat blootstelling aan de omgeving een aanzienlijke invloed heeft op deze materialen.

Uit het onderzoek kan worden geconcludeerd (hoofdstuk 6) dat zowel microbiële als chemische risico's inherent zijn aan de productieprocessen en toepassingen van nieuwe bio-composiet materialen die in dit proefschrift werden bekeken. Deze risico's ontstaan door het gebruik van specifieke grondstoffen, waaronder calciet uit drinkwater, cellulose uit afvalwater, riet en gras afkomstig uit oppervlaktewaterbeheer uitgevoerd door waterschappen, en de harsen en additieven die in nieuwe materialen worden gebruikt. Het in dit onderzoek ontwikkelde raamwerk, dat laboratoriumtesten, modellering en risicobeoordelingsmethoden omvat, is gevalideerd als zijnde toepasbaar op de in dit werk gebruikte biocomposietmateriaal toepassingen. Omdat het raamwerk generiek van aard is, toont het ook potentieel voor risicobeoordelingen voor de menselijke gezondheid en het milieu met betrekking tot verschillende toekomstige toepassingen van nieuwe bio-composiet materialen.

1

INTRODUCTION

1

1.1. OVERVIEW

At present, there is a growing interest in developing water-smart solutions that enhance sustainability, resource efficiency and reduce greenhouse gas emissions. They are grounded in the principles of the circular economy, which emphasizes reusing and recycling resources to minimize waste and environmental impact. This aligns with the United Nation's sustainable development goals 6 and 12 (SDG) [1], in which innovative approaches to water management and conservation are mentioned as specific goals to meet contemporary challenges such as climate change and water pollution.
The water sector is in the middle of a transformation. It is no longer solely concerned with managing and supplying water, but also with reclaiming valuable substances from it. Today, the wastewater treatment industry utilises advanced technology to capture and reuse a range of resources, including energy, nutrients, metals, and organic compounds [2]. Additionally, the drinking water industry employs the recovery of valuable materials from the drinking water processes [3, 4]. There is a growing interest in the value of various materials found in water. This interest is driven by a focus on sustainable and circular water use. Various resources can be recovered from water and reused in multiple ways. In this thesis the focus is on resources recovered from drinking water, wastewater, and surface water management for the production of a new type of bio-composite material, which can be used in the construction sector. Bio-composite materials are a promising frontier in sustainable water treatment, derived from resources recovered from the water cycle.

1.2. BIO-COMPOSITE MATERIALS

Composite materials are composed of a combination of different materials, including glass fibres or carbon, which serve as reinforcement agents, and a matrix structure, which is typically a thermoset or thermoplastic resin, such as polyester or epoxy resin [5]. However, these composite materials, as well as petroleum-based polymers, are recently not considered the best option anymore in terms of environmental impact. The main common composite materials made from petroleum-based polymers are highly valued for their strength, flexibility, and chemical resistance. However, the growing issue of disposing of these polymers has become a pressing concern for society. Scientists estimate that a plastic bag could take up to 500 years to decompose [6]. This highlights the long-term environmental impact of such materials. There are additional concerns regarding the environmental impact of producing and disposing of these products, including their contribution to global warming and potential toxicity risks [6]. Thus, research lead to bio-composite materials made from natural, renewable, and fully biodegradable sources [7]. Bio-composite materials (or green composites) are generally composed of a matrix (resin) and reinforced with plant fibers, mostly cellulose fibres from crops or waste paper [8]. In order to enhance the performance that might not otherwise be achieved by the reinforcement and resin ingredients alone, a filler is employed to improve mechanical properties [9]. These materials have received significant research attention due to the need to innovate to conserve fossil-based resources and to reduce carbon dioxide emissions into the environment.

1.2.1. NEW WATER RESOURCE RECOVERY-BASED BIO-COMPOSITE MATERIALS

New bio-composite materials have been developed in the Netherlands, which use residuals from water treatment systems. These innovative materials are made from natural fibers, such as cellulose derived from untreated wastewater or reed fibers harvested during surface water management. Additionally, calcite, a by-product of the drinking water softening process, is used as a filler alongside bio-fillers sourced from agricultural waste, such as coconut shells, olive powder, food residue, etc. The material's structural integrity is achieved by binding fibers and fillers with resins, including polyester or furan resins, which can contain bio-based constituents. Polyester resin with bio-based content is characterized by reduced styrene content, approximately 35%, compared to the 50% found in conventional unsaturated polyester resins. Another option for a binding agent is furan resin, which is also bio-based and notable for its higher concentration of furfuryl alcohol, a volatile substance. This development represents progress in material science and highlights a sustainable approach to waste utilization and environmental sustainability. Four alternatives of the new bio-composite materials are object of this study. The alternatives are described in 1.1.

Table 1.1.: Composition of bio-composite materials analysed in this dissertation.

Materials	M1	M2	M3	M4
Natural fibers	Reeds	Reeds	Wastewater cellulose	Grass
Filler	Mined calcite	Calcite[1]	Calcite	Bio-filler from agricultural waste
Resin	Polyester resin	Polyester resin with bio-based content	Polyester resin with bio-based content	Furan resin
Additives	Additives[2]	Additives	Additives	Additives

[1]Calcite: This study analyses bio-composite samples that consist of a blend of calcite obtained from mining operations and recovered from drinking water softening. Some samples use only calcite reclaimed from drinking water softening. The following chapters of this thesis will systematically provide a comprehensive elaboration of

These novel materials find potential application in the water environment such as canal bank protection and water level scale, and in the construction field such as façade building elements. The new bio-composites represent a valid alternative for similar elements made of hardwood in case of canal bank protection and water level scale, and as an alternative for aluminium, ceramic, glass, and wood for construction elements.

1.2.2. POTENTIAL CONCERNS ABOUT THE USE OF RESOURCES RECOVERED FROM WATER TO PRODUCE THE NEW BIO-COMPOSITE MATERIALS

From drinking water treatment, more exactly from softening process, it is possible to recover calcite pellets [10], that will be used as a filler in the composite materials.

The softening process is part of the drinking water treatment process with the aim of reducing the total hardness of the water to a standard value of $1.00 - 1.5$ mmol/l [11]. The hardness of water is defined as the sum of calcium and magnesium ions present in the solution. The water influent into the softening process may be contaminated with heavy metals, including zinc, copper, cadmium, arsenic and nickel. Consequently, the calcite pellets recovered as a by-product of the softening process may be contaminated with these heavy metals, thereby reducing their potential for reuse in agriculture, for example, due to the toxicity of the metals [12].

In the context of natural fibres, cellulose can be recovered from toilet paper contained within wastewater. This can be achieved through the primary treatment of wastewater, which involves the use of a sieve with a fine mesh, or alternatively, through the use of activated sludge [13]. Sewage sludge is the residual, semi-solid material that is produced as a by-product during sewage treatment of industrial or municipal wastewater. The cellulose is recovered from sludge via the hydrolysis of the sludge sample and the application of autoclave treatment. As was the case with the calcite pellets, the quality of the source water where the raw materials are collected has a crucial role in the potential reuse of the recovered materials. Influent wastewater is contaminated with a variety of substances, including pathogens, heavy metals, residual drugs, and others. Consequently, the recovered cellulose fibres may also be contaminated. The same can be affirmed for surface water

these variations.

[2]Additives: used as catalyst to stimulate the chemical reaction (polymerization) of the resin, improve impact resistance (impact agents), release agents to prevent sticking to the mould and allow releasing the part (release agents). Zinc stearate was used as release agent for material M1, M2 and M3, olive pamoate was used as release agent for M4.

contamination, specifically chemical contamination, where the natural fibres can also be collected, such as grass and reeds. The fibres are collected from water boards using specific operating machines and in accordance with the protocols set out in the Flora and Fauna Law [14].
The collected raw materials are bonded together with a synthetic resin, such as polyester or furan resin, in order to produce the bio-composite products, as described in section 1.2.1.
The recovery and reuse of these resources may present concerns regarding the potential hazards of the recovery process, including exposure to chemical substances and/or microbial pathogens.

1.3. KNOWLEDGE GAPS AND RESEARCH QUESTIONS

In light of the considerations outlined in section 1.2.2, regarding potential microbial and chemical contamination of the raw materials used to produce the new type of bio-composite materials, it was identified that research was required to address the identified knowledge gaps. Each identified knowledge gap gives rise to a research question, which are detailed in this section.
A comprehensive literature review was conducted to evaluate the methodology of risk analysis on wastewater treatments and the processes of resource recovery from water. However, it is unclear how the new bio-composite materials can impact human health and the environment. Additionally, the available previous studies on bio-composite materials are related to a different material (made from plant resources). Accordingly, the first knowledge gap was identified in the novelty of these bio-composite materials. This has led to the finding that the existing health and environmental risk assessment tools have not yet been studied for their applicability on bio-composite materials. Therefore, it is challenging to determine the most suitable risk assessment methodology for identifying hazards and creating a map of the key risks involved in the production of bio-composite materials and their application. In light of the aforementioned initial knowledge gap, the first research question was formulated as follows:
Research question 1: *What are the main risks and related hazards associated with the production of new resource recovery-based bio-composite materials and their applications and how are these interlinked? What existing methods can be potentially used (and with what modifications) and which new ones need to be developed to assess these risks?*
The objective of this part of the research is to establish the most effective strategy for identifying key risks in the process of recovering and reusing raw materials from the water sector to produce new bio-composite materials. The evaluation covers the entire life cycle of these materials, from recovery to application, with the objective of understanding the

potential environmental and health hazards. The aim is to develop a comprehensive framework for the systematic identification, assessment, and management of hazards and related risks, with the aim of ensuring the safe and sustainable use of bio-composite materials in various applications.

A review of previous studies provides an overview of the functionality of wastewater treatment plants (WWTPs) and the main hazards and associated risks related to water treatment. In light of the aforementioned findings, a second research gap was identified, namely the uncertainty surrounding the quantification of these risks and their integration into the production process of bio-composite materials. Consequently, the necessity arises for the development of a novel framework for the assessment of the human health risks associated with the reuse and recovery of wastewater for the production of bio-composite materials and related end-use products. This leads to the second research question:

Research question 2: *What is the best approach to define and quantify the human health risks involved in the production of bio-composite materials?*

The goal for addressing this research question is to develop a new human health risk assessment framework that can be used to assess the human health risks associated with the production of water resource recovery-based bio-composite materials.

The presence of chemical contamination in raw materials, and consequently in bio-composite materials, as confirmed by human health risk assessment, gives rise to concerns regarding not only human health but also the potential environmental impact. This is particularly pertinent when considering their application in the context of canal bank protection, which prevents soil from collapsing into the water. A common alternative to bio-composite materials is traditional materials, which are typically made from hardwood. This leads to the third identified knowledge gap, namely the absence of a comprehensive environmental risk assessment for these new bio-composite materials in this application. In light of the aforementioned considerations, the third research question was as follows:

Research question 3: *What is the environmental risk associated with the utilisation of novel bio-composite materials in aquatic environments? In particular, what is the associated risk in the context of the use of canal bank protection elements made from these new materials?*

The research objective, within the scope of the identified knowledge gap and corresponding research question, is to investigate the applicability of the novel materials for canal bank protection and to evaluate the potential risks of water pollution associated with these materials.

A different scenario emerges when the new bio-composite materials are used as façade building elements, which leads to the last identified knowledge gap of this research. Extended exposure to environmental factors such as sunlight, rain, snow, and wind may result in the deterioration of the material quality, potentially leading to environmental concerns due to the potential release of pollutants. In this case, as well, a systematic methodology for assessing environmental risk is of the utmost importance. However, such a framework is notably lacking. In accordance with the aforementioned considerations, the fourth research question was as follows:

Research question 4: *What is the environmental risk associated with using new bio-composite materials as building façade elements and how does the weathering of these elements affect this risk?*

The objective of this final research question is to assess the suitability of these novel materials as construction elements, with a particular focus on the impact of weathering on chemical leaching and the subsequent environmental impact on surface water.

1.4. DISSERTATION OBJECTIVES AND OUTLINE

Having identified the principal knowledge gaps, the overall aim of this research project is to develop an approach for the evaluation of potential risks to human health and the environment that may result from the production and application of the new bio-composite materials. Table 1.2 provides an overview of the structure of this dissertation, indicating the knowledge gaps that have been identified and the research questions addressed in each chapter.

1

Table 1.2.: Dissertation outline.

Chapter	Knowledge Gap	Research Question	Specific Thesis Objective
Chapter 2: Risk Assessment methods for water resource recovery for the production of the bio-composite materials: Literature review and future research directions	The existing health and environmental risk assessment tools have not yet been studied for their applicability on bio-composite materials	What are the main risks and related hazards associated with the production of new resource recovery-based bio-composite materials and their applications and how are these interlinked? What existing methods can be potentially used (and with what modifications) and which new ones need to be developed to assess these risks?	The objective is to establish the most effective strategy for identifying key risks in the process of recovering and re-using raw materials from the water sector to produce new bio-composite materials
Chapter 3: Human Health Risk Assessment Framework for new water resource recovery-based bio-composite materials	Lack of human health risk assessment framework for producing the new bio-composite materials	What is the best approach to define and quantify the human health risks involved in the production of bio-composite materials?	The research goal is to develop a new human health risk assessment framework that can be used to assess the human health risks associated with the production of water resource recovery-based bio-composite materials
Chapter 4: Environmental Risk Assessment related to using resource recovery-based bio-composite materials in aquatic environment with new laboratory leaching test data	Lack of environmental risk assessment framework in using the new bio-composites as canal bank protection elements	What is the environmental risk associated with the utilisation of novel bio-composite materials in aquatic environments? In particular, what is the associated risk in the context of the use of canal bank protection elements made from these new materials?	The research objective is to investigate the applicability of the novel materials as canal bank protection and to evaluate the potential risks of water pollution associated with these materials

Table 1.2.: Dissertation outline (continued).

Chapter	Knowledge Gap	Research Question	Specific Thesis Objective
Chapter 5: Risk of Rainfall Caused Leaching from Bio-Composite Material based Building Façades into the Aquatic Environment	Lack of systematic methodology to assess environmental risk assessment for using these new materials as façade building elements	What is the environmental risk associated with using new bio-composite materials as building facade elements and how does the weathering of these elements affect this risk?	The objective is to examine the suitability of these new materials as construction elements, and in particular, how weathering affects chemical leaching and the resultant environmental impact on surface water
Chapter 6: Conclusions and outlook		Integrated answer to the research questions resulting in key findings	The objective is to discuss the implications of the research and to offer recommendations for future work

The identified knowledge gaps and the related research questions have been addressed in a systematic manner, with each gap and question being addressed in a separate chapter.

The first research question is addressed in Chapter 2, which provides a comprehensive literature review. The literature study examines previous studies and provides an overview of the main risks associated with wastewater and drinking water treatment plants, resource recovery and water reuse. The chapter evaluates the applicability of the risk assessment methodologies documented in the literature to the production of new bio-composite materials. The literature review provides a detailed description of the study of literature, which is an essential tool to begin with. This information can help in assessing the main expected risks involved in bio-composite production.

Chapter 3 presents a framework for the assessment of human health risk associated with the production process of bio-composite materials. The framework employs both qualitative and quantitative methodologies to assess human health risks, addressing the research question two. The chemical and microbial risk assessments are central to this framework, as they identify and characterize the principal health hazards associated with the production of bio-composite material. The study employed Quantitative Chemical Risk Assessment (QCRA) and Quantitative Microbial Risk Assessment (QMRA) using data on chemical and microbial contaminants in raw materials. Looking at the various applications of these new bio-composite materials, canal bank protection and façade building elements were selected as case studies of this research. The use of bio-composite materials has been identified as a potential source of concern with regards to chemical risk assessment and the potential for adverse environmental impact. Therefore, it is necessary to conduct a chemical risk assessment to address these environmental risks.

The third research question is addressed in Chapter 4, which presents the environmental risk assessment framework for evaluating the use of new bio-composites as canal bank protection elements. The framework employed column leaching tests to obtain input data for the evaluation of the potential release of chemicals into the aquatic environment and to evaluate the potential environmental risk under real-world conditions. The environmental risk assessment framework was conducted in accordance with European guidelines [15], employing both deterministic and stochastic approaches to assess the uncertainties associated with the lack of on-site data, including background concentrations of chemicals in the surface water and flow water velocity variation.

Chapter 5 continues with experimental work, which involves the selection of two bio-composite materials for use in building façade elements and their exposure to various rainfall intensities. Leaching tests were conducted on both new (i.e., initial application) and weathered (i.e., samples subjected to weathering conditions) bio-composite samples to assess the impact of ageing and degradation on leaching. The chapter concludes with an evaluation of a real-world scenario in which the bio-composite materials were used in façade elements of a pumping station and the environmental risks were determined. This chapter addresses the final research question of this dissertation.

At the end, Chapter 6 summarizes the key findings of this research and delineates its principal scientific contributions. Furthermore, the study discusses the implications of the research and offers recommendations for future work, setting the stage for subsequent investigations and the continued development of the field.

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2

RISK ASSESSMENT METHODS FOR WATER RESOURCE RECOVERY FOR THE PRODUCTION OF BIO-COMPOSITE MATERIALS: LITERATURE REVIEW AND FUTURE RESEARCH DIRECTIONS

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This chapter is based on: Nativio, A., Kapelan, Z., & van der Hoek, J. P. (2022). Risk assessment methods for water resource recovery for the production of bio-composite materials: Literature review and future research directions. Environ. Challenges 9, 100645. doi: 10.1016/j.envc.2022.100645 [1]

2

2.1. ABSTRACT

Bio-composite materials made from resources recovered from the water cycle are the future of the holistic approach towards sustainable wastewater treatment. The raw ingredients for these materials are coming from contaminated sources such as wastewater resources, water plants from surface water etc. Thus, different risks like human health, environmental and product quality risks need to be assessed. Existing literature was analysed regarding these risks, especially methods concerning the risk assessment in wastewater and drinking water treatment and water/wastewater-based resource recovery for reuse. The reviewed literature identified several risk assessment methods such as FMEA, FMECA, FTA, QMRA and QCRA as frequently used ones for these purposes. However, no dedicated methods were identified for the corresponding risk assessments related to bio-composite materials representing key knowledge gaps. The literature review also showed that the above identified risk assessment methods cannot be directly applied for bio-composite materials as many required input data are missing. To overcome above gaps, future research directions have been identified. These include use of qualitative risk assessment methods such as HAZOP and ETA to first identify hazards and map the risks. Once this is done, QMRA and QCRA could be used in combination with Monte Carlo analysis to assess the actual risks. However, before this can be done, additional work should be carried out to collect the missing data required for the use of these methods in the context of bio-composite materials. In addition, additional experimental work such as column leaching tests should be carried out to assess the environmental risks, in particular, looking at the release of toxic chemical compounds such as heavy metals in the aquatic environment. Finally, a list of quality requirements for bio-composite material and related products (e.g., requirements for mechanical properties, purity of raw materials, etc.) should be made, so that the related product quality risks can be assessed.

2.2. INTRODUCTION

New water smart solutions aiming at improved sustainability, increased resource efficiency, reduced greenhouse gas emissions and based on principles of circular economy are becoming popular and are increasingly developed [2, 3]. These include solutions based on various resources recovered from water and wastewater. For example, it is possible to reuse wastewater as a resource and produce energy [4, 5], bio-gas from sludge digestion [6] or recover raw materials such as bio-fertilizer, bio-plastic [7], nitrogen [7], phosphorus [8], struvite [4], cellulose [9] and calcite [10]. Recovery and reuse of resources from wastewater and water can also have a positive impact on the ecosystem hence providing benefits to both society and nature [2].

In terms of reducing negative environmental impact, bio-composite materials are becoming a sustainable alternative on the global market. Bio-composite materials are made from natural ingredients derived from sustainable resources [11] like natural fibres such as cellulose fibres from crops or waste paper and glued together with a matrix (resin). The use of bio-composite materials will reduce the negative environmental impact compared to the use of composite materials made from polymeric resin and synthetic fibres [12]. Therefore, these materials can be better alternatives to polymer composite materials made from synthetic fibres (non-renewable resources). Bio-composite materials have found their applications in the automotive, pharmaceutical and food industries [13, 14] so far.

Recently, a new type of bio-composite material, made from resources recovered from water and wastewater, is starting to be produced. The raw materials for this new material are recovered from the water cycle as follows: (i) calcite pellets recovered as residual product from the drinking water softening (i.e. treatment) process [10]; cellulose fibres collected from the toilet paper contained into untreated wastewater treatment and recovered through fine mesh sieving [9]; (iii) natural fibres recovered from grass, reeds and aquatic plants collected during surface water management. Once recovered, these raw materials are glued together with different types of resins. The mixed product is moulded using high pressure and temperature into a bio-composite material. A new material like the one described here can have multiple applications such as building construction elements for riverbank protection, creating nautical signs or elements for building facades.

Having said the above, surface water, raw drinking water and wastewater can be contaminated with pathogens and chemical compounds such as heavy metals, residual drugs, hormones, Persistent Organic Pollutants (POP) and agro-chemicals that can potentially make their way into the bio-composite material. It should be noted that environmental toxicity of chemical contaminants (listed above) should be evaluated based on the toxicity of degradation products detected in nature, rather than parent compounds. This applies to chemicals that undergo structural changes as a result of environmental factors. An example of this can be found in the recent study by Remy et al. [15], where the authors detected levels of chromium as high as 20 mg/kg in the cellulose fibres recovered from the wastewater, i.e. at the level that is ten times higher than the acceptable limits of 2 mg/kg [16]. If contaminated, the raw materials used to make a bio-composite material can result in several undesirable effects such as workers will be exposed to the pathogens and/or heavy metals during the bio-composite material production via ingestion, inhalation or dermal contact through the dust formed from raw materials. Contaminated raw materials can also pose a threat to the natural environment as these substances may be released into the environment, e.g., via leaching of heavy metals like arsenic, lead and chromium into the river and soil from the riverbank protection elements made using the aforementioned bio-composite material. Finally, the contaminated raw materials can also result in a lower quality in terms of mechanical properties of the produced bio-composite material.

Given above, it is necessary to assess the human health, environmental and other risks associated with the production and application of bio-composite materials made by resource recovery from the water cycle. For this purpose, relevant risk assessment methods, available in the published literature, were first summarised and analysed. This was done separately for the risks related to wastewater and drinking water treatment plants (section 2.3) and resource recovery and water reuse (section 2.4). The applicability of these methods for the production and application of bio-composite materials made by recovering resources from the water cycle is discussed in section 2.5. The resulting knowledge gaps are presented in section 2.6. Future research directions to address these gaps are provided in section 2.7. Finally, the key findings are summarised in section 2.8.

2.2.1. REVIEW SCOPE, OBJECTIVES, AND METHODOLOGY

This scientific review focused on previous studies in which risk assessment methodologies have been developed and illustrated on case studies concerning primarily wastewater and drinking water treatment, followed by cases on resource recovery and water/wastewater reuse. The aims of the literature review were as follows: (i) identify methodologies developed for assessing risks in **drinking water treatment** and **wastewater treatment**, and **water/wastewater reuse** and **resource recovery**; (ii) assess the applicability of these methodologies for reuse of resources collected from water to produce **bio-composite materials**; (iii) identify related **knowledge gaps**.

The literature research was performed using Google Scholar, TU Delft repository database and scopus. Concerning reports about standards, thresholds and methodologies, these were searched using U.S.E.P.A. and W.H.O. websites. Furthermore, technical reports were searched on the STOWA (Foundation for applied water research STOWA website).

Relevant papers were identified using keywords such as risk assessment methodologies, water sector, water treatments, and/or wastewater reuse, resource recovery from water, etc. A total of 19 papers were collected concerning wastewater and drinking water treatment and a total of 14 papers were collected for resource recovery and water reuse.

Once relevant papers were identified, these were critically analysed to first identify the types of risk assessment methods used. The identified methods are shown in section 2.3 and section 2.4, respectively for wastewater and drinking water treatment and for resource recovery and water reuse. It was decided to start with risk assessment methodologies applied on wastewater treatment plants (WWTPs) and drinking water treatment plants (DWTPs) as they represent the source water where the raw materials, of our bio-composites, are collected. Then the focus moved on the resource recovery processes and the reuse of water, to obtain an overview of the main potential issues that can be involved in the production of these new bio-composite materials.

The previous studies have been analysed critically and, in more details, to understand the specific aspects of these methods, and how well these methods have been tested/validated on real case studies. Previous studies were analysed and contextualized for the risk assessment methodology applied with the specific case study examined, availability of input data and exposure scenario. Furthermore, several studies were collected in which no risk assessment methodology was applied, but in where an explanation of the way in which raw materials could be recovered from the water sector was provided. These papers proved to be useful to understand what the main hazards and associated risks could be, in terms of human health and environment, during the collection of raw materials from different types of water, such as wastewater, raw drinking water and surface water. Thereafter, in section 2.4 the methodologies applied in the previous studies are analysed in terms of how they compare to each other, and how these methods can be used to contribute to the knowledge required for the assessment of various risks related to bio-composite materials and their products.

Once the review was completed, key gaps in knowledge were identified by means of further critical analyses and deduction based on the literature review carried out such as which type of methods have been applied in the past, which risks have been assessed so far and what it is missing in literature and why. All of this is compared and reported to the bio-composite case study.

The expected outcome of this review was to find one or more risk assessment methodologies applied in the water sector that can be applied or be adapted to risk assessment for the production and application of bio-composites. The focus was on risks to human health, the environment and water quality, but previous studies in which operational risks were assessed were also evaluated.

2.3. RISK ASSESSMENT IN WASTEWATER AND DRINKING WATER TREATMENT PLANTS

This section contains a review of previous studies in which risk assessment methodologies were developed for wastewater and drinking water treatment plants. Many authors have used similar risk assessment methods, as the main potential risks appear to be the same (presence of chemical and pathogens in source water). However, each study has important differences both in terms of the input data used, the risk receptors analysed, and finally in terms of the goal of the study. Therefore, it was decided to cite the same studies several times, as they were applied in different areas for different purposes. Table 2.1 lists previous studies collected on risk assessment methodologies applied to wastewater and drinking water treatment plants.

2.3.1. RISK ASSESSMENT IN WASTEWATER TREATMENT PLANTS

Wastewater treatment plants (WWTPs) are used to treat wastewater to meet the discharge standards for various applications such as discharge into surface water, direct or indirect water reuse, etc. Risk analysis in wastewater treatment plants is quite important to prevent possible incidents in the treatment processes, as incidents occurring in these plants strongly affect the efficiency and effectiveness of the system and the health of employees [17].

Evaluating previous studies on risk assessment methodologies applied on WWTPs allows the identification of the main risks involved during wastewater treatment and consequently to recover materials from wastewater like cellulose.

In this subsection the most relevant references concerning risk assessment methods used in WWTPs were analysed. The main risk assessment methods found in literature are as follows:

- FMEA: Failure Mode Effects Analysis.
- SMRA: System Modelled Risk Analysis.
- FTA: Fault Tree Analysis.
- Bow-Tie.
- QMRA: Quantitative Microbial Risk Assessment.
- HQ: Hazard Quotient.

The first four risk assessment methods were used focusing on operational risk assessment, however, in WWTPs, as well as DWTPs, there are also other type of risks. In fact, when looking at human health risks and natural environment, the main two risk categories associated with these water treatment plants are microbial and chemical risks due to the presence of pathogens and chemical contaminants in the untreated water.

Failure Mode Effects Analysis (FMEA). FMEA is used to detect and prevent possible incidents in system based on experts' opinion and system databases which record failures that have occurred in the same or similar systems [18]. This qualitative risk assessment methodology is commonly applied to prevent operational issues. Figure 2.1 provides a scheme of how FMEA methodology works. Nazh Gulum et al. [17] used this methodology to prevent possible incidents in co-generation system of a wastewater treatment plants. Wastewater treatment plants require huge amounts of thermal and electrical energy and some of this energy can be provided from co-generation plants [17]. The authors applied the FMEA methodology by calculating the Risk Priority Number (RPN) which consists of attributing values scaled from 1 to 5 in three different categories to a specific event. The categories are: (i) severity (impact/effects of the event), (ii) detectability (possibility to detect the failure) and (iii) occurrence. The experts attribute a value for each category defining failure modes/effects and report them in a table.

One of the main drawbacks of this method is that it is not able to define

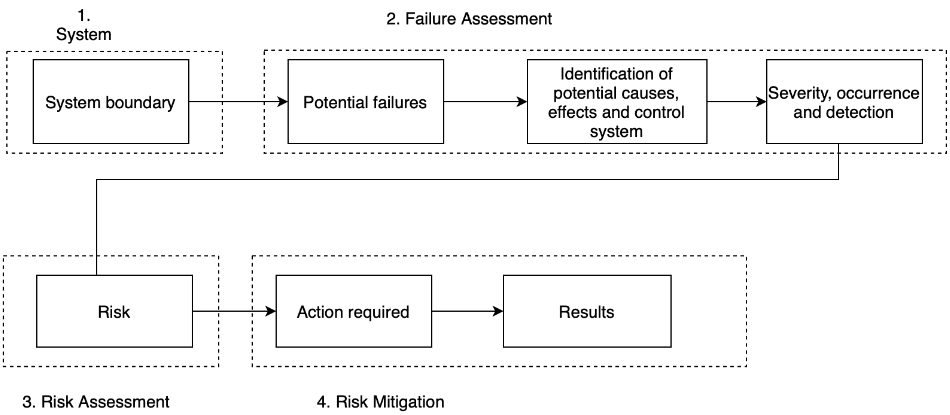

Figure 2.1.: Scheme to summarise FMEA methodology.

the combination of failures that lead to the first hazardous event (defined as event that occurs when a hazard is realized), resulting in a harm [19]. Also, this method may only identify major failure modes in a system [18]. Furthermore, the FMEA method requires a detailed knowledge of the system and its devices/equipment, including their response to the failure which is not always available.

Even though quantitative risk assessment methodologies are usually preferred, the qualitative risk analysis methodologies such as FMEA can provide a clear overview of what the main process criticality are. Furthermore, FMEA methodology proved to be an effective method to assess operational risks arising from failures of devices and/or system, as it has been demonstrated with the study carried out by Nazh Gulum et al. [17]. There is extensive use of both design and process FMEA inside the automotive, aerospace, medical, nuclear and other manufacturing industries [18].

System Modelled Risk Analysis (SMRA). SMRA is a methodology developed by Trubetskaya et al. [20] in order to address the risks associated with the industrial wastewater treatment plants. In this study the authors decided to perform the risk assessment in a closed loop as shown in Figure 2.2.

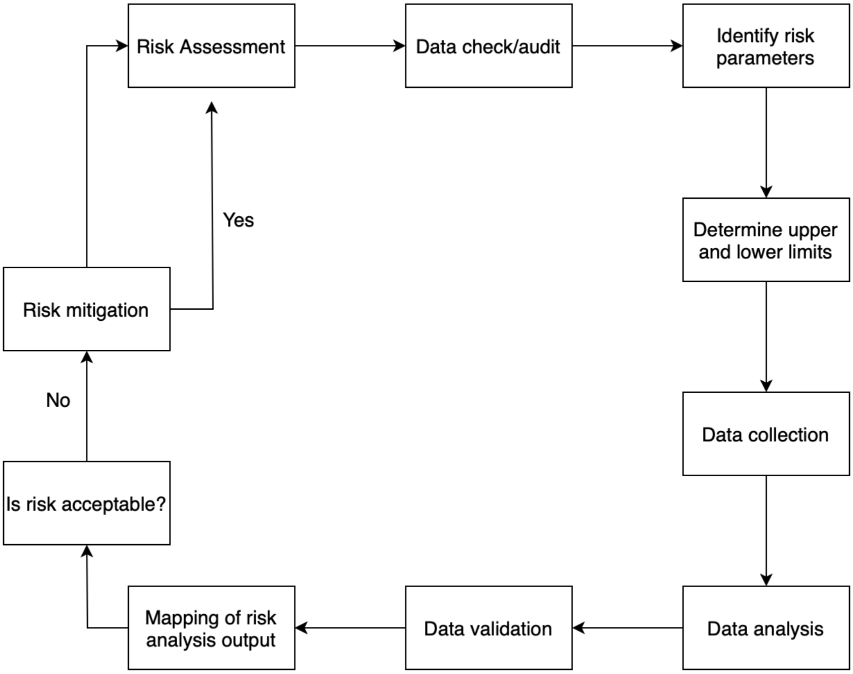

Figure 2.2.: Developed framework with modified FMEA (SRMA) for risk assessment for industrial wastewater treatment [20].

Focusing on the risk assessment stage, a modified FMEA (SRMA) has been applied by the authors to prioritizing the risks, as an improvement of the traditional FMEA [20]. The SMRA consists in 7 steps:

1. Identification of potential Failure Mode.
2. Description of potential Effects.
3. Calculation of a β coefficient (that quantifies the effects).
4. Determine the Current Process Control (USL) using literature.
5. Sensitivity analysis of parameter causing any associated risks.

6. Calculation of RPN.
7. Fill out FMEA form.

Concerning the last step, the form was filled out using a colour scale from green (low risk) to red (highest risk), as it is usually done with the Risk Matrix (Subsection 2.3.2). The importance of this work consists in a development of a new risk assessment framework able to predict and minimize the risks at WWTPs, improving the traditional FMEA methodology. In addition, the authors have highlighted that the risk assessment carried out with this type of risk assessment methods needs to be improved with additional tools like heat map, statistical analysis, sensitivity analysis, etc. This methodology, as well as FMEA, are type of risk assessment methods specific for assessing operational risks and failure modes. Thus, these are not the best recommended methodologies for assessing other risk categories like human health and/or environmental risks unless these are caused by an operational failure mode.

Fault Tree Analysis (FTA). FTA is another common risk assessment method that can be applied both qualitatively and quantitatively. This methodology is commonly used to define the causes behind an occurred incidents defining the probability of occurrence of an incident. The FTA can also be applied preventively in the design phase of the system, identifying the potential causes based on Boolean algebra of an incidents finding also the possible solution and mitigation measures. Taheriyoun and Moradinejad [21] applied the FTA combined with Monte Carlo method to assess the reliability of wastewater treatment plants: the Top Event considered for the FTA is the violation of the allowable Biological Oxygen Demand (BOD) effluent concentration. Monte Carlo method was used to simulate the occurrences of the primary event (Top Event).

FTA allows the frequency of the occurrence of the Top Event (first hazardous incident) to be estimated, using a logical model of the system failure mechanism. The use of this method begins with the definition of the Top Event and then all causes will be defined from the top to the bottom of the tree. The starting point to build the tree is the upper part (Top Event) and the end point is the lowest part of the tree and the events at the last level of the tree are called *bottom events*. This means that analysts must be familiar with the system and its possible failures. In order to link and combine the failures of several basic components of the system, logic gates (AND, OR) are used.

FTA finds its applicability mainly in the chemical process industry, and it is used for addressing safety and reliability [19]. Moreover, this method is also able to identify human errors during an industrial process, and its use is not limited for operational risks. The main weakness is related to the development of the tree, and there is a potential for error if failure paths are omitted, also changing the results of the analysis. This method requires considerable experience to generate useful, well-structured trees in a reasonable period. The choice to use this methodology will depend on the scope of the risk assessment: if the aim is to define the main causes that lead to the first hazardous event, this is the best suitable methodology to proceed with. On the other hands, if the purpose of the risk assessment is to address the consequences due to the occurrence of a first hazardous event, other methodologies (e.g., Event Tree Analysis) are recommended. As mentioned above, the main drawback of this methodology concerns the development of the tree, so before to choose if this method is suitable or not it is preferable to clarify the objective of the risk assessment.

Monte Carlo. Monte Carlo approach is a stochastic method and is one of the most effective methodologies for reliability assessment due to its ability to express well the statistical nature of events [19, 21]. This approach is a mathematical technique, which is used to estimate the possible outcomes of an uncertain event. Monte Carlo simulations have assessed the impact of risk in many real-life scenarios, such as in artificial intelligence, stock prices, sales forecasting, project management, and pricing. They also provide several advantages over predictive models with fixed inputs, such as the ability to conduct sensitivity analysis or calculate the correlation of inputs. Sensitivity analysis allows decision-makers to see the impact of individual inputs on a given outcome and correlation allows them to understand relationships between any input variables [22]. Taheriyoun and Moradinejad [21] have proven the effectively of the combination of these two methods for assessing the reliability of wastewater treatment plants and, in particular, for the reuse of the effluent for irrigation. Indeed, the object was to define the major failure modes in terms of quality of effluent, determining which failure modes can occur, focusing on operational issues of the system.

Bow-Tie. This method was applied by Analouei et al. [23] with the aim of assessing health risks and other adverse impacts of wastewater treatment. The Bow-Tie method consists of a combination of the described above Fault Tree Analysis (FTA) and Event Tree Analysis (ETA). The latter is an inductive risk assessment methodology able to identify the main effects from an occurred hazardous event [19, 24].

An example of the scheme of the Bow-Tie method is illustrated in Figure 2.3, where the first hazardous event (Top Event) is placed in the centre from where two tree diagrams are constructed. On the left the tree diagram is represented by the FTA, this part is also referred as prevention, since the basic event (Bottom Event) leading to the Top Event are identified. Therefore, by assessing the causes it would be possible to prevent the occurrence of the Top Event. The tree diagram on the right side is represented by the ETA and corresponds to the *risk map* and *mitigation phase*. In this way the possible effects (scenario) are identified and by evaluating these it would be possible to reduce the negative impacts. The Bow-Tie method results the best complete risk assessment method

to apply, if the aim is to analyse causes and effects of a certain hazardous event. At the same time, the application of this method can take more time than expected, especially if there are several first hazardous events to analyse, as it is for bio-composite materials.
The main drawbacks of the Bow-Tie methodology are as follows: (i) experience and knowledge of the system by the analysts (for both methods), (ii) strong dependency on experts 'opinion (for both methods), (iii) presence of potential for error if failure paths are omitted (FTA), (iv) identification of all effects from first hazardous event, including failure of safety barriers.

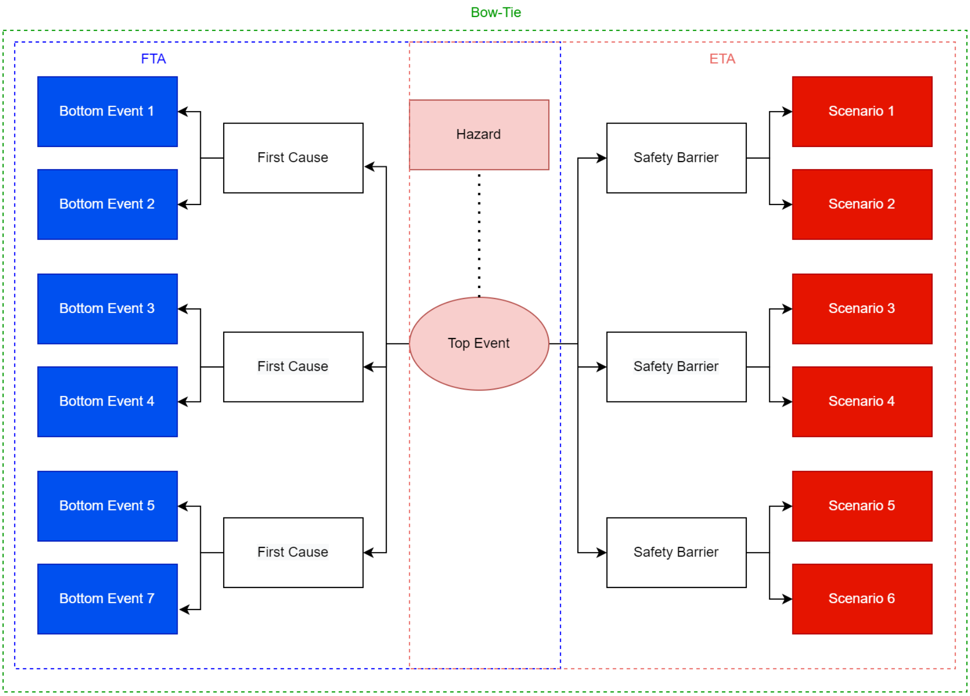

Figure 2.3.: Scheme of a typical FTA, ETA, and Bow-Tie methodology.

Quantitative Microbial Risk Assessment and Quantitative Chemical Risk Assessment. There are several risk assessment methodologies to assess microbial and chemical risks, starting with the common qualitative risk assessment methodologies such as Check List and Risk Matrix to the quantitative risk assessment methods like FTA and ETA. In addition to the common methodologies, Quantitative Microbial Risk Assessment (QMRA), of which a detailed description is provided by W.H.O. [25] and also by Bassett et al. [26], is specifically used to quantify the level of human health risks due to the presence of pathogens. Whereas, chemical risks are assessed by using the Quantitative Chemical Risk Assessment (QCRA) described by U.S.E.P.A. [27, 28].

QMRA methodology is a quantitative risk assessment method, which combines scientific knowledge in terms of presence pathogens and their nature, human exposure, and the health effects that may result from the exposure [25]. This methodology is organised in four steps: (a) Hazard Identification; (b) Exposure Assessment; (c) Dose-Response Assessment; (d) Risk Characterization. In the last stage, risks are quantified in terms of probability of infection/illness.

QMRA is often combined with other methodologies such as deterministic modelling, using probabilistic density functions (PDF), more suitable for a specific case, to assess the exposure to the microorganisms or the dose-response relationships [25]. However, as it is possible to notice in the studies mentioned below, in most cases microbial risks cannot be assessed by using only a deterministic model due to uncertainties related to the type of pathogens, their concentration and uncertainties in predicting exposure and dose-response relationships. Therefore, QMRA is usually combined with a stochastic model, in particular the Monte Carlo method.

Hazard Quotient. Another common methodology for assessing microbial risks is the Hazard Quotient (HQ) method based on U.S.E.P.A. guidelines [27, 29]. This is a risk assessment methodology that consists of calculating the ratio between the average daily dose rate and the allowed reference dose which is likely to be without an appreciable risk of deleterious effects during a lifetime [30]. This ratio must be less than 1.00 to consider the risk acceptable. This method, is typically also used for assessing chemical risks, which guidelines are provided by U.S.E.P.A. guidelines [27].

The QMRA and HQ methods have been also combined when assessing some specific risks such as the risk of bio-aerosol formation at WWTPs [29]. Exposure to bio-aerosols is one of the main risks that affects workers and nearby population since it results in exposure to microorganisms from sewage sludge. Bio-aerosol generated from WWTPs may contain *Legionella pneumophila*, fungi and other airborne bacteria. In this study the QMRA was used in order to assess the probability of infection and illness, defining a dose-response model. The HQ was used for evaluating if the microbial risk. Han et al. [31] applied the HQ method in their study. The objective of their work was to evaluate the seasonal variation of the health risks due to the human exposure to the bio-aerosol formed from untreated wastewater. In order to carry out this study, several species of pathogens have been found in bio-aerosol such as *Chryseobacterium*, *Stenotrophomonas*, *Alcaligenes*, *Micrococcus*, *Micrococcus*, *Enterobacter* and *Escherichia-Shigella*, increasing the risk of exposure from bio-aerosol [31]. In contrast, a different approach was followed by Chen et al. [32] combining the QMRA with Monte Carlo method to assess the health risks for workers exposed to *S. Aureus* or *E.coli* bio-aerosol in two different

WWTPs. In this study, Monte Carlo method was used to assess the variability and uncertainty of QMRA method input values.
Based on the previous studies mentioned above, QMRAis the most common methodology for assessing microbial risks. This method takes into account all components of the water system, providing valuable information on the effects of each component on the human health risks from exposure to waterborne pathogens [25]. The limitation of QMRA methodology is related to the availability of the data on presence, transport, and removal of pathogens in water treatment processes. When the data are absent, QMRA has to work with assumptions [25], so analysts must have experience in this area.

2.3.2. APPLICATION OF RISK ASSESSMENT METHODS TO DRINKING WATER TREATMENT PLANTS

In the previous section the published literature has been reported, focusing on the risk assessment methodologies applied in wastewater treatment plants. In this section the focus is on the risk assessment methodologies applied in drinking water treatment plants.
The World Health Organization (WHO) has developed the Water Safety Plan (WSP) [25] to achieve safe drinking water through proper control of drinking water sources, treatments and distribution. The capacity of the total system to provide safe drinking water and the activities required to verify water safety are assessed in the WSP since even a short period of unsafe drinking water can have a great impact on the risk of infection to human health [33]. With regard to drinking water treatment, the focus on risk assessment is about human health risk, in terms of chemical (Quantitative Chemical Risk Assessment) and microbial risks (Quantitative Microbial Risk Assessment), both described in the previous section. The main risk assessment methodologies found in literature are as follows:

- Accumulation Index & Hazard Index.
- Quantitative Chemical Risk Assessment & Hazard Quotient.
- Quantitative Microbial Risk Assessment.

Accumulation Index & Hazard Index. Liu et al. [34] carried out a multi-phase criterion to assess the health risk, due to the presence of toxic compounds in drinking water, by considering drinking water treatment efficiency and effluent quality, including carcinogen classification based on the International Agency for Research on Cancer standards (as carcinogenic risks), Accumulation Index (AI), and Hazard Index (HI) as the multi-phase evaluation variables. In this study several samples were collected both from the influent (raw water) and effluent and analyzed chemically. Then, quantitative chemical risk analysis was performed with the aim to assess health risks. To summarize the results the authors made a heat map of the priority of chemical compounds for both raw and treated water with the aim of colour-coding the heavy metals found to be harmful to human health. The difference between raw and treated water implies that many chemicals can be removed during the drinking water treatment, but by-products were generated during disinfection processes [34]. This study represents a novel method and scientific support for drinking water safety (DWS). Furthermore, the authors highlighted the importance to prevent raw water contamination and enhance removal processes reducing by-products formation by introducing advanced treatment technologies during the purification processes.

Quantitative Chemical Risk Assessment & Hazard Quotient. QCRA & HQ methodologies proposed by U.S.E.P.A. guidelines [27] consists to calculate the daily intake dose (exposure assessment) selecting a specific exposure pathway such as ingestion, inhalation or dermal contact. Once the daily intake dose is calculated, this value is compared to the reference allowed dose (RfD) for ingestion and dermal exposure [30] or to the reference allowed concentration (RfC) for inhalation exposure [30], by dividing the daily intake dose by RfD. This ratio is called Hazard Quotient (HQ) (Risk Characterization). If the HQ is lower than 1.00, the risk can be considered acceptable, otherwise measures to reduce the risk are required [27]. In order to define the total risk, the single calculated HQ (based on exposure pathways) are summed calculating the Hazard Index (HI) [27].

QCRA in drinking water treatment plants is mostly applied to investigate the amount of heavy metals in source water (e.g., surface or ground water) and to assess whether that may be toxic for human health. Cantoni et al. [35] developed a new method for assessing chemical risks in drinking water treatment and supply. They proposed a new probabilistic procedure of the QCRA, with the aim to assess potential health risks associated with the presence of contaminants of emerging concern (CECs) in drinking water. The QCRA estimates the probabilistic distribution of CECs concentrations in drinking water based on their concentration in source water and simulating the breakthrough curves of a granular activated carbon (GAC) treatment process [35]. This new methodology was combined with the Monte Carlo method, resulting in a successful approach highlighting the advantages of a stochastic approach to risk assessment. The method developed by Cantoni et al. [35] is based on Hazard Quotient described by U.S.E.P.A. [27]: the daily reference dose was calculated by estimating the Drinking Water Target Level (DWTL), which represents the concentration of a compound that does not result in the exceeding of the tolerable exposure (e.g. RfD) of a consumer over lifetime [35].

Selvam et al. [36] investigated the change in the amount of toxic heavy metals in the river system during the COVID-19 pandemic. The Hazard Quotient (HQ) method was applied, including the carcinogenic risk assessment for both children and adults through ingestion and dermal adsorption exposures. Samples were collected both in pre-lockdown period ($28-29$ January 2020) and during the lockdown ($6-7$ May 2020). Finally, the HMPI (Heavy Metal Pollution Index) was evaluated providing a classification of heavy metal pollution in surface water bodies into three categories such as low contamination (HMPI<15), medium contamination (HMPI=$15-30$) and high contamination (HMPI>30) with the aim of assessing water quality. To assess human health risks the Chronic Daily Intake (CDI) was calculated for ingestion and dermal contact respectively and then divided by the Reference Dose (RfD) in order to define the hazard Quotient (HQ). The final step was to calculate the Hazard Index (HI) by summing the HQ for ingestion and dermal contact of a specific heavy metal. Toxic metals with HQ and HI greater than 1.00 may have adverse effects on human health. The same procedure was applied to assess carcinogenic risks by calculating the CDI and multiply it by the Slope Factor (SF) to define the Cancer Risk [37]. The acceptable value for cancer risk is in the range $10^{-6}-10^{-4}$. The importance of this study concerns the assessment of water quality by calculating the amount of pollution due to the presence of toxic heavy metals. Furthermore, the combination of a quantitative methodology such as Hazard Quotient to assess human health risks with a procedure to assess quality risks, using the results as input for QCRA, was validated.

Quantitative Microbial Risk Assesment (QMRA). With regard to microbial risk in drinking water systems, the concentration of pathogens is usually below the detection limit, but a QMRA is still necessary to assess the safety of the drinking water supply. The QMRA method is already described in subsection 2.3.1 hence this subsection shows and discusses applications of this method to drinking water systems.

Gizaw et al. [38] in their study carried out a cross-sectional study for households with children in the rural village of Ethiopia. The potential for external exposure of children to intestinal parasites was assessed by determining the presence of faecal indicator organism (*E. coli*) in drinking water. The exposure was also monitored using a questionnaire to assess behaviours that result in high risk of exposure. No common risk assessment methodologies were applied in this study, but the epidemiological study was conducted to assess the risk of exposure, especially for children. This methodology did not provide a level of risk of infection but was able to assess exposure to faecal contamination in drinking water. Epidemiological studies are often carried out to obtain input data for performing QMRA, sometimes the QMRA is carried out and the outputs are compared with the results of an epidemiological studies.

Smeets [33] monitored the presence of pathogens in raw water and the reduction of pathogen by treatment was stochastic modelled using Monte Carlo simulations. This method was tested in a case study with *Campylobacter* monitoring data from a rapid sand filtration and ozona-

tion process. The results lead to an overestimation, so an improved method was developed by using complementary cumulative distribution function (CCDF) graphs, combining with a stochastic approach. The results were then presented in frequency number curves (F-N curves) [33]. Using F-N curves is useful in terms of risk assessment, since it is possible to visualize graphically the frequency of the incidents and the related number of people involved. This method is usually applied for building construction risk assessment after the Event Tree Analysis application, but it can be applied in different context if all data are available.
Microbial risks in drinking water treatment were also carried out by van Lieverloo et al. [39], by applying the QMRA methodology for distributed drinking water. In order to estimate the infection risk, the cumulative probability density function (CDF) was used. In this study, the concentrations of faecal contamination, such as *E.coli*, *Campylobacter*, enteroviruses and other faecal indicators, were used to estimate the infection risk to consumers in the affected areas [39].The results indicated that the infection risk may be very high, especially from *Campylobacter* and enteroviruses, but also that the uncertainties are significantly high.
Zhiteneva et al. [40] carried out a review summarizing common assumptions in statistical distribution selection for dose-response models for risk assessments applied to potable and non-potable reuse scenarios. The objective was to evaluate the evaluate how the dose-response model choice affects the level of risk. The benefit of using PDFs for describing concentrations is that it allows a more comprehensive assessment of final risks [40]. For many waterborne bacteria such as *Legionella*, *E.coli*, rotavirus, fungi, the dose-response relationship is provided in literature [41].

Table 2.1.: Summary of risk assessment methodologies for wastewater and drinking water treatment.

Methodology	Reference	Application
Failure Mode and Effects Analysis (FMEA)	Failure modes and effects analysis for co-generation unit in a wastewater treatment plant [17]	FMEA is a qualitative risk assessment methodology based on experts' opinion and literature database. This method finds its applicability mainly on operational risk assessment due to the failure modes of components of a system and/or subsystems. It is not recommended to use this method for human health and environmental risk assessment unless these are caused by an operational failure.
Modified FMEA: System Modelled Risk Analysis (SMRA) and statistical analysis	A methodology for assessing and monitoring risk in the industrial wastewater sector [20]	As mentioned for FMEA methodology, SMRA finds its application to assess operational failure modes and the related effects. However, the improvements made by authors (e.g. heat map) lead this method to be used for different scenarios, but other methods might be preferred for the simplicity of their application.
Fault Tree Analysis (FTA)	Reliability analysis of a wastewater treatment plant using fault tree analysis and Monte Carlo simulation [21]	This method is able to identify and quantify the main causes of a first hazardous event. The drawback is in the tree development. The scope of the risk analysis should be defined before choosing the methodology to apply, especially if it is required to study the causes or the effects of a hazardous event.
Bow-Tie (FTA combined with ETA)	Risk assessment of an industrial wastewater treatment and reclamation plant using the Bow-Tie method [23]	This method is recommended if the aim is to analyse causes and effects of a certain hazardous event. At the same time, the application of this method can take more time than expected, especially if there are several first hazardous events to analyse.
Quantitative Microbial Risk Assessment (QMRA) - Guidelines	Quantitative Microbial Risk Assessment: Application for Water Safety Management [25, 27, 42]	These references concern the guidelines provided by World Health Organization (WHO) and U.S. Environmental Protection Agency (USEPA) about the application of QMRA in the water sector. Examples of case studies are provided in these guidelines.
Hazard Quotient (Guidelines)	Risk Assessment Guidance for Superfund Volume I - Human Health Evaluation Manual (Part A) [27]; Human Health and Ecological Risk Assessment [42]	These references are guidelines published by USEPA. These guidelines explain the Hazard Quotient (HQ) method for chemical and microbial risk assessment respectively providing examples.

Table 2.1.: Summary of risk assessment methodologies for wastewater and drinking water treatment (continued).

Methodology	**Reference**	**Application**
Hazard Quotient	Bio-aerosols emission and exposure risk of a wastewater treatment plant with A^2O treatment process [31]	HQ method applied to define the microbial risks for human exposure in several contexts. This method can be applied alone or combined with other risk assessment methodology based on the data input availability. HQ is not complete as QMRA is, but it provides all information required in a proper risk assessment analysis.
QMRA & Hazard Quotient	Bio-aerosol in a typical municipal wastewater treatment plant: concentration, size distribution, and health risk assessment [29]	QMRA is the most common risk assessment method used to assess microbial risks. This method can be combined with other methodologies, as in this case to HQ in order to obtain more consistent results in terms of probability of infections.
QMRA & Monte Carlo	Quantitative microbial risk assessment and sensitivity analysis for workers exposed to pathogenic bacterial bio-aerosols under various aeration modes in two wastewater treatment plants [32]	As mentioned above, QMRA can be combined with Monte Carlo in order to address uncertainties for example due to the lack of consistent input data. This study has proven that the combination of these two methods can provide consistent results and an optimization of normal QMRA.
Multiphasic QCRA	Multiphasic screening of priority chemical compounds in drinking water by process control and human health risk [34]	A multiphasic evaluation analysis was carried out in this study to assess health risks due to the presence of toxic compounds. This study represents a novel method and scientific support for Drinking Water Safety (DWS). Furthermore, this method highlights the importance to prevent raw water contamination and enhance removal processes reducing by-products formation by introducing advanced treatment technologies during the purification processes.
Quantitative Chemical Risk Assessment (QCRA)	Development of a quantitative chemical risk assessment (QCRA) procedure for contaminants of emerging concern in drinking water supply [35]	This new approach has been proven to be efficient concerning the water sector, in particular drinking water treatments. This new approach of QCRA was combined with Monte Carlo resulting in a successful approach highlighting the advantages of a stochastic approach to risk assessment.

Table 2.1.: Summary of risk assessment methodologies for wastewater and drinking water treatment (continued).

Methodology	**Reference**	**Application**
RQ and Quality Risk Assessment	Human health risk assessment of heavy metal and pathogenic contamination in surface water of the Punnakayal estuary, South India [36]	QCRA, already mentioned above, has been combined with a quality risk assessment method, in particular using index to quantify the quality of the water. This study has proven the possibility to combine QCRA with other methods different than Monte Carlo, obtaining good and consistent results in terms of human health risks and quality of source water.
Epidemiological study	Faecal indicator bacteria along multiple environmental exposure pathways (water, food, and soil) and intestinal parasites among children in the rural northwest Ethiopia [38]	Epidemiological study is not a risk assessment methodology, but it can provide good results, also reused as input for risk assessment methodology especially for QMRA and QCRA in terms of human health. The main drawback concerns the availability of input data or previous epidemiological studies performed for a previous outbreak.
QMRA + Monte Carlo method combined with F-N curves	Stochastic modelling of drinking water treatment in quantitative microbial risk assessment [33]	In this study, the presence of pathogens in raw water and reduction of pathogens with treatment was modelled stochastic with Monte Carlo simulations. Using F-N curve it was possible to assess both variation in risk and the uncertainty. In addition, societal risk calculations can lead to the evaluation of the likelihood of simultaneous infection of a large number of people, referred to as an outbreak.
QMRA combined with epidemiological study	Quantitative microbial risk assessment of distributed drinking water using faecal indicator incidence and concentrations [39]	As already mentioned above, epidemiological study can be combined with QMRA leading to more consistent results and a validation of the QMRA method itself.
QMRA combined with empirical literature data and probability distribution functions (PDFs)	Trends in conducting quantitative microbial risk assessments for water reuse systems: A review [40]	This review summarizes common assumptions in PDF selection for source water and treatment steps and dose-response models for risk assessments applied to two different scenarios. The use of PDFs allowed to assess how the dose-response model choice affects the level of the risks in terms of infection (human health risks).

2.4. RISK ASSESSMENT METHODS FOR WATER/WASTEWATER REUSE AND RESOURCE RECOVERY

This section focuses on the review of methods used for assessment of risks related to the reuse of water/wastewater and resource recovery. A summary of the applied methods in the studies examined in this section is listed in Table 2.2.

Concerning the resource recovery, only a few references have been found regarding risk assessment methodologies. Most of the previous studies in literature focus on recovery processes, the quality of the recovered materials and their potential reuse. Only some of them focus on the main human health problems resulting from resource recovery from water, but no risk assessment methodologies have been applied. Examples are Hammes et al. [43] who studied the microbial contamination of calcite pellets, Remy et al. [15] who focused on chemical contamination with residual drugs and heavy metals of cellulose fibres collected from wastewater treatment plants, and Tang et al. [44] who studied the chemical contamination such as heavy metals of calcite pellets collected from different drinking water treatment plants. Although risk assessment methodologies were not applied in these studies, they are a useful tool to understand what the main issues are during collection of raw materials from water, and that the recovery process and the reuse of these materials can lead to various risks, especially for human health.

In this section, as already done in the previous sections, the collected references are listed starting from qualitative and semi-qualitative risk assessment methodologies, followed by the hybrid methodologies (if applicable) and finishing with the quantitative risk assessment methods. This section is focused firstly on resource recovery process, then on water reuse. The main risk assessment methodologies found in literature are as follows:

- FMECA: Failure Mode Effects and Criticality Analysis.
- IWSQI: Irrigation Water Security Quality-based Index.
- Risk Matrix
- QMRA: Quantitative Microbial Risk Assessment.
- QMEA: Quantitative Microbial Exposure Assessment.
- RQ: Risk Quotient.
- QCRA & HQ: Quantitative Chemical Risk Assessment and Hazard Quotient.

FMECA. Schetters et al. [10] applied the Failure Mode Effects and Criticality Analysis (FMECA) for the transition from garnet sand to calcite in the drinking water pellet softening process. All possible failures of process elements in the water and the seeding material stream were evaluated according to their effects on water quality, safety, and environment. The FMECA methodology used by Schetters et al. [10] is an improvement of conventional FMEA method applied by Nazh Gulum et al. [17] and mentioned in subsection 2.3.1. The FMECA method is composed of two separate analyses: the FMEA and Criticality Analysis (CA) [45]. The RPN calculation is one of the benefits of the FMECA method, as it is able to prioritize (qualitatively) issues for corrective action starting with the worst failure mode to the mildest [18].

The benefits of using FMECA are mainly in the outputs: this method can identify potential failure modes for an individual product or process, rank the failure modes and quantify the effects. On the other hand, as already mentioned in subsection 2.3.1 this methodology is entirely dependent from the experience of the analysts. In addition, this method is not suitable for multiple failures, as in the case of larger systems.

IWSQI. The rising of the population leads to increase of water demands of all aspects of water uses, including agricultural, so this implies the research of new sources of water. The reuse of water includes the verification of “Water Security Index” to reflect the water use sustainability. Demerdash et al. [46] developed the IWSQI method that is suitable for defining a sustainable irrigation water system in Egypt. This security index considers both the water quantity and quality. If the parameter causes harm for a specific indicator, it is given an objective index value of zero, otherwise a value of 1.00. The probability of harm was used in the risk assessment and the results of this study showed water insecurity that needs to be improved. In this study no common risk assessment methodologies were applied, but the risk was assessed by evaluating the quality and quantity of water sources for irrigation.

By assessing the quality of the source water, it is possible to predict the potential contamination in terms of chemicals and pathogens that might be present in the resource recovered from the source water. This is a useful tool in case consistent input data for carrying out a risk assessment are missing, and the analysis must be based on assumptions. In that case, the assumptions can be made by using data of source water, where the materials/resources are collected.

A similar approach based on the analysis of water samples and comparison of them to the European standards, has been carried out by Bonetta et al. [47]. In this study, the aim was to investigate the role of wastewater treatments in microbiological contamination by evaluating the possible risks associated with wastewater effluent reuse, considering new EU legislation (2020/741) on minimum requirements for water reuse. Objective of this study was to assess the human exposure to the microbial contamination: all samples were analysed for total *Coliform*, *Enterococci*, *E. coli* and *Clostridium perfringens* spore counts. Then, a statistical analysis was performed to define the concentrations of pathogens. The results were compared with the EU thresholds [47]. This study showed the risk of exposure to the pathogens according to the type of treatments carried out in different WWTPs, highlighting which treatment seems to be the best for achieving the requirements proposed by new European regulations. This is critically important to prevent the possible microbial risk to public health.

Risk Matrix. Talking about the reuse of wastewater, in particular for irrigation, Elgallal et al. [48] used a risk matrix methodology in order to assess environmental and health risks associated with the presence of chemicals in wastewater used for irrigation. This study shows that inappropriate management of wastewater irrigation can contribute to serious environmental and health problems. The risk matrix ranks on a scale from 1 to 5, the occurrence and severity of a specific event according to the experts ‘opinion. Figure 2.4 shows the five categories of risk: Catastrophic (red); Unacceptable (orange); Undesirable (yellow); Acceptable (green) and Desirable (light green) [49].

Severity	Catastrophic	5	5	10	15	20	25
	Significant	4	4	8	12	16	20
	Moderate	3	3	6	9	12	15
	Low	2	2	4	6	8	10
	Negligible	1	1	2	3	4	5
Catastrophoc [16-25] =STOP			1	2	3	4	5
Unacceptable [15] = Urgent action			Improbable	Remote	Occasional	Probable	Frequent
Undesiderable [8 - 15] = Action							
Acceptable [4 - 6] = Monitor							
Desiderable [1 -3] = No action			Likelihood				

Figure 2.4.: Risk Matrix and the five risk categories based on the risk matrix colour code.

Risk Matrix is probably the most common risk assessment method used in literature. This method provides a semi-quantitative risk characterization, since it can rank the risk based on two important categories: (i) occurrence of a dangerous event; (ii) severity of effects of the occurred dangerous event. The risk is indeed calculated as product of likelihood and severity ($R = LxS$) [24]. This method provides a general overview of the main risks involved in a system or subsystems, but it is strongly dependent on experts ‘opinion and the availability of literature data or record database of previous incidents. However, some case studies require the application of quantitative risk assessment method, so the Risk Matrix is commonly used also as preliminary qualitative risk analysis before the quantitative methodologies are applied.

QMRA. Looking at quantitative risk assessment methodologies applied in resource recovery and water reuse, Mara et al. [50] assessed the human health risks associated with the use of wastewater for crop irrigation in two different scenarios (unrestricted and restricted irrigation) using standard QMRA combined with Monte Carlo method. The results were compared with the output of an epidemiological study. The study was focused on human exposure to the rotavirus and *E. coli*. The infection risks estimated by Monte Carlo simulations from $10,000$ - trials generally showed relatively good agreement (no more than one order of magnitude) with epidemiologically determined incidences. On the other hand, the assumptions made for QMRA calculations were close to the conditions in the epidemiological field studies [50]. This study gave satisfactory results when the analytical risk assessment methodology, QMRA in this case, was compared with an epidemiological study. Epidemiological study is not a risk assessment methodology itself, but it is a useful tool to measure the proportion of infected people in an exposed group compared with a control group, measuring the incidence of disease. QMRA quantifies the infection risk in an exposed group of people.

The weakness of using an epidemiological study rather than QMRA concerns the availability of consistent input data. Therefore, the feasibility of a combination of QMRA and epidemiological study is highly dependent on the case study, where at least the epidemiological study must have already been carried out.

A similar study was conducted by An et al. [51] who investigated human exposure to *E. coli* in reclaimed wastewater irrigation, considering two types of scenarios: (1) wastewater treated with UV disinfection; (2) wastewater treated without UV disinfection. In this study the QMRA was applied, defining the dose-response model by applying β-Poisson model to estimate the microbial risk of pathogen ingestion among farmers and nearby children [51]. This methodology was combined with Monte Carlo simulations ($10,000$ - trials). The results of this study showed that water treated with UV disinfection significantly reduced microbiological risks. The main problem to use this disinfection treatment concerns the costs because this treatment requires a large amount of energy. In addition, UV disinfection is effective in killing microorganisms, but it does not work for chemical removal. It can also be ineffective in killing microorganisms if not used appropriately.

QMRA has also been applied to investigate the microbial risk of *E.coli* and rotavirus in treated wastewater for different applications such as irrigation, landscape, industry and urban non-potable water. Persson and Liu [52] have evaluated if the treated water after tertiary treatment combined with a pond system could be reused for different applications from a microbial point of view. Also in this case, the QMRA was combined with Monte Carlo method, which is based on statistical sampling techniques to produce a stochastic approximation of the result and evaluate the uncertainty surrounding estimated values represented by credibility intervals [52].

QMEA. Allende et al. [53] proposed QMEA as an alternative approach to the use of QMRA, to assess the impact of different surface water sources as irrigation water and seasonality on the *E. coli* load of field-grown leafy greens. One of the limitations of QMRA concerns the limited availability of microbiology models describing the behaviour of these pathogens in agricultural settings [53]. The authors proposed this new approach for assessing the contamination of *E.coli* during the production of baby spinach, evaluating the potential impact of weather conditions. The results were analysed by using @*Risk* software (extension of Microsoft Excel) able also to assess the variability of pathogens based on seasonality. The effective of this new approach concerns the focus on the Exposure Assessment, without investigating on the risk characterization. The results of this model are valid input data for both other risk assessment methods and epidemiological study. Furthermore, the QMEA can also assess the impact of safety measures provided for different risk mitigation strategies. Another potential output of this model might also be the assessment of the impact of safety measures provided for different risk mitigation strategies.

RQ. Authors such as Adegoke et al. [54] have investigated the microbial risk for farmers, their family and consumers, due to the use of wastewater effluent for irrigation. The aim of this study was a review of the previous epidemiological studies and health risks associated with the reuse of wastewater for irrigation. The risk assessment was carried out considering the different routes of exposure and the characteristics of the individual who became ill. The risk was characterized by applying the RQ method also known as Hazard Quotient (HQ) (see section 2.3.1 and 2.3.2), proposed by U.S.E.P.A. guidelines [27]. The ratio is measured is calculated between the measured concentration of antibiotic in wastewater and the predicted no effect concentration (PNEC) [54]. If $RQ < 0.1$ the risk is low, $0.1 < RQ < 1.00$ means medium risk and $RQ > 1.00$ means high risk [54]. This study assessed not only human health risk, but also environmental risk due to the antibiotic residues and their impact. The authors improved the RQ method from the original assigning different risk levels based on the parameters to calculate the risk quotient. In the original method the risk was considered acceptable or not by assigning the value 0 and 1 respectively. The introduction of different risk index levels is an improvement of the method that considers different risk mitigation strategies, which can now be specific according to the level of risk as a result, perhaps also leading to a reduction in costs.

QCRA & HQ. Liu et al. [55] assessed the chemical risks of heavy metal contamination in paddy soil due to irrigation with reclaimed wastewater. The risk assessment was carried out by collecting samples from sites upstream (control) and downstream of the electroplating wastewater outlet. Electroplating wastewater means the wastewater that comes from the surface plating operations. The metal is dipped in an electroplating solution of various types of metals and then rinsed. It originates from washing, rinsing, and batch dumps. The technological processes of electroplating wastewater treatment are classified according to the reactions and chemical composition of the electrolytes, which are the source of wastewater forming [56]. Risk assessment code (RAC) was used to evaluate the environmental risks of heavy metals in soils. The health risk index (HRI) and hazard index (HI) were calculated to assess potential health risks to local populations through rice consumption. In this study the focus was on concentration of heavy metals such as copper, chromium, nickel, lead and cadmium in water, paddy soils and rice. If RAC is < 1%, the soil is not at risk to the environment. Low risk, medium risk, high risk, and very high risk are associated with RAC values of 1 – 10%, 11 – 30%, 31 – 50%, and > 75%, respectively. The HRI was calculated as the ratio of estimated rice exposure to the oral reference dose. The HI is a measure of the potential risk of adverse health effects from a mixture of chemical constituents in rice. This value is the sum of all HRIs for a specific receptor/pathway (e.g., ingestion). This methodology is an improvement on the HQ method proposed by U.S.E.P.A. guidelines [27], where in this case the authors used different terminology (which is more specific than the original) and assigned different risk levels. Looking at the Risk Matrix, there are 5 risk levels divided into different colours according to the severity of the consequences and the probability of occurrence. In this specific case study, the importance of having different risk levels concerns a better assessment of the consequences for human health and consequently also a reduction in the costs of safety barriers during the risk mitigation phase.

Table 2.2.: Summary of risk assessment methodologies used for water/wastewater reuse and resource recovery.

Methodology	**Reference**	**Application**
FMECA: Failure Mode Effects and Criticality Analysis	Circular economy in drinking water treatment: reuse of ground pellets as seeding material in the pellet softening process [10]	The application of FMECA for this specific case study concerns the identification and assessment of operational risks during the softening process. The comparison of the results with those of a different risk assessment methodology is useful to compare the two methods and evaluate the pros and cons according to their application to the specific scenario assessed.
Irrigation Water Security Quality-based Index	Development of a quality-based irrigation water security index [46]	Water Security Index is not a proper risk assessment methodology, but in this study the application of this method has provided good results in terms of potential hazards and human exposure to the contaminants. In addition, it is useful to evaluate the quality of source water when input data for risk assessment are missing.
Microbial risk assessment on wastewater effluent reuse	Impact of wastewater treatment plants on microbiological contamination for evaluating the risks of wastewater reuse [47]	In this study no risk assessment methods were applied, but disinfection treatments of wastewater were evaluated in terms of efficiency in order to assess the exposure and potential risks for human health. These studies are useful when consistent input data for risk assessment are missing, and assumptions might be made as results of water quality assessment.
Risk Matrix	Assessment of potential risks associated with chemicals in wastewater used for irrigation in arid and semiarid zones: A review [48]	Risk Matrix in this study has proven to be one of the most effective qualitative risk assessment methods. In fact, Risk Matrix, unlike the FMEA and FMECA, provided a risk map in terms of operational, human health and environmental risks.
QMRA combined with Monte Carlo and comparison with epidemiological study	Health risks in wastewater irrigation: Comparing estimates from quantitative microbial risk analyses and epidemiological studies [50]	This study demonstrated the effectiveness of the combination of QMRA and epidemiological study, validating the QMRA method itself. The main disadvantage of this combination concerns the feasibility of carrying out or using an existing epidemiological study combined with QMRA, due to the lack of consistent input data from a previous outbreak (needed for the epidemiological study and outputs comparison for QMRA validation).

Table 2.2.: Summary of risk assessment methodologies used for water/wastewater reuse and resource recovery (continued).

Methodology	**Reference**	**Application**
QMRA and Monte Carlo	Estimating the Microbial Risk of *E. coli* in Reclaimed Wastewater Irrigation on Paddy Field [51]	QMRA was carried out in this study with the aim of assessing the human health risks as a result of exposure to *E. coli* in reclaimed wastewater irrigation. The method was combined with stochastic approach to estimate the risk associated with uncertainties. UV-disinfected irrigation water showed a lower risk value than others. The main problem concerns the amount of energy requirement (and costs) to use UV-Disinfection treatment.
QMRA	Estimating microbial risk in treated wastewater for reuse: a case study in Lund, Sweden [52]	QMRA has been applied to estimate the microbial risk of *E. coli* and rotavirus in treated wastewater for different reuse. The QMRA as already mentioned is the best method for assessing microbial risk quantitatively. In this case the method provided also a good first estimate of where an increased risk may occur for the different modes of water reuse practices.
QMEA (Quantitative Microbial Exposure Assessment)	Quantitative microbial exposure modelling as a tool to evaluate the impact of contamination level of surface irrigation water and seasonality on faecal hygiene indicator *E. coli* in leafy green production [53]	This study describes QMEA as an alternative approach to the general QMRA method when the necessary data are lacking. One of the outputs of this method was the verification that the selection of irrigation water sources affects *E. coli* loads in leafy vegetables at harvest. Another potential output of this model might also be the assessment of the impact of safety measures provided for different risk mitigation strategies.

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Table 2.2.: Summary of risk assessment methodologies used for water/wastewater reuse and resource recovery (continued).

Methodology	Reference	Application
Review of Epidemiological studies and Risk Quotient	Epidemiological Evidence and Health Risks Associated With Agricultural Reuse of Partially Treated and Untreated Wastewater: A Review [54]	The authors improved the RQ method from the original method assigning different risk levels based on the parameters considered to calculate the risk quotient. The introduction of different risk index levels is an improvement of the method that considers different risk mitigation strategies, which might now be specific according to the level of risk as a result, perhaps also leading to a reduction in costs in terms of risk mitigation measures.
Quantitative Chemical Risk Assessment – Health Risk Index (RHI) and hazard Index (HI)	Heavy metal contamination and risk assessment in water, paddy soil, and rice around an electroplating plant [55]	This methodology is an improvement on the HQ method proposed by USEPA [27], where in this case the authors used different terminology (which is more specific than the original) and assigned different risk levels. In addition, in this specific case study, the importance of having different risk levels concerns a better assessment of the consequences for human health and consequently also a reduction in costs in terms of risk mitigation measures.

2.5. POTENTIAL APPLICATION OF RISK ASSESSMENT METHODS FOR BIO-COMPOSITE MATERIALS

As already mentioned in section 2.2, the bio-composite materials considered in this study are completely new as they are made from resources recovered from the water sector. Therefore, with the aim of finding the best suitable methodology for risk assessment on the bio-composite production process and the application of these materials, this review was carried out looking at risk assessment methodologies applied in the water sector (wastewater treatment, drinking water treatment, resource recovery and water/wastewater reuse). Some of the risk assessment methodologies applied in studies concerning the water sector cannot be directly applied for bio-composite materials as most of the required input data are missing such as the number of pathogens and/or heavy metals contained as impurities in the raw materials. Therefore, assumptions and analysis have to be performed, since these data are not available in literature. This affirmation concerns the applicability of ETA, QMRA and QCRA. As far as other risk assessment methodologies are concerned, these can be applied for the risk assessment of the production and application of bio-composite products based on the available data and the objective of the risk analysis. The following subsections describe if (and how) these methodologies (listed in Table 2.3) can be applied for bio-composite production process and application, including their pros and cons.

2.5.1. SEMI-QUALITATIVE RISK ASSESSMENT METHODOLOGIES

FMEA and FMECA are two semi-quantitative methodologies based on experts 'opinion and literature database. These methodologies find their best applicability in operational risk assessment, identifying potential failures and their effects [24].

Looking at the bio-composite materials, objective of this study, the FMEA methodology could find its application with regards to the manufacturing processes like raw materials recovery processes, mixing process and moulding to obtain the bio-based product, looking for potential operational risks. The application of this method for bio-composite materials risk assessment will provide an overview of the main potential operational failure modes, without assessing the other risks in terms human health and environment, unless they are caused from a failure mode. Thus, other methodologies to assess these risks will be required and the risk assessment framework might be not easy to develop. In conclusion it is possible to affirm that this methodology is not the best suitable risk assessment method to use for the purpose of the human health and environmental risk assessment for bio-composite materials.

Risk matrix is a semi-qualitative methodology, which requires the experience of the analyst to rank from 1 to 5, as shown in Figure 2.4, the probability of occurrence of a specific hazardous event and its severity. This method could be applied to the production process of bio-composites, including the process of collecting raw materials. Risk matrix is able to classify outcome risks regardless of the type of risk (human health risk, quality risk or environmental risk). The limitation of the applicability of this method is mostly based on experts 'opinion and literature database and as mentioned above, these materials are completely new, so no references are available. However, the Risk matrix might be applied to assess the potential environmental risk due to the application of the bio-composite product by referring to similar incidents in the literature due to the release of toxic substances to the environment, in particular release of heavy metals into aquatic environment.

2.5.2. HYBRID RISK ASSESSMENT METHODOLOGIES

Fault Tree Analysis (FTA), Event Tree Analysis (ETA) and Bow-Tie methods are defined as hybrid methodologies since these methods can be applied both for qualitatively and quantitatively risk assessment. The choice of FTA rather than ETA depends on the purpose of the risk assessment: if the objective of the risk assessment is prevention, then FTA is the most appropriate methodology. Otherwise, if the objective of the risk assessment is protection, the ETA is the best choice. In both cases, depending on the availability of data to perform a full quantitative risk assessment, the Bow-Tie methodology might be the best choice, as this method is able to define the causes and effects of the Top Event, quantify the probability of occurrence of the Top Event (solving FTA stage) and the effects (solving ETA stage). Looking at the case study of this study, bio-composite materials, the purpose of the risk assessment protection. The risk assessment will be performed by evaluating and assess the consequences of reusing materials recovered from the water cycle to produce bio-composite materials and the effects of the application of related products in terms of human health, quality of materials and environmental impact.

Thus, Event Tree Analysis seems to be the most suitable methodology for qualitative risk assessment in order to obtain an overview (map) of the main risks involved during the collection of raw materials and then for the bio-composite production process. ETA can also be applied quantitatively, depending on the available data and the type of risks mapped by the qualitative risk analysis. In fact, for each type of risk there is a methodology that is best suited to assess the specific risks (e.g. QCRA and QMRA). Therefore, the FTA and Bow-Tie methodologies do not appear to be the most appropriate methods for carrying out risk assessment for the production and application of bio-composite materials.

2.5.3. QUANTITATIVE RISK ASSESSMENT METHODOLOGIES

Quantitative Microbial Risk Assessment (QMRA) and Quantitative Chemical Risk Assessment (QCRA) are the quantitative risk assessment methods found in literature concerning risk assessment in water sector and resource recovery.

The applicability of these methodologies for assessing chemical and microbial risks are valuable tools for defining and assessing risks to human health and environment.

QMRA. Looking at the bio-composite materials, the main issues (described in section 1.2) related to the production and applicability of the new bio-composite materials are focused on the potential chemical and microbial contamination of the raw materials and consequently of the bio-composites themselves. With regards on microbial contamination, QMRA is so far the best risk assessment methodology that can be applied for bio-composite materials risk assessment, especially in terms of human health risks. In fact, workers may be exposed to these contaminants in different exposure routes such as ingestion, inhalation and dermal contact. Exposure can be caused by the dust formed by the raw materials. The main issue with this method concerns the availability of input data, but as mentioned above this method works with assumption quite well. Thus, input data can be collected from the raw material producer (e.g., provided safety data sheet) or field studies of the source water and making assumptions. Once the amount and type of pathogens present in the raw materials are known/assumed, it would be possible to calculate the probability of illness through the dose-response model. Finally, the risk can be characterized in terms of the probability of infection. The uncertainties due to the lack of consistent input data might be addressed by combining QMRA with Monte Carlo stochastic approach.

In previous study described above, the QMRA is sometimes combined with epidemiological study for both validate the QMRA methodology and also to assess the dose-response model. With regards to the new bio-composite materials it is not possible to perform epidemiological studies for two main reasons: (i) no available data in literature concerning infection from bio-composite materials contaminated with pathogens; (ii) no outbreaks had occurred so far because of the production and application of these new materials.

QCRA. QCRA finds its application in several sectors with appropriate changes based on the specific case study. With regards to the bio-composite materials, this method can assess chemical risks in terms of both human health and environment. Indeed, the presence of the chemicals is not dangerous only for human exposure, but also for the environment. The main chemical pollutants present in the raw materials concern heavy metals. Therefore, some input data such as potential ingestion and inhalation rate, RfD and RfC are available on the guidelines and safety data sheet provided by U.S.E.P.A. To support what mentioned above, the previous studies present in literature mentioned above and in sections 2.2 and 2.3, have proven that the HQ is the best methodology to assess chemical risks in water sector, especially when combined with a stochastic approach to assess the uncertainties associated with exposure assessment when consistent input data are not available and assumptions had to be made. Furthermore, chemicals contamination might have also negative effects on environment. An example can be the application of bio-composite product as riverbank protection and the potential release of chemicals into the aquatic environment might lead to negative environmental effects. Thus, a specific risk assessment methodology for assessing chemical risks is required.

Table 2.3.: Summary of literature review regarding risk assessment methodologies for drinking water and wastewater treatment.

Methodology	Risks	Topic	Applicability for bio-composites
Qualitative: FMEA	Operational risks	Wastewater treatment plant	FMEA is usually applied to assess operational risks of a system or component of a system in the design phase. This method can be applied for bio-composite materials case study, with regard to their manufacturing process focusing on the potential failure modes of the equipment required for both raw materials recovery process and bio-composite product production (e.g., mixer and compression moulding machine), but it is not indicated to assess human health, quality and environmental risks, unless they are caused by a specific operational failure mode.
Semi-quantitative: FMECA	General risks	Resource recovery from drinking water: calcite pellets	FMECA, as already said for FMEA, is a methodology usually applied to assess operational risks. As already said for FMEA this method might be applied for bio-composite materials risk assessment looking at operational risk and failure modes that can lead to a human health and/or environmental risks.
Semi-quantitative: Risk Matrix	Health and environmental risks	Resource recovery from wastewater: reuse of wastewater	The risk matrix is a methodology that can be applied for risk assessment on bio-composite production and use. Considering that the materials are completely new, no historical data or records of previous incidents are available. Thus, it would be preferable to apply this method in specific case where it is possible to refer a similar previous incidents reported in literature.

Table 2.3.: Summary of literature review regarding risk assessment methodologies for drinking water and wastewater treatment (continued).

Methodology	**Risks**	**Topic**	**Applicability for bio-composites**
Quantitative: FTA & Monte Carlo	Operational risks	Wastewater treatment plant	FTA is a valuable tool for assessing risks both qualitatively and quantitatively by defining the causes of the Top Event and its frequency of occurrence. The objective of this methodology is to prevent the occurrence of a such dangerous event (TE). When considering risk assessment for the production and application of bio-composite materials, the objective of which is to assess human health and environmental risks, this method is not the best choice. Indeed, the objective of risk assessment on bio-composites is to assess the consequences of the occurrence of TE.
Quantitative: Bow – Tie	Operational risks	Wastewater treatment plant	The Bow-Tie methodology is one of the most complete risk assessment methodologies as it can assess the causes and effects of a single first hazardous event. The aim of this method is to define the main causes and effects of a system at the same time resulting in one of the most exhaustive methodologies to apply for risk assessment. In this case study, as explained above, FTA is not applicable for the purpose of this study, so Bow-Tie method results not the best choice as well.
Quantitative: QMRA	Microbial risk	Wastewater treatment plant and wastewater reuse	QMRA method can be applied to assess microbial risks due to the potential contamination of raw materials. The exposure might be via different exposure routes and the dose-response model can be defined by using QMRA. If input data are missing, assumptions might be made and assessed by combining QMRA with stochastic approach (e.g., Monte Carlo method).

Table 2.3.: Summary of literature review regarding risk assessment methodologies for drinking water and wastewater treatment (continued).

Methodology	Risks	Topic	Applicability for bio-composites
Quantitative: Epidemiological study	Microbial risk	Resource recovery from water cycle: reuse of wastewater	Epidemiological study is not a valid tool for assessing human health risks associated with the production and application of bio-composite materials, as these materials are completely new, no references and record of previous incidents are available.
Quantitative: QCRA and Hazard Quotient	Chemical risk	Drinking water treatment plant	General QCRA represents the tool to assess quantitatively chemical risks in a certain system, including bio-composite production and application. This method may also be combined with a stochastic approach (e.g., Monte Carlo method) in order to assess the uncertainties due to the lack of input data and enhance the assumptions made to assess the exposure.

2.6. SUMMARY OF KEY REVIEW FINDINGS

The existing risk assessment methodologies proved to be effective for assessing human health (e.g., microbial and chemical risks), water quality, environmental and also operational risks in wastewater and drinking water treatment and also in water/wastewater reuse and resource recovery.

Since the bio-composite materials are new, existing human health, environmental and quality risk assessment methods and tools used in drinking water treatment, wastewater treatment, water and wastewater reuse and resource recovery have not yet been studied for their applicability to bio-composite materials. Thus, it is still difficult to define the most suitable risk assessment methodology for production of the bio-composite materials and their application. However, some suggestions are provided in Table 2.3.

Outputs of this review can be summarised in the following key knowledge gaps:

- Not many studies exist on risk assessment related to water and wastewater-based resource recovery. Some of these methods could be potentially used to assess the risks associated with the extraction of raw materials required to produce new bio-composite materials but it is unclear if and how these methods could be used/modified to serve that purpose.

- No methods nor studies for the specific assessment of human health risks associated with new bio-composite materials and related products have been found in the literature. Some existing methods have the potential to be used for this, but it is unclear if and how these methods could be used/modified to enable new application.
- No methods nor studies for the specific assessment of environmental risks associated with bio-composite materials and related products have been found in the literature. Some existing methods have the potential to be used for this, but it is unclear if and how these methods could be used/modified to enable new application.
- No methods nor studies for the specific assessment of quality risks for bio-composite materials and related products have been found in the literature. Some existing methods have the potential to be used for this, but it is unclear if and how these methods could be used/modified to enable new application.

The identified knowledge gaps can be summarised as the need for a solid risk assessment framework capable of assessing the human health, quality and environmental risks associated with the production and application of bio-composite materials. The framework should be able to perform a complete risk assessment from the hazard identification stage, through the risk mapping and finally the risk quantification. Each risk must be assessed using a specific methodology.
The proposal of this framework is described in section 2.7, as a direction to address the identified knowledge gap.

2.7. FUTURE RESEARCH DIRECTIONS

2.7.1. KNOWLEDGE GAP 1: EXISTING RISK ASSESSMENT METHODOLOGIES FOR WATER-BASED RESOURCE RECOVERY ARE LIMITED

Several resources are recovered from the water cycle, with the aim of reusing them for producing energy, bio-fertiliser, industrial application, nutrients recovery etc. [5, 7–10, 57]. From these studies it was possible to assume that the main risks associated with the recovery of resources from the water sector concern human health risk (in terms of microbial and chemical risk), but also environmental risk and quality of the recovered materials. Therefore, a framework to assess risks associated with water-based resource recovery is required. One of the most important steps to start with is a preliminary qualitative risk assessment for hazard identification and risk mapping. The objective of qualitative risk analysis is to define the main hazards and the associated risks. The latter must be mapped and categorized in order to define the best suitable methodology based on risk category. The qualitative risk assessment should be carried out starting from the resource recovery process, then the risk assessment should focus on the production of bio-composite material (as intermediate product) and finally the focus should be about the final product and its application (e.g. river bank protection). Then, specific quantitative risk assessment methodologies will be applied based on the risk type (see sections 2.7.2, 2.7.3 and 2.7.4).

Hazard identification in the case of bio-composite materials and related products might be conducted by applying one of the qualitative or semi-quantitative risk assessment methodologies applied in previous studies such as FMEA, FMECA or Risk Matrix. However, as mentioned in section 2.5.1 these methodologies are not the best choice to assess qualitatively risk related to human health, quality and environment for bio-composite production process and application, but they find their best applicability to detect and assess operational failures. Furthermore, the main challenge of assessing risks associated with the production and application of bio-composite materials concern the input data that are missing.

In relation to the above, it would be preferable to use a methodology that is structured, methodical and possible to apply when potential hazards are only assumed and not really known. One of the methodologies that might best suit this case study is Hazard & Operability (HAZOP), which is usually applied for hazard identification and qualitative risk assessment [19]. The HAZOP methodology was not applied in the previous studies found in literature, but it seems to be a better solution to carry out the hazard identification stage for bio-composite production process. The HAZOP methodology is usually applied at the first stage of the design process, where hazards and associated risks are not really known, in this way this method is able to provide an overview of the main hazardous events that can occur during the process analysed.

Once the list of all potential process deviations with their potential causes and effects has been made, it is possible to create a map of risks. To characterize the risks, the Event Tree Analysis might be one of the best methodology to apply, as it can be used both qualitatively and quantitatively [24]. As described in section 2.3, the ETA is a structured and inductive methodology that can define the effects of an hazardous event, taking into account the intermediate incidents and the safety barriers (both their functionality or their failure) [58]. At this stage, it would be interesting to have a map of all risks associated with the process of recovering resources from water cycle. It would also be valuable to categorize the risks according to the type of risk (e.g., environmental risk, human health risk, and quality risk), in order to have an overview of what would be the best suitable methodology for quantitative risk assessment.

2.7.2. Knowledge gap 2: Risk assessment methodologies to assess health risks associated with new bio-composite materials and related products are missing

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In subsection 2.7.1, we explained the importance of carrying out a qualitative risk assessment methodology to define the main hazards and risks associated with recovering resources from the water cycle, in order to reuse them for bio-composite production. Once the raw materials have been collected, what would be the main risks to human health originating from the production process of the new bio-composites and from the use of products made from this bio-composite material?

Outputs of qualitative risk assessment might be analysed in terms of type of risk. Concerning human health risks, one of the main expected results of the qualitative risk assessment concerns the presence of pathogens and chemicals. Thus, QMRA and QCRA might be carried out to assess risks associated with the reuse of raw materials to produce bio-composite and the application of the bio-based products.

Concerning QCRA, as already mentioned in Table 2.3, the Hazard Quotient (HQ) would be the most suitable methodology to assess chemical risks related to the production and application of the bio-composite materials. The potential chemical contaminants, in particular for raw materials, concern heavy metals. Therefore, the major risk would be the human exposure to these contaminants via three potential pathways (ingestion, inhalation and dermal contact) through the dust formed from the raw materials. The input parameters, needed to characterize the risk, such as RfD, RfC, ingestion and inhalation rate, exposure duration, etc. are provided by U.S.E.P.A. guidelines to assess chemical risk [27, 28, 30].

QMRA, as mentioned in Table 2.3, can be applied to assess microbial risk during the production process of bio-composite materials and their application. This methodology is described by W.H.O. [25] that provides Guidelines with several examples of the application of this methodology in the water sector. The input parameters such as the distribution to simulate the dose-response model for a specific group of pathogens is given in online database by Q.M.R.A.Wiki [41].

As already mentioned, the main issues to perform a risk assessment on bio-composite materials, concern the availability of input data, in particular those regarding the concentrations of pathogens and/or chemical compounds in the raw materials. One of the solutions to this issue might be the use of safety data sheets provided by the suppliers of the raw materials or referring to literature data about the quality of source water where these materials are collected. In addition, QCRA, as well as

QMRA, might be combined with a stochastic approach (e.g., Monte Carlo method), to assess the uncertainties related to the assumptions made due to the unavailability of consistent input data in order to assess the exposure. Another solution to get consistent input data can be provided by physically and chemically analysing the raw materials prior to their application. This experimental work can provide more details about the concentration of pathogens and chemicals in the raw materials and what kind of disinfection treatment could be applied to obtain a raw material with higher purity. These analyses should be done by the producer and this information should be shared with the research team in order to define which type of risk assessment method should be performed according to the type of risk present (e.g., chemical or microbial). Knowing the actual amount of chemicals (as well as of pathogens) reduces the uncertainties linked to the exposure assessment and leads to more consistent results.

2.7.3. Knowledge gap 3: There are no risk assessment methodologies to assess environmental risks associated with the new bio-composite material and related product

Outputs of qualitative risk assessment, described in section 2.7.1, show the type of risks involved in the production process of bio-composite materials and their application. One of the risk types resulted concerns the environmental risk.

Environmental risks, unlike the health risks, concern mainly the related products of bio-composite material and their application in the natural environment. An example of this is the river (or canal) bank protection element made from new bio-composite material and installed in the natural (aquatic) environment. If the raw materials used for the production of bio-composite material that these elements are made of are contaminated, certain toxic substances (e.g., chemical compounds) could be released to the environment. For future research, it would be interesting to carry out leaching tests. Leaching assessment procedures have been used to determine the leaching of heavy metals as input for evaluating the risk from sewage sludge compost land application [59].

The application of these tests on samples of bio-composite material aims to simulate the leaching of inorganic and organic compounds (e.g., heavy metals and/or organic micro-pollutants) and to assess the corresponding environmental risks. Furthermore, bio-composite materials with different compositions should be analysed, in order to compare different materials and see which one results in lower leaching in the aquatic environment.

Output of leaching tests is the amount of chemicals, in particular heavy metals, which are released from the bio-composite material and leach into the environment. These values can be used as input for Environmental Risk Assessment (ERA). The ERA can be done by using quantitative Event Tree Analysis based on availability of data (e.g., frequency of first hazardous event and intermediate events) or also using the Risk Matrix that classifies risks according to experts' opinion. The application of the risk matrix may be effective if the effects of the application of bio-composite materials (e.g., canal bank protection) are compared with previous similar incidents such as the release of toxic substances into the aquatic environment due to the application of the bio-based product. This may be a better solution if the data necessary to perform a quantitative ETA are missing.

The results of leaching test can also be used as input for assessing human health risks related to the application of the bio-composite materials by knowing their leaching behaviour. Furthermore, it should also be interesting to assess the environmental risks due to the transport of raw materials to the bio-composite factory and the environmental impact related to the recovery process.

2.7.4. Knowledge gap 4: There are no risk assessment methodologies to assess quality risks for bio-composite materials and related products

Other outputs of qualitative risk assessment may concern quality risks, in particular quality of materials in terms of mechanical properties, purity, etc. Quality risks are different from human health and environmental risks, because before starting to assess quality risks the quality concept must be defined [60]. As bio-composite materials are new and their applications are not fully known, quality requirements are not yet well defined. Looking at how these materials are made, and the potential applications ranging widely from river/canal bank protection elements to building facade elements and road traffic signs, one of the quality requirements might be related to the mechanical properties. For those bio-composite products, whose application is in the outdoor environment, an example of quality requirements might be resistance to adverse climatic conditions and impacts. Another example of potential quality requirement could be in terms of the purity of raw materials used for the production of bio-composite, since the presence of contaminants as impurities can reduce the adhesion with other ingredients (e.g., resin) and reduce the mechanical properties of the bio-composite product. Therefore, a list of quality requirements, related to the application of the bio-composite material, should be provided and then it should be checked whether the requirements are met by the new bio-composite materials.

Once the list of quality requirements is made, these could be evaluated by the ETA application. The Event Tree analysis, as described above, is able to logically define the effects for each hazardous event, defining the potential risk scenario. ETA can be applied both qualitatively and quantitatively to address quality risks of bio-composite materials: qualitatively it is possible to define the worst case scenario due to non-compliance with the list of quality requirements, quantitatively it is possible to quantify the probability of occurrence of each intermediate event and related scenario starting from the first hazardous event. If no data are available to perform a quantitative risk assessment, the risk matrix can be applied, ranking the risk level according to expert opinion.

2.8. CONCLUSIONS

Bio-composite materials made from resources recovered from the water sector are new and they are just starting to be produced and used in the Netherlands and other countries. Given that raw resources for the production of these materials are coming from sources with potential contaminants (e.g., wastewater treatment), their use may lead to potential human health risks, environmental risks and product quality risks.

Previous studies regarding the assessment methods for these types of risks in the water sector were identified and reviewed. In particular, related methods concerning the risk assessment in wastewater and drinking water treatment and water/wastewater-based resource recovery for reuse were analysed. No dedicated methods were identified for the assessment of human health, environmental and quality risks related to the production (and application) of bio-composite materials representing the key knowledge gaps.

Despite above some of the existing, more general risk assessment methods seem to have a potential to be used to assess the above risks and have been identified as possible future research directions. For example, the HAZOP method could be applied/adapted to perform the qualitative risk assessment, i.e., to identify key hazards and map the associated risks using the qualitative Event Tree Analysis method. Once the key risks are mapped and categorized, QMRA and QCRA methods could be used to assess the actual microbial and chemical risks to human health. Before this can be done additional work should be carried out to collect the missing information required for the use of QMRA and QCRA methods in the context of bio-composite materials. Stochastic approach could also be adopted in order to take into account the uncertainties associated with limited input data available which is likely to prevail in the future. With regard to the risks posed to the natural environment, it is clear that additional field and laboratory work needs to be conducted to help with the assessment of this risk category. For example, column leaching tests could be carried out to assess the risks related to uncontrolled release of toxic chemical compounds such as heavy metals into the aquatic environment and soil. Finally, a list of quality requirements for bio-composite product (e.g., specific requirements for mechanical properties, purity of raw materials, shape, etc.) has to be made, so that the related material quality risks can be assessed. Our future work will focus on the development of above three risk assessment methods and related experimental work.

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HUMAN HEALTH RISK ASSESSMENT FRAMEWORK FOR NEW WATER RESOURCE RECOVERY-BASED BIO-COMPOSITE MATERIALS

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This chapter is based on: Nativio, A., Javanovic, O., Kapelan, Z., & van der Hoek, J. P. (2024b). Human health risk assessment framework for new water resource recovery-based bio-composite materials. Journal of Water & Health 22(4), 652-672. doi: 10.2166/wh.2024.168 [1]

3.1. ABSTRACT

A new type of bio-composite material is being produced from water-recovered resources such as cellulose fibres from wastewater, calcite from drinking water softening process and grass and reed from water-board sites. These raw materials may be contaminated with pathogens and chemicals such as *E. coli*, heavy metals, and resin compounds. A novel risk assessment framework is proposed here, addressing human health risks during the production of new bio-composite materials. The developed framework consists of a combination of existing risk assessment methods and is based on three main steps: hazard identification, qualitative risk mapping and quantitative risk assessment. The Hazard & Operability and Event Tree Analysis methodologies were used for hazard identification and risk mapping stages. Then, human health risks were quantitatively assessed using Quantitative Chemical Risk Assessment, evaluating cancer and no-cancer risk, and Quantitative Microbial Risk Assessment. The deterministic and the stochastic approach were performed for this purpose. The contamination of raw materials may pose human health concerns, resulting in cancer risk above the threshold. Microbial risk is also above the safety threshold. Additional analysis would be significant as future research to better assess the microbial risk in bio-composites production. The framework has been effectively used for chemical and microbial risk assessment.

3.2. INTRODUCTION

Bio-composite materials are increasingly used in various applications, such as food packaging and the automotive industry. These materials are emerging as replacement for natural and conventional synthetic composites and plastic-derived materials. A trend driven by the increasing awareness about green products by customers, government programs, and new directives on waste management and recycling [2]. The most common bio-composites are made from natural fibres obtained from natural resources (e.g., cellulose), and their mechanical properties are comparable to those composites made from synthetic fibres [3].

Water and wastewater are considered valuable resources as they contain organic and inorganic substances that can be used for energy production and nutrient recovery [4]. In addition, the water smartness and sustainability of the technical solutions for reuse and resource recovery aligns with the United Nation’s sustainable development goals n. 6 and n. 12 (SGD) [5].

A new type of bio-based materials defined as water resource recovery-based bio-composite is emerging on the market and starting to be produced in the Netherlands.

These novel bio-composite materials are mostly made from renewable resources and, at the end of their life, can be ground and reused as a filler (up to 50% of the blend) in the new bio-composites. According to data provided by the producers, these new materials are expected to remain durable for at least 30 years in aquatic environments. The use of natural fibres recovered, for example, from cellulose from wastewater, requires significantly less energy to produce and fewer chemicals to adhere to the binder.

These novel materials are made from resources recovered from the water cycle, such as cellulose fibres from wastewater treatment plants [6], calcite pellets from drinking water treatment plants [7] and materials from surface water management, such as aquatic plants. Once processed these are bonded together using some polyester or bio-based resin to form a bio-composite material that can be used as a replacement for hardwood or other materials.

The production of bio-composite materials based on water resource recovery poses potential risks to human health. Several previous studies [8–10] on surface water and wastewater reuse have clearly demonstrated the existence of these risks, with the main hazards arising from chemical and microbial contamination of various components. Zhang and Weng [11] conducted a study on the potential hazards and associated risks in the production of plant fibre-derived bio-composite food-packaging. The results indicated the potential for harmful substances, including melamine, to migrate from the packaging into the food, thereby posing a risk to human health. The presence of these substances can be attributed to the varying composition of plants, influenced by their respective environments. It is essential to consider these findings when evaluating the safety and viability of bio-composite food-packaging. Thus, certain harmful compounds, such as poisons like cyanide and melamine, are obtained from plants. Other hazardous substances may derive from the use of additives and synthetic resins (e.g., monomers or polymers) to produce the bio-composites. Therefore, bio-composite materials based on water resource recovery should be assessed for their impact on human health risks, during their production and use.

The present study aims to identify potential hazards and associated risks to human health that may arise during the production of a bio-composite material. The production process of bio-composite material typically involves the following steps [12]: (i) Raw materials preparation: the natural fibres, some of which may contain pathogens and chemicals, are cleaned, dried, and sometimes treated or disinfected to remove impurities or contaminants; (ii) Matrix material preparation: the matrix material is dissolved in a solvent to create a liquid form. (iii) Mixing: during this stage, the raw materials are blended with the liquid matrix component, resulting in the formation of dust that comprises pathogens and chemicals such as heavy metals. This dust can be ingested or inhaled by a worker or transferred by skin contact, posing a health risk; (iv) Moulding: The mixture is poured or pressed to create the desired shape (e.g., plates); (v) Curing: the mixture is left to harden and solidify, this process may require the material to be heated or cooled. (vi) Finishing: the finished product may be sanded, painted, or coated to improve its appearance or functionality. The first four steps described above are the subject of this study. Curing and finishing steps are not included as these are highly dependent on the application of the bio-composite material.

During the moulding process, the mixed dough is pressed by a pressing machine (140˚C – 160˚C) for $1-2$ minutes per mm of material thickness. This is a total of $4-8$ minutes considering the thickness of the different bio-composite materials. It is expected that heat transfer would inactivate the remaining pathogens in the dough. However, the actual inactivation rate was not determined due to the lack of initial pathogen contamination data in the raw materials. In addition, no pre-treatment to reduce the heavy metal concentration has been carried out. The manufacturer can choose the quality of the raw material (e.g., utilize water board grass fibres instead of motorway grass fibres, which contain heavy metals and are unsuitable for use).

No concerns regarding exposure to drinking water, wastewater, or surface water are addressed in this study, nor are other risks such as environmental or material quality-related ones. Nevertheless, it should be pointed out that the final drinking water, treated wastewater, and surface waters, from which raw materials are obtained, meet legal and environmental requirements/standards. This study examines the potential threats to human health from exposure to hazardous substances derived from raw materials or from the use of resins (e.g., monomers and polymers).

A risk assessment framework is needed to assess the health risks associated with the production of water resource derived bio-composite materials. A previous study [13] concluded that such a framework does not currently exist for these new materials and that the existing frameworks cannot be applied directly due to different means of human exposure and risk scenarios. For example, in the study conducted by Zubair et al. [14], authors concluded the necessity of Standard Operating Procedure and Hazard and Operability Study (risk assessment) to identifying possible hazards associated with the production of bio-composites and minimize the risks during production. In another study Singh and Lee [15] evaluated the necessity of risk assessment due to the heavy metals contamination in Automobile Shredder Residue (ASR), that is considered a dangerous waste in Europe. Based on above, the purpose of this study is to develop such a risk assessment framework, i.e., a framework that can be used to assess the human health risks associated with the production of water resource recovery-based bio-composite materials.

The chapter is structured as follows. Section 3.3 describes the materials and methods for producing these new bio-composite materials. Then, the new human health risk assessment framework is presented together with associated methods used (sections 3.4). Section 3.5 presents the results obtained when applying the new framework to the new materials, including a discussion for the obtained results. Section 3.6 details the study's conclusions, outlining the functionality of the developed framework, the results obtained on human health risks, and the need for further research.

3.3. MATERIALS AND METHODS

In this section a description of how the new materials are produces is provided in section 3.3.1, then, the developed framework is described step by step in the following sections.

3.3.1. NEW BIO-COMPOSITE MATERIALS PRODUCTION PROCESS

This work assesses the human health-related risks for four bio-composite materials (M1, M2, M3, M4) shown in Table 1.1. These materials are produced using the following manufacturing steps:

1. The bio-composite production begins with the preparation of the dough. The resin (fluid) is added to the filler (e.g., calcite) and mixed for 20 minutes. The fibres are then added in the batches and mixed for $2-4$ minutes. The fibres are added last and mixed for a shorter time to avoid breaking them. The mixing process allows the cohesion of all the raw materials, ensuring compatibility and adhesion. The mixing of raw materials can produce dust which may contain contaminants such as pathogens and heavy metals. In addition, the resin used in the production process can be toxic to human health due to the presence of hazardous substances such as styrene and furfuryl alcohol. These two substances are classified as hazardous to human health for both non-cancer and cancer risk. In addition, the use of the mixer requires training and the application of safety protocols (e.g., ventilated laboratory room). Therefore, Personal Protective Equipment (PPE) such as organic vapour filtering respirators and butyl rubber or neoprene gloves [16], depending on the exposure time, must be used to reduce exposure when handling raw materials, especially resins.

2. The dough obtained is then vacuum sealed in bags and left to mature in the refrigerator for a few days before being pressed. For M4, the Bulk Moulding Compound (BMC), For M4, the bulk moulding compound (BMC), except for polyester resin materials (M1, M2 and M3), some heat is added during mixing to reduce the water content.

3. Finally, a moulding process is applied to give the product shape (e.g., panels). The materials are placed under the press (for bulk

moulding process). The dough is weighed and fed in, then the material is pressed for the time required to cure before the part is removed from the mould. At this stage, the safety protocols and training of the workers are required for the use of this type of machine. The use of this machine involves a risk of crushing, abrasions, cuts and burns between man and machine. Therefore, the use of PPE is also required in this case.

4. The resulting moulds can then be machined according to the specific application of the material. this stage is not covered in this study.

This list shows that the main potential hazards are the presence of materials classified as hazardous to human health and the use of operating machinery that can lead to risks to human health. Specifically, in the production process of bio-composite, major concerns are the potential pollution due to the presence of pathogens, and chemicals such as heavy metals and resin constituents. Evaluation of operational machinery typically follows safety protocols provided by suppliers and personnel are trained on correct usage. Thus, this topic does not fall under the scope of this study. Additionally, using appropriate personal protective equipment (PPE) can reduce exposure and alleviate related effects.
This study considers the handling of raw materials and resins without the use of PPE. The aim is to define the level of risk in the bio-composite production process by considering the worst-case scenario in terms of human health effects.

3.4. HEALTH RISK ASSESSMENT FRAMEWORK

This study uses the human health risk assessment framework to evaluate the potential risks associated with the production of bio-composites based on water resource recovery. The framework makes use of several existing methodologies that have been adapted and integrated together for this purpose. The framework is based on two main steps: (i) health risk mapping; (ii) quantitative risk assessment.

3.4.1. HEALTH RISK MAPPING: HAZARD IDENTIFICATION AND QUALITATIVE RISK MAPPING

Risk assessment starts with hazard identification. Several methods have been used to identify hazards in the water sector, but not all of them seem to be directly applicable to hazards identification for the recovery of raw materials for the production of bio-composites [13]. After an evaluation of different methods for hazard identification, such as Failure Mode, Effects and Criticality, Analysis (FMEA and FMECA), and What If Analysis, it was decided to use the Hazard & Operability (HAZOP) method here. The HAZOP method was originally developed to analyse chemical process systems in the early stages of process design in a chemical treatment plant, but it has since been extended to other types of systems [17]. The generic nature of the HAZOP method, combined with the ability to identify hazards using a structured, well-established methodology, makes it a preferred method for identifying hazards associated with the production of bio-composite materials based on water resource recovery. The HAZOP method is usually applied in the design phase, due to the novelty of the subject. Thus, the key hazards and associated risks are not really known due to the novelty of the topic.

The HAZOP analyses are usually performed by building a spreadsheet where the deviation is identified by combining guide words (e.g., *as well as* - an additional event occurs.) with a process parameter (e.g., *influent water*). The combination of the guide words with the process parameters leads to additional events (in the example above: *as well as influent water*). This means that an additional event can occur such as the influent water not being disinfected, so the hazard is the potential growth of microbial biofilm that will have consequences. Once the deviation has been identified, the causes, effects and safety measures are defined. Considering the production process of bio-composite, biofilm may be present on raw materials such as calcite pellets recovered from drinking water. The presence of biofilm implies the presence of microorganism and can lead to contamination of the pellets and, consequently, the contamination of the bio-composite material causing a risk for human health.

The HAZOP method for bio-composite production was conducted; the scope was the identification of the hazards (deviations) and the potential effects based on a qualitative assessment. In this study, the main deviations that may lead to risks to human health are selected. The aim is to identify the main potential hazards from the beginning of the process: preparation of raw materials used as fibers and/or filler to produce the bio-composite. The importance of this step is to define where the hazard that can cause a risk is present, and if necessary, where the safety guards or other safety barriers should be placed.

Once the hazards have been identified, they need to be linked to associated human health risks. This requires mapping the hazards to risks by identifying relevant intermediate cause and effect type events. The obtained result is a risk map that can be used to quantify the risks in the next stage of the assessment.

There are several methods for doing the mapping, including the Failure Mode Effects and Criticality Analysis (FMECA), Fault Tree Analysis (FTA), Risk Matrix and Event Tree Analysis (ETA). FTA focuses on the cause identification, which is not the object of this hazard mapping step in the risk assessment framework. Furthermore, both FMECA and Risk Matrix are semi-quantitative risk assessment methodologies. The output of these methods is a semi-qualitative characterization of the risk by assigning numbers describing the probability of occurrence and the severity of the risk. However, a semi-quantitative risk characterization is not the main objective of health risk mapping at this stage of the framework; rather a methodology is required that produces a map of all potential risks associated with the bio-composite production process. To obtain such a map, an inductive methodology is required. This method must be able to define the impact of an identified deviation from the associated potential risks.

Based on above ETA was selected as the method for mapping the hazards to risks producing bio-composite material based on water resource recovery. ETA is an inductive methodology that enables the definition of intermediate events that can lead to a scenario, which may or may not involve a risk, starting from an initial hazardous event. Usually, the standard ETA consists of a logical chain of events from the first hazardous event to the outcome. Furthermore, knowing the frequency of the first dangerous occurrence, it is possible to calculate the probability of each possible outcome [18].

In this framework, the ETA methodology is only applied qualitatively. To develop the qualitative ETA, only the branches that can lead to a potential risk scenario are considered. The common ETA scheme has an initial hazardous event, and a series of intermediate events, and safety barriers. In this qualitative ETA framework, the potential causes replace safety barriers and lead to the final scenario, which represents the risk. The identification of potential risks determines the appropriate measures needed to manage them.

The qualitative ETA scheme provides an overview of the hazardous events, the induced consequences, and the potential causes. Furthermore, a risk map can be created by collecting all the potential risks. The risk map shows which risks need to be assessed quantitatively based on the occurrence of the same risk category (e.g., chemical contamination).

The outcome of the hazard and qualitative risk analyses is a risk map shown in Figure 3.1.

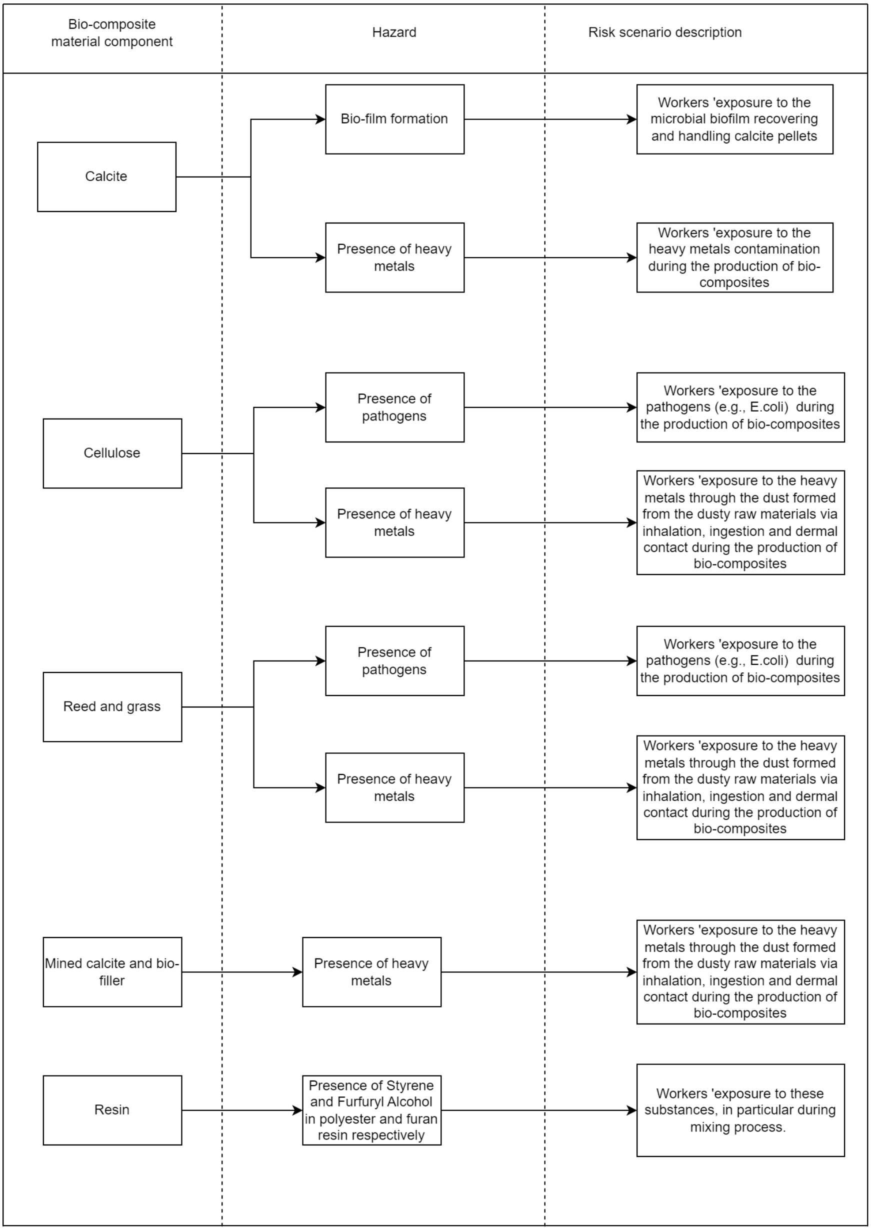

Figure 3.1.: Risk map as the result of the qualitative risk mapping for bio-composite material production process.

As shown in Figure 3.1, the human health risks are related to chemical and microbial contamination of the raw materials. The main risks associated with the presence of microorganisms and chemicals, hazardous to human health, are assessed both qualitatively and quantitatively.

The health risk mapping mainly addresses raw materials collected from the water sector, such as cellulose from wastewater treatment, calcite pellets from drinking water treatment and reed and grass from surface water management. Mined calcite, bio-filler and resins at this stage were only considered based on safety data sheets from suppliers. In addition, bio-fillers are recovered from agricultural waste and dried. Thus, it was assumed that no biofilm formation will occur. The only concern for the bio-filler, as well as mined calcite, as raw materials used for the bio-composite production, is about the chemical contamination. The safety data sheets identify the main hazards and associated risks related to the use of these materials, including instructions that need to be followed for the preparation and handling. However, mined calcite, bio-fillers and resins may contain chemicals classified as hazardous to human health. Therefore, all the raw materials, except for resins, were analysed for heavy metals using Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Atomic Fluorescence Spectroscopy (AFS). For this purpose, samples were made from all available batches of raw materials. For example, calcite is delivered in several bags, and a quantity of about 30 g of material was collected from each bag of each raw material to prepare the sample for the analysis. Samples were prepared by filtration through a micro-filter with pore size of 0.45 μm, followed by acidification with nitric acid prior to analysis. Determination of mercury (Hg) was performed with a fluorescence spectrometer following the standards, US EPA 245.7, EN ISO 17852. Other elements were measured using the ICP-MS technique following the standards US EPA 200.8, EN ISO $17294-2$, US EPA $6020A$, CSN 757358. The ICP-MS was carried out in an accredited external laboratory. The obtained results are presented in Table A.1 of the Supplementary material (A).

The ICP-MS results are used for quantitative risk assessment. The resins are addressed by means of safety data sheets from which it is possible to calculate the amount of styrene and furfuryl alcohol for polyester and furan resin respectively, based on the specific composition of the bio-composite material.

The risk assessment is based on the worst-case scenario: no personal protective equipment (PPE) and safety protocols are used in the bio-composite production process. The mixing phase is the object of this study, where the workers are exposed to the dust generated by the raw materials and to the resins. The quantitative risk assessment is described in section 3.4.2

3.4.2. QUANTITATIVE RISK ASSESSMENT

The risk map produced in the previous step was used as a basis for the quantitative risk assessment. As shown in Figure 3.1, the risks are human health risks related to the presence of chemical and microbial contaminants in the raw materials. Therefore, the Quantitative Chemical Risk Assessment (QCRA) and the Quantitative Microbial Risk Assessment (QMRA) methods are used here to quantify different aspects of human health risk.

Quantitative Chemical Risk Assessment (QCRA).

QCRA is performed according to the USEPA method [19]. The QCRA is structured as follows:

1. Hazard identification: chemicals with the potential to cause harm to humans (e.g., workers) have been detected at this stage. In this phase, the stressors such as heavy metals (e.g., arsenic, cadmium, chromium, lead, etc.), styrene, and furfuryl alcohol are identified.

2. Dose-response: this stage evaluates the numerical relationship between the stressors and the human response, which defines the effects.

3. Exposure assessment: this stage characterises the exposure based on the concentration of the stressors. Then the exposure routes through which the exposure occurs are defined, such as indoor or outdoor environment, and exposure duration.

4. Risk characterization: in this stage, the level of risk is determined, which consists of (i) risk estimation and (ii) risk description. The first concerns the estimation or measurement of the level of exposure for each stressor. The second is used to interpret the results: adverse effects, uncertainties, reasonable alternative interpretations, etc.

The framework is described in the handbooks published by USEPA guidelines [20, 21].

In this work the object is the quantitative risk assessment due to the presence of heavy metals and toxic/dangerous chemicals such as styrene and furfuryl alcohol. In particular, chemical exposure may result in non-cancer and cancer type risks, based on the chemical properties of the chemicals present in the raw materials. The classification as hazardous chemical is available in the literature and published by USEPA-IRIS [22].

In this work, the QCRA aims to determine whether the levels of chemicals present in the raw materials, and subsequently in the bio-composite material, could adversely affect the human health for a given exposure scenario. As mentioned above, exposure was assumed to occur by accidental ingestion, inhalation and/or dermal contact with the contaminated dust generated from the raw materials during the mixing process. The exposure dose was calculated according to the guidelines published by U.S.E.P.A. guidelines [20].

The U.S.E.P.A. Handbook [23] provides literature data concerning the human exposure to contaminated soil and dust for different age groups and gender. The relevant parameter values may vary depending on the scenario in which the framework is applied. For example, the exposure during the bio-composite production occurs in an indoor environment for one working day (8 hours per day) is in the range of 200 − 300 days per year with an average value of 250 days/year. The other input parameters such as ingestion, inhalation rate, available skin area and body weight, these are also available in the U.S.E.P.A. Handbook [23]. Several parameters such as ingestion, inhalation rate, adherence factors, body weight and available skin area, are selected in a range between an age of 21 and 61 years of age for both male and female groups. An average value is then calculated for each parameter and used to apply the deterministic approach of the QCRA to assess the exposure and the final human health risk.

Given the uncertainty present in many of the input values for the QCRA method, a sensitivity analysis was performed to analyse how different values of the input variables (e.g., chemical concentration, body weight, ingestion rate, etc.) may affect the risk index of each chemical and the bio-composite material. The sensitivity analysis is performed using the Monte Carlo method as described in section 3.5.1.

Non-cancer risk assessment. Non-cancer risk, defined by calculating the Hazard Quotient (HQ) and Hazard Index (HI) [19], includes acute, sub-chronic and chronic effects based on the exposure scenario and chemical properties. The HQ, ratio between the exposure dose and the reference allowable dose at which no adverse effects are likely to occur [24] and HI, sum of the HQs of chemicals to which a person is exposed [24], are generally used as indicators of the likelihood of harm resulting from the non-cancer effects of chemicals [25]. The value of HI below the threshold value of 1.00 [20] is generally considered to be an acceptable risk. In contrast, values above 1.00 would indicate a likely negative effect. However, by definition [20] the HI is only qualitative related to the likelihood of adverse effects except in qualitative terms. Therefore, neither the HI nor the HQ can be translated into a probability of the occurrence of adverse effects. However, the HI and HQ still represent the non-cancer risk, not in terms of probability but in qualitative terms [20, 24].

To calculate the HQ for each exposure route, the resulting exposure assessment is compared with the Reference Doses (RfDs). These reference doses are specific to each exposure route and represent the maximum allowable dose of a toxic substance at which no adverse health effects are expected to occur from a lifetime exposure [19]. The RfDs vary according to the duration of exposure, such as acute, sub-chronic, and chronic. In this risk assessment framework chronic exposure is considered. Chronic exposure is repeated exposure to a toxic substance over a long period of time (months or years). Chronic exposure is defined when chemicals are used every day at work, so that workers are exposed to these chemicals every day.

The RfDs values (for ingestion, inhalation, and dermal contact) are obtained from the safety data sheets for each chemical provided by IRIS database [22] and from several public databases such as the Risk Assessment Information System, Informative Furan Chemicals and the Screen Regional Level [16, 26, 27]. The RfDs for both dermal and inhalation exposure for chemicals for which data is not directly available in the literature are calculated as follows:

1. Dermal exposure: the reference value (RfD$_{derm}$) is calculated using the reference dose for ingestion exposure (RfD$_{ing}$), [mg/kg/d] and the Gastro-intestinal Absorption Factors (GIABS) [−]. The latter was collected for each chemical from the standard and guidelines database [16, 26, 27]. The gastrointestinal adsorption factor represents the rate at which a chemical is absorbed in the gastrointestinal tract of the human body. This value is divided between the skin and a solid medium, for example, dust [26]. The dermal reference dose is calculated as follows:

$$RfD_{derm} = RfD_{ing} \cdot GIABS \tag{3.1}$$

2. Inhalation exposure: the reference value (RfD$_{inh}$) for inhalation exposure is derived from the Reference Concentration (RfC) [mg/m^3] [21, 26]. The RfC is defined as the concentration inhaled over a continuous inhalation exposure (acute, chronic, or sub-chronic) to a chemical at which no adverse effects are expected to occur [21, 24]. The RfD for inhalation exposure is calculated as follows [26]:

$$RfD_{inh} = \frac{RfC \cdot InhR}{BW} \tag{3.2}$$

   where InhR is the inhalation rate [m^3/day] and BW is the average body weight for adults [kg].

The HQ is calculated separately for each chemical and exposure route. The HI for a chemical is then calculated as the sum of all HQs for that chemical. The overall HI value for a bio-composite material is calculated as the sum of all HIs for all chemicals present in the material. The overall HI value represents the human health risk associated with the analysed bio-composite material during its production. This value obtained this way is then compared with the threshold value of 1.00 for non-cancer risk [20]. If the value obtained is less than 1.00, the risk is considered acceptable. Otherwise, safety measures must be taken.

Cancer risk assessment. Cancer Risk (CR) is calculated by considering the long-term (lifetime) effects as recommended by standard guidelines [28] as an appropriate measure of exposure to a carcinogen. The CR is

defined by the probability that a person will develop cancer over a lifetime as a result of exposure to one or more carcinogens [25]. The CR is calculated by multiplying the calculated exposure (for different exposure routes) by the cancer Slope Factor (SF). The slope factor is defined as the upper 95% confidence limit of the probability of developing a cancer over a lifetime exposure [25]. Further details on the calculations and formulae for both non-cancer and cancer risk are provided in the Supplementary Material A.
Some of the chemicals are also known human carcinogens. The cancer risk is assessed according to the standard U.S.E.P.A. guidelines [28]. As explained above, to assess the cancer risk the average lifetime (e.g., 70 years) has to be taken into account, as cancer risk is a long-term effect. To calculate the cancer risk for each exposure, the slope factors for ingestion and inhalation are obtained from the above-mentioned RfDs databases [16, 26, 27]. The dermal cancer slope factor is derived from the ingestion cancer slope factor, as follows [26, 29]:

$$SF_{derm} = SF_{ing} \cdot GIABS \tag{3.3}$$

where the SF_{ing} is the ingestion cancer slope factor [mg/kg·day]$^{-1}$. The cancer risk is then calculated in a similar way to the non-cancer risk. Detailed calculations can be found in the Supplementary Material A. The overall cancer risk index (CRI) is compared with the threshold value of 10^{-6} for that risk [28]. If the cancer risk index obtained is below the threshold, the risk can be considered acceptable.
Table 3.1 lists the RfDs and SFs used for dose-response model calculations.
Quantitative Microbial Risk Assessment (QMRA). The aim of QMRA is to investigate the risk that could be posed to human health by the presence of pathogens in the raw materials. Literature data [30] were used in the calculations to perform the QMRA assessment. Data from untreated cellulose fibres were chosen as the worst-case scenario.
QMRA is carried out according to the W.H.O. guidelines [31, 32]. The methodology is structured as follows:

1. Problem formulation: this step defines the purpose and the scope of the investigation. This step includes hazard identification (selection of reference pathogens based on local conditions, source water characteristics, and incidence and severity of waterborne disease).

2. Exposure assessment: in this stage, exposure is characterized by defining and quantifying the exposure pathways. The exposure is then characterized by quantifying the severity and frequency of exposure based on the case study.

3. Health effects assessment: in this step the health effects are assessed by collecting the health effects data for the identified haz-

Table 3.1.: RfDs and SFs values collected from USEPA database [16, 26, 27].

Chemical	RfD_{ing} [mg/kg·day]	RfD_{oral} [mg/kg·day]	RfC [mg/m^3]	GIABS [-]	RfD_{derm} [mg/kg·day]
Si	No data	$6.14 \cdot 10^{-4}$	$3.00 \cdot 10^{-3}$	No data	No data
Al	$1.00 \cdot 10^{0}$	$1.02 \cdot 10^{-3}$	$5.00 \cdot 10^{-3}$	$1.00 \cdot 10^{0}$	$1.00 \cdot 10^{0}$
Fe	$7.00 \cdot 10^{-1}$	No data	No data	No data	No data
Mg	$1.10 \cdot 10^{1}$	$2.05 \cdot 10^{-2}$	$1.00 \cdot 10^{-1}$	$1.00 \cdot 10^{0}$	$1.10 \cdot 10^{1}$
Na	$1.90 \cdot 10^{1}$	No data	No data	$1.00 \cdot 10^{0}$	$1.90 \cdot 10^{1}$
Ti	$3.00 \cdot 10^{0}$	No data	No data	No data	No data
P	$4.90 \cdot 10^{1}$	No data	No data	$1.00 \cdot 10^{0}$	$4.90 \cdot 10^{1}$
Be	$2.00 \cdot 10^{-3}$	$4.09 \cdot 10^{-6}$	$2.00 \cdot 10^{-5}$	$7.00 \cdot 10^{-3}$	$1.40 \cdot 10^{-5}$
Cr	$3.00 \cdot 10^{-3}$	$2.05 \cdot 10^{-5}$	$1.00 \cdot 10^{-4}$	$2.50 \cdot 10^{-2}$	$7.50 \cdot 10^{-5}$
Co	$3.00 \cdot 10^{-4}$	$1.23 \cdot 10^{-6}$	$6.00 \cdot 10^{-6}$	$1.00 \cdot 10^{0}$	$3.00 \cdot 10^{-4}$
Pb	$4.00 \cdot 10^{-3}$	No data	No data	No data	No data
Mn	$2.40 \cdot 10^{-2}$	$1.02 \cdot 10^{-5}$	$5.00 \cdot 10^{-5}$	$4.00 \cdot 10^{-2}$	$9.60 \cdot 10^{-4}$
Mo	$5.00 \cdot 10^{-3}$	$4.09 \cdot 10^{-4}$	$2.00 \cdot 10^{-3}$	$1.00 \cdot 10^{0}$	$5.00 \cdot 10^{-3}$
Ni	$1.10 \cdot 10^{-2}$	$2.87 \cdot 10^{-6}$	$1.40 \cdot 10^{-5}$	$4.00 \cdot 10^{-2}$	$4.40 \cdot 10^{-4}$
V	$5.04 \cdot 10^{-3}$	$2.05 \cdot 10^{-5}$	$1.00 \cdot 10^{-4}$	$2.60 \cdot 10^{-2}$	$1.31 \cdot 10^{-4}$
Zn	$3.00 \cdot 10^{-1}$	No data	No data	$1.00 \cdot 10^{0}$	$3.00 \cdot 10^{-1}$
Ba	$2.00 \cdot 10^{-1}$	$1.02 \cdot 10^{-4}$	$5.00 \cdot 10^{-4}$	$7.00 \cdot 10^{-2}$	$1.40 \cdot 10^{-2}$
B	$2.00 \cdot 10^{-1}$	$4.09 \cdot 10^{-3}$	$2.00 \cdot 10^{-2}$	$1.00 \cdot 10^{0}$	$2.00 \cdot 10^{-1}$
Li	$2.00 \cdot 10^{-3}$	No data	No data	$1.00 \cdot 10^{0}$	$2.00 \cdot 10^{-3}$
Sn	$6.00 \cdot 10^{-1}$	No data	No data	$1.00 \cdot 10^{0}$	$6.00 \cdot 10^{-1}$
Bi	No data	No data	No data	No data	No data
C_8H_8	$2.00 \cdot 10^{-1}$	$1.84 \cdot 10^{-1}$	$9.00 \cdot 10^{-1}$	$1.00 \cdot 10^{0}$	$2.00 \cdot 10^{-1}$
$C_5H_6O_2$	$7.57 \cdot 10^{-4}$	$1.25 \cdot 10^{-3}$	$6.09 \cdot 10^{-3}$	$1.00 \cdot 10^{0}$	$7.57 \cdot 10^{-4}$

ards and the specific study population. This step includes the dose-response model, the probability of illness, and the burden of disease.

- Dose-response: this step consists of identifying the relationship between exposure to the agent and the estimated effects (either infection or disease). A model must be selected from the literature database [33].
- Probability of illness: people can be infected by pathogens without showing symptoms. Thus, when using an infection-based dose-response model, it is important to consider the probability of illness once infected [32].
- Burden of disease: the metric used in the W.H.O. guidelines is disability-adjusted life years (DALY). This measure is expressed per person per year (pppy).

4. Risk characterization: Exposure and health effects assessments are combined, and calculations are made to quantify and characterize risk.

To assess the microbial risk, the main potential pathogens such as *E. coli* and *Clostridium* that may be present in cellulose fibres collected from wastewater [30] and incidentally ingested through the hand-mouth route from workers' hands (or gloves) during the bio-composite production are considered here. The dose-response models specific to each pathogen were obtained from the QMRA database [33]. The dose-response analysis provides a relationship (quantitative) between the probability of adverse effects and the level of microbial exposure (severity). This is fundamental as input data for risk characterization. The risk characterization combines the dose-response model and the exposure assessment to estimate the level of microbial risk, and the uncertainties. The uncertainties of this model are related to the level of measured pathogens concentration. Furthermore, disinfection treatments of raw materials prior to their use in bio-composite production are not precise in terms of pathogens reduction.

The amount of the fraction ingested may vary due to human factors (changing of gloves, washing hands, taking care not to touch the face during the mixing process, etc.) which are not predictable. The exposure scenario used in the guidelines [32] is based on accidental ingestion of contaminated food due to the use of contaminated surface water or wastewater for irrigation. Thus, the exposure assessment is modified based on the bio-composite production process. The input parameters must be suitable for the case study. Therefore, based on the available data and the bio-composite production scenario, only ingestion route is considered in the QMRA. No data are available for taking into account inhalation and dermal contact routes. The ingestion rate is defined as in the QCRA, with a value of 0.03 g/day, taking into account the accidental ingestion of contaminated dust. The exposure duration in this case is also considered to be 8 hours per day (working day) for an average of 250 days/year for the indoor environment as exposure frequency.

3.4.3. SENSITIVITY ANALYSIS

The input data for the risk assessment were collected from the literature [10, 34, 35] and interviews with industry experts involved in water resource recovery processes. As many of these input parameters are uncertain, sensitivity analysis using Monte Carlo method [36] was carried out to assess the impact of these uncertainties on the estimated human health risks. The following five cases are analysed in the assessment of chemical and microbial risks:

1. Sensitivity case 0 (s0): the concentrations of chemicals (QCRA) and pathogens (QMRA) detected in raw materials, are simulated using a uniform distribution. The uniform distribution is used as an approximation where little or no data are available.

2. Sensitivity case 1 (s1): exposure rate parameters such as ingestion rate, inhalation rates, and skin area are simulated using a lognormal distribution, as suggested by the USEPA Handbook [23]. Different values are chosen for each parameter depending on the age and gender. The geometric mean and standard deviation values are calculated for the inhalation rate and the available skin area for the head and hands. Concerning the ingestion rate, only a single value for dust ingestion is available in the literature, so the 96% confidence interval is used as standard deviation. With regards to the QMRA model, only the ingestion route is considered, as described in section 3.4.2 Therefore, only the ingestion rate is simulated as done for the QCRA.

3. Sensitivity case 2 (s2): the exposure frequency is modelled using the lognormal distribution [23]. The exposure frequency considered is for 200, 250, and 300 days per year. The average value of 250 days per year is calculated and the 96% confidence interval is used as standard deviation. This model is the same for both QCRA and QMRA.

4. Sensitivity case 3 (s3): for QCRA body weight is simulated using a lognormal distribution as above. The parameters for the distribution are gander based. The geometric mean and standard deviation are calculated. For QMRA, body weight is not an input parameter for QMRA. Thus, this case of sensitivity analysis is not included in the QMRA stochastic approach.

5. Sensitivity case 4 (s4): all input parameters are simulated simultaneously as uncertain to evaluate the maximum acceptable risk. This case is represented as “s3” for QMRA.

The input parameters used for both the QCRA and QMRA sensitivity analyses, simulated using Monte Carlo method, are listed in Table 3.2. The number of trials is chosen based on the stability of the output achieved. The procedure of selecting the number of trials is carried out by iteration. Different numbers of trials are tested such as 10,000, 20,000, 50,000, and 100,000 trials. The stability of the outputs is reached from 10,000 trials.

3.5. RESULTS AND DISCUSSION

3.5.1. QCRA RESULTS

The QCRA was first carried out using a conventional (deterministic) approach, and then a stochastic approach to assess the impact of the above uncertainties.

Table 3.2.: Input parameters employed in sensitivity analysis.

Input	Unit	Mean	Std	Distribution	Ref.
Chemical [C]	mg/kg	Exp. values		Uniform	
IngR	mg/day	$3.00 \cdot 10^{-2}$	$1.20 \cdot 10^{0}$	Lognormal	[23]
InhR	m^3/d	$1.552 \cdot 10^{1}$	$7.5 \cdot 10^{-1}$	Lognormal	[23]
SA hands	cm^2	$9.80 \cdot 10^{2}$	$1.273 \cdot 10^{2}$	Lognormal	[23]
SA head	cm^2	$1.00 \cdot 10^{0}$	$1.55 \cdot 10^{2}$	Lognormal	
Frequency	day/year	$6.8 \cdot 10^{-1}$	$2.7 \cdot 10^{-2}$	Lognormal	[23]
BW	kg	$7.56 \cdot 10^{1}$	$5.94 \cdot 10^{0}$	Lognormal	
Pathogens [C]	CFU/mL	Exp. values		Uniform	

The results of the deterministic approach for chemical risk assessment per 1 kg of material, are presented in Table 3.3. Observing the HI, all values are below the threshold value of 1.00 for all four materials, leading to an overall hazard index as acceptable risks. The highest hazard index is obtained for dermal exposure. The production of the bio-composites involves the manipulation of raw materials, in particular resins, to obtain a uniform mixture which is then pressed to produce bio-composite panels. The raw materials used in this process tend to generate dust, making dermal exposure the most likely route during the mixing phase. This dust can potentially settle on hair, clothing, and hands, posing a risk of dermal contact also after the mixing stage.

The Cancer Risk Index (CRI) shows values above the threshold value of 10^{-6}. Also, in this case the dermal contact is the major contributor to the overall risk for the reasons given above.

The results presented in Table 3.3 are graphically presented in Figure 3.2, highlighting the chemicals with the most significant contributions to the overall non-cancer risk for the four bio-composite materials studied. The predominant heavy metal contributing to the overall HI for all four alternatives is manganese. This significant contribution is a result of the noticeable amount of manganese present in most of the raw materials, excluding reed. This high prevalence of manganese in the raw materials is the main reason for its significant influence on the HI for heavy metals in all four materials. Furthermore, chromium and vanadium play a significant role in the non-cancer risk, especially for the M1 and M4 alternatives. The increased contribution of these two elements can be directly related to their detection in mined calcite, which accounts for a larger proportion of M1, and in grass, which is used as a natural fibre for M4, as shown in Table 1.1. These results underline the significant influence of the initial chemical composition of the raw materials on the risks to human health, including both non-cancer and cancer risk assessments. Interestingly, chromium emerges as the major contributor to cancer risk for heavy metals M1 and M4 (Figure 3.3), which is consistent with the above observations for non-cancer risk. In particular, material M4 ap-

Table 3.3.: QCRA results for all four materials in terms of hazard index (HI) and cancer risk index (CRI).

Material	Exposure routes	Hazard Index (HI)	Cancer Risk Index (CRI)
M1	Dust ingestion	$5.03 \cdot 10^{-4}$	$4.66 \cdot 10^{-7}$
	Dust inhalation	$4.18 \cdot 10^{-7}$	$9.42 \cdot 10^{-13}$
	Dermal contact	$6.93 \cdot 10^{-3}$	$6.15 \cdot 10^{-6}$
	Total	$\mathbf{7.40 \cdot 10^{-3}}$	$\mathbf{6.61 \cdot 10^{-6}}$
M2	Dust ingestion	$3.53 \cdot 10^{-4}$	$3.26 \cdot 10^{-7}$
	Dust inhalation	$2.59 \cdot 10^{-7}$	$5.23 \cdot 10^{-13}$
	Dermal contact	$4.82 \cdot 10^{-3}$	$4.29 \cdot 10^{-6}$
	Total	$\mathbf{5.20 \cdot 10^{-3}}$	$\mathbf{4.26 \cdot 10^{-6}}$
M3	Dust ingestion	$3.65 \cdot 10^{-4}$	$3.38 \cdot 10^{-7}$
	Dust inhalation	$3.06 \cdot 10^{-7}$	$5.41 \cdot 10^{-13}$
	Dermal contact	$5.00 \cdot 10^{-3}$	$4.45 \cdot 10^{-6}$
	Total	$\mathbf{5.40 \cdot 10^{-3}}$	$\mathbf{4.79 \cdot 10^{-6}}$
M4	Dust ingestion	$5.10 \cdot 10^{-3}$	$5.78 \cdot 10^{-8}$
	Dust inhalation	$4.76 \cdot 10^{-7}$	$1.14 \cdot 10^{-12}$
	Dermal contact	$6.71 \cdot 10^{-2}$	$2.42 \cdot 10^{-6}$
	Total	$\mathbf{7.20 \cdot 10^{-2}}$	$\mathbf{2.48 \cdot 10^{-6}}$

proaches the critical threshold of 1.00 for total non-cancer risk, mainly due to the presence of furfuryl alcohol in the furan resin.

Furfuryl alcohol poses a significant risk to human health in both non-cancer and cancer-related contexts. For materials M1, M2, and M3, styrene stands out as the main chemical contributing to the overall non-cancer risk. This hazardous chemical is commonly found in polyester resins. Similarly, furfuryl alcohol, known for its volatility and adverse effects on human health, contributes significantly to the non-cancer and cancer risks.

Heavy metals such as manganese, chromium, vanadium, barium, and beryllium play a key role in the non-cancer risk indices, affecting the overall non-cancer risk in all four bio-composite alternatives. Notably, these elements (as detailed in Table A.1 of the Supplementary Material A) are detected in grass and mined calcite, resulting in higher hazard quotients and, consequently, hazard indices for materials M1 and M4.

It would be interesting to investigate the specific preparation treatments of the raw materials prior to their reuse in bio-composite production. Knowledge of the specific preparation treatment, may help to define whether the metals, mentioned above, are the results of contamination due to the preparation treatments, or whether they were present where the raw materials were collected. Furthermore, chemical treatment to remove heavy metals may be carried out before the raw materials are reused. The calculations have been made by considering 1 kg of bio-composite material (pilot scale). Thus, in the real case, the exposure might be higher because a higher quantity of raw materials is handled, which increases the exposure. Therefore, safety measures must be taken to protect the health of the workers, such as the use of specific personal protective equipment (PPE) when handling raw materials, especially resins.

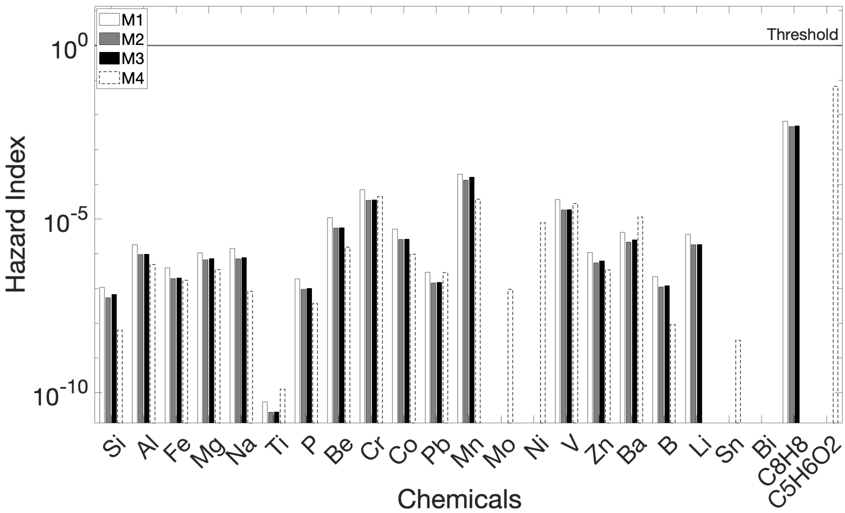

Figure 3.2.: Comparison non-cancer risk as hazard index (HI), for all four bio-composite materials.

Concerning the cancer risk (Figure 3.3), as mentioned above, the risk level is above the threshold for all four materials due to the presence of styrene and furfuryl alcohol. As it is done for non-cancer risk, the assessment is carried out by considering 1 kg of bio-composite product (pilot scale). Furthermore, the amount of styrene and furfuryl alcohol is assumed based on safety data sheets from resin suppliers. As mentioned above, both styrene and furfuryl alcohol are dangerous to human health and are defined as carcinogens.

In order to get more precise results, the sensitivity analysis by using Monte Carlo method has been carried out as described in section 3.5.1

The findings of the sensitivity analysis for non-cancer and cancer risks are shown in Figure 3.4 and Figure 3.5 respectively. The analysis includes all four materials analysed and for the sensitivity case s4, in which all input parameters are modelled simultaneously using the Monte Carlo method. The boxplot in these two figures represent the risk values for

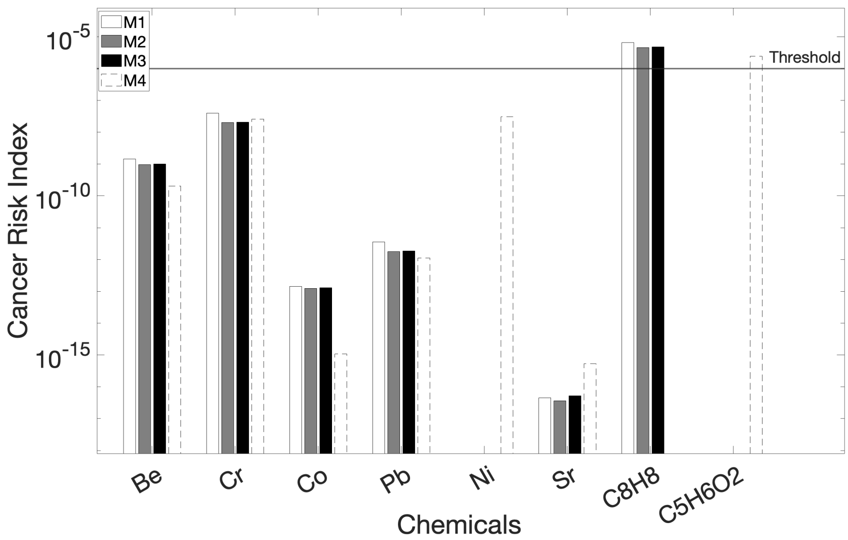

Figure 3.3.: Comparison of cancer risk index (CRI), for all four bio-composite materials.

the 25th and 75th percentiles. The horizontal line inside the box plot represents the median (50th percentile) and the signs "+" and "—" represent the minimum and maximum values obtained. The signs "+" and "—" are visible only for s1, s2 and s3 cases (shown in Figure 3.6), where the uncertainty is higher due to the narrow range of the boxplot obtained with these simulations.

Figure 3.4 and Figure 3.5 show that the overall risk level varies between different materials, but the risk level is always below the threshold for the non-cancer risk and above the threshold for cancer risk for most uncertain samples. The simultaneous consideration of all input parameters in our simulations results in a remarkably wide range of output values, especially when assessing the overall risk for both non-cancer and cancer risks. Material M4 has the highest risk index for non-cancer risk, confirming the results of our deterministic approach. This increased risk level is mainly due to the presence of furfuryl alcohol, which is the largest single contributor to the overall risk in this context. It is interesting to note that when examining the maximum value obtained from the sensitivity analysis (especially the s4 case) for the M4 material, the resulting risk is very close to the results obtained from the deterministic approach. This similarity underlines the robustness and consistency of the obtained results. Finally, the analysis performed underlines the central role of the initial chemical composition of the materials. This factor emerges as the most critical determinant in the context of QCRA. In other words, the ini-

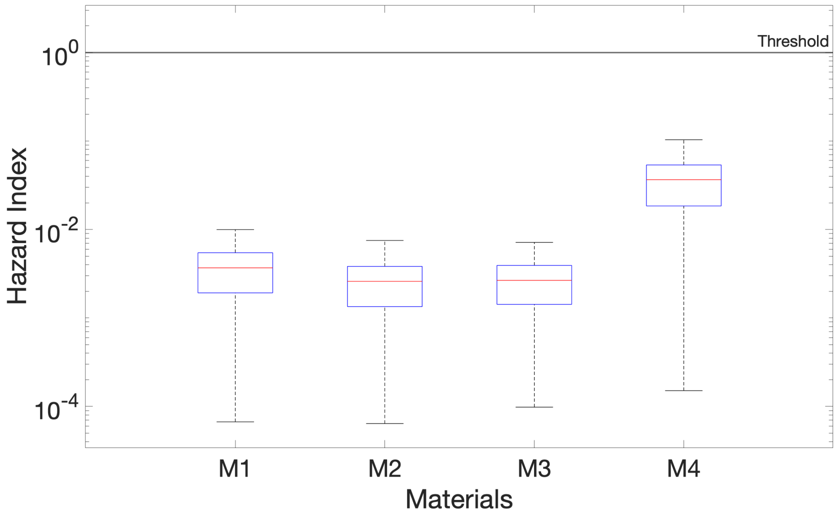

Figure 3.4.: Comparison of total non-cancer risk (HI) for all materials based on sensitivity case s4. The boxplot represents the risk values for the 25th and 75th percentiles. The horizontal line inside the box plot represents the median (50th percentile) and the signs "—" represent the minimum values obtained.

tial chemical content of materials is the key parameter that significantly influences the risk associated with both non-cancer and cancer risks.

The overall risk for all four materials is above the threshold. This is due to the presence of styrene and furfuryl alcohol in polyester and furan resin, respectively. These two substances are toxic for human health for both non-cancer and cancer risk. The assessment of cancer risk must take into consideration lifetime exposure, which is a longer period of exposure than non-cancer risk. The cancer potency factors, and unit risk factors are estimated using long-term data from epidemiological studies [37]. Furthermore, these compounds pose a greater risk of causing cancer rather than non-cancer risk. Personal protective equipment and safety protocols are therefore essential to reduce the exposure.

Materials M1, M2 and M3 are made of polyester resin, which contains styrene. M1 has a slightly higher non-cancer and cancer risk level than M2 and M3, due to the higher amount of styrene in the resin. Material M4 has the highest non-cancer and cancer risk due to its composition with furan resin, which contains furfuryl alcohol. Figure 3.6 shows the cancer risk trend of M4 for all sensitivity cases.

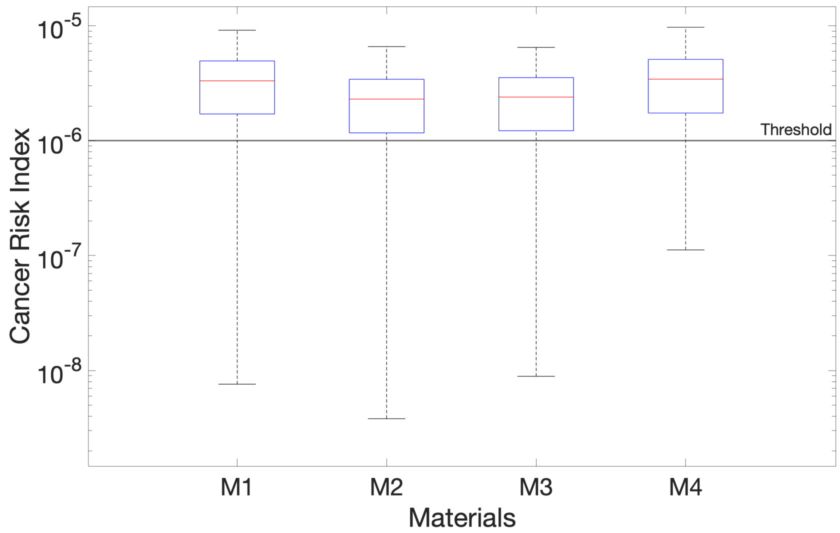

Figure 3.5.: Comparison of total cancer risk index (CRI) for all materials based on sensitivity case s4. The boxplot represents the risk values for the 25th and 75th percentiles. The horizontal line inside the box plot represents the median (50th percentile) and the signs “—” represent the minimum values obtained.

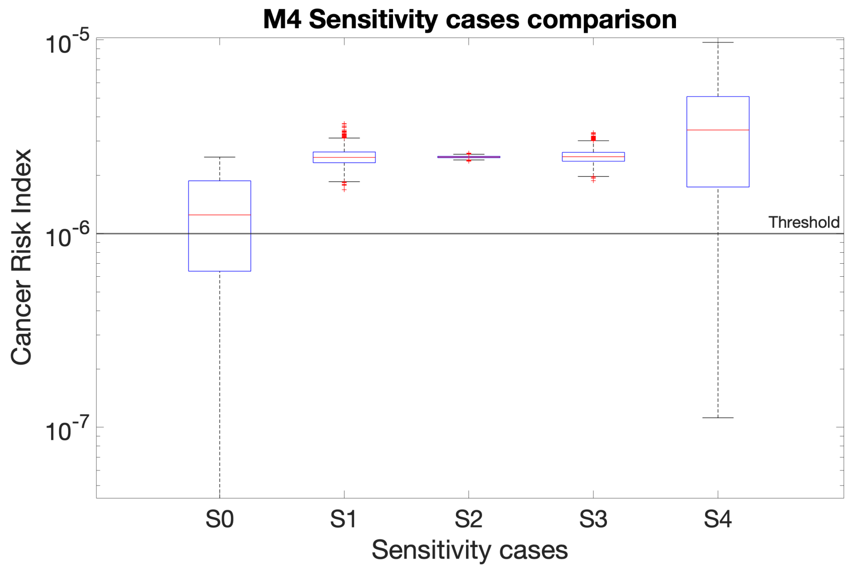

Figure 3.6.: M4 sensitivity models comparison, cancer risk index (CRI). The boxplot represents the risk values for the 25th and 75th percentiles. The horizontal line inside the box plot represents the median (50th percentile) and the signs “—” represent the minimum values obtained.

As it can be seen in this figure, the widest range of risk values (100-fold) is obtained in the s0 case with many uncertain risk values below the threshold. This can be attributed to the large variation in the modelled concentration of all the heavy metals detected in the raw materials by ICP-MS analysis. This indicates that the measured values of chemical contaminants have the greatest influence on the width of the risk interval, and therefore monitoring of the raw material quality, and the use of large data sets for the risk assessment are recommended. This result confirms that the original chemical composition of the material being the most influential parameter in terms of overall risk.

The narrowest range between the minimum and the maximum risk values, observed in case s2, indicates that the frequency of the exposure has a minimal effect on overall risk. The distributions of the cancer risk values in cases s1 and s3 are also rather narrow. These variations are attributed to the simulation of ingestion, inhalation rate, skin surface area, and body weight, respectively. This demonstrates that when risk assessment relies on average data that do not consider physical variations, such as differences in body weight, or skin surface area, there is a possibility of underestimating or overestimating the risk by a small margin ($1-2$-fold). The input parameters simulated in cases s1, s2 and s3 are selected on the basis of the USEPA handbooks [23]. The selected values for each input parameter differ from each other by a small interval. Thus, unlike the chemical concentrations in case s1, a large variation cannot be observed between the minimum and maximum values of each input parameter. The chemical concentrations are based on observed values, therefore the largest range between minimum and maximum values is reached in case s0 and not in other cases.

In model s4, all input parameters were simulated simultaneously. Concentrations of chemical contaminants influenced the wide range of results that spans over 50-fold, while other parameters influenced the average overall risk. Based on the results obtained from both deterministic and stochastic approaches, the cancer risk levels are above the threshold. Appropriate personal protective equipment must therefore be used. This highlights the importance of human health risk assessment, not only for these four particular bio-composites, but for all novel materials.

3.5.2. QMRA RESULTS

Only the data related to cellulose fibres were available in literature about microbial contamination hence only material M3 was analysed. The obtained results from deterministic model are shown in Figure 3.7.

Figure 3.7 shows that *E. coli* is the only pathogen of concern for material M3. The effectiveness of the disinfection treatments of raw materials after recovery is unknown. Thus, as worst-case scenario, for this QMRA application, the observed data published by Heuvel [30] of raw cellulose

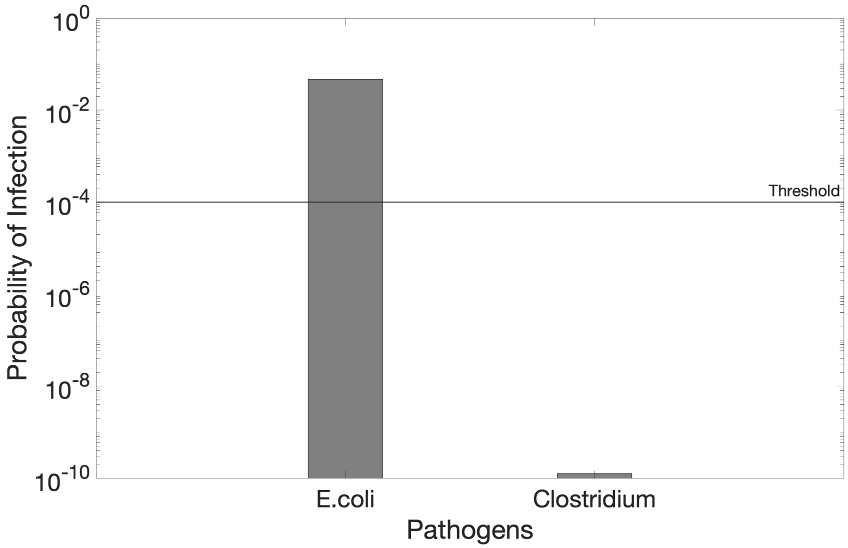

Figure 3.7.: Deterministic results of QMRA model for material M3.

fibres (untreated) recovered from a wastewater treatment plant were considered.

The microbial risk results obtained tend to overestimate the actual microbial risk when untreated cellulose fibres recovered from wastewater are considered. At this stage, the cellulose fibres are inevitably contaminated with a variety of pathogens, a contamination profile that is closely linked to the characteristics of the wastewater source. To prepare these cellulose fibres for reuse, they are subjected to a drying and heating process at elevated temperatures, the main aim of which is to significantly reduce the number of pathogens present. It is important to note that this chapter does not deal with the specifics of the disinfection treatments applied to the raw materials, nor with the quality of the water from which these materials are recovered. However, the disinfection treatment of raw materials, particularly in the case of cellulose fibres, plays a key role in reducing the microbial risk to human health. For a more comprehensive assessment of microbial risk, it is essential to consider the disinfection process of raw materials and the quality of the water sources from which these materials are derived. Proper disinfection protocols are an integral part of ensuring the safety and suitability of recovered cellulose fibres and other materials for various applications. This includes not only the removal of pathogens, but also the maintenance of the desired quality standards for the end product in accordance with health and safety regulations.

As explained earlier, the original initial of pathogens is the most uncertain parameter in this analysis. Thus, the sensitivity analysis was performed as in QCRA.

Pathogen concentrations were simulated using a uniform distribution to assess the risk at the lowest and highest concentrations. The results of the sensitivity analysis are shown in Figure 3.8.

QMRA sensitivity analysis provides remarkable insights into the microbial risk associated with different cases. The widest range of microbial risk values is observed for case s0, highlighting the considerable variability in the results. This variability is mainly driven by variations in pathogen concentration, a parameter with the greatest influence on model output. As discussed in previous sections, it is advisable to use larger datasets for risk assessment in cases such as this, as pathogen concentrations contribute significantly to the observed wide range of results, spanning more than 10^5-fold.

Similarly, in case s3, where all input parameters are simulated simultaneously, it was observed a considerable range of risk values, indicating the complex interplay between these factors in microbial risk assessment. Conversely, in cases s1 and s2, where parameters such as ingestion rate and exposure frequency are modelled explicitly, the impact on microbial risk appears to be relatively minimal. This is evident from the narrow range of risk values, with differences between the minimum and maximum values of about 1.2 and 1.1 times, respectively.

It is important to note that this QMRA was conducted based on data from the literature [30] and takes a worst-case scenario approach by considering untreated cellulose fibres. This approach results in an overestimation of the overall risk compared to a real-world scenario, as already observed. Although cellulose fibres undergo a drying process at high temperatures, it is not currently possible to quantify the reduction in pathogens due to this disinfection treatment. To improve the accuracy and specificity of the QMRA model, it would be valuable to apply it to measured data or to collect additional information on the disinfection treatments applied to all raw materials prior to their use.

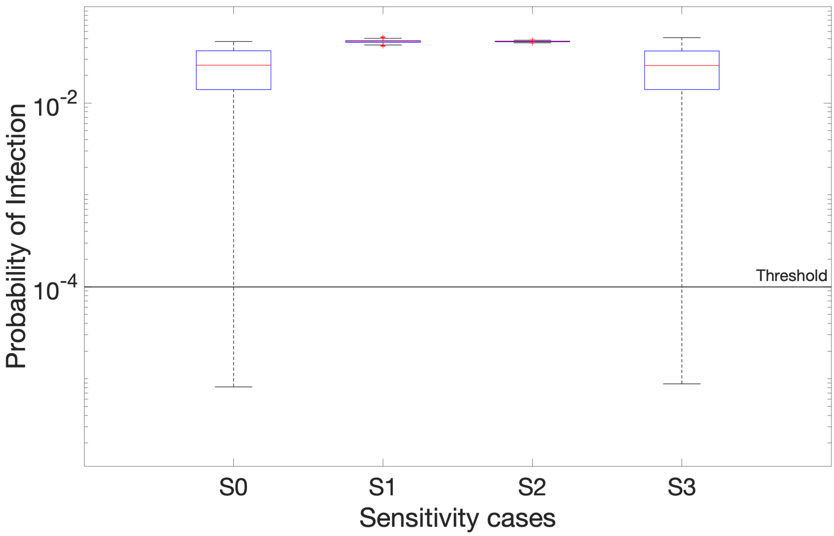

Figure 3.8.: Microbial Risk results for material M3, sensitivity analysis. The boxplot represents the risk values for the 25th and 75th percentiles. The horizontal line inside the box plot represents the median (50th percentile) and the signs "+" and "—" represent the minimum and maximum values obtained.

3.6. CONCLUSIONS

The chapter presents a new framework for assessing human health risks associated with the production of bio-composite materials made by recovering resources from the water cycle (e.g., calcite from drinking water treatment and cellulose from wastewater treatment). The framework consists of two steps. The first step is to identify the key health hazards using the HAZOP methodology. These are then used to create a risk map linking the hazards to potential health consequences via key risk exposure mechanisms, i.e., cause-effect type events. The map was constructed using the ETA qualitative risk analysis methodology. In the second stage of the risk assessment framework, the risk map obtained in the first stage was used to quantify different aspects of human health risks. The objective here is the health risks arising from chemical and microbial contamination of raw materials and their transfer to a worker. The corresponding non-cancer risk, cancer risk, and microbial risk were assessed using the QCRA and QMRA methods respectively. Sensitivity analysis was used to overcome the lack of some input data for the risk assessment and to assess the robustness of the results obtained.

The framework was applied to a case study where four bio-composite materials currently prototyped in the Netherlands were assessed for potential human health risks. The results obtained lead to the following conclusions:

- The proposed framework for assessing risks to human health operates effectively. Using this framework, the primary hazards and associated risks can be identified, mapped, and then quantitatively assessed. As a result, it is possible to identify problems associated with different components of bio-composite material and to detect weaknesses in their production.

- The toxicological aspect of human health risk was assessed using the QCRA method with adapted inputs. The overall non-cancer risk is below the safety threshold for all four materials analysed. Material M4 is representative of the worst-case due to a presence of furfuryl alcohol in the furan resin used in this material. Regarding the cancer aspect of human health risk, all four materials have the total risk value above the threshold. This is mainly caused by exposure via dermal and ingestion routes to the contaminated dust generated during the mixing of various components. However, all this can be easily addressed by asking the workers to wear masks and gloves during the production process. Furthermore, adequate safety procedures and PPE for handling resins must be applied.

- The microbial aspect of human health risk was assessed using the QMRA method with adapted inputs. The results obtained show that *E. Coli* is a pathogen of concern, based on the data used in this study for QMRA. This is a potential issue only in material M3 because of use of cellulose fibres recovered from wastewater treatment in this material. However, this risk assessment was conducted based on a worst-case scenario assuming untreated cellulose fibres. In reality, these fibres will be treated by using a drying process at high temperature which is likely to remove *E. Coli* and bring the overall risk below a safe threshold. In addition, the moulding process through the heat transfer would inactivate the remained pathogens in the dough.

- Sensitivity analysis proves to be a valuable tool for addressing the absence of certain input data in risk assessment. The results of the sensitivity analysis indicate that the concentrations of chemicals and pathogens are the most influential input parameters, as variations in their respective concentrations produce the widest range of health risk outcomes. In scenarios s4 and s3 for QCRA and QMRA respectively, all uncertain inputs are simulated concurrently. This approach yields a broader range of estimated risk values compared to scenario s0, where only the concentrations of chemicals and pathogens are simulated while the other input parameters remain fixed.

Future research should consider the implementation of the framework. Firstly, analysing the quality of the air in the laboratory, where the bio-composites are produced, is crucial for better evaluate the inhalation exposure. Therefore, further research is necessary to assess the validity of this approach for other exposure routes. Additionally, the QMRA model was only performed by considering the ingestion exposure route and relied on previously researched pathogen concentrations from literature. To improve the QMRA, it is essential to gather additional microbial data and incorporate other pathogens and exposure routes like inhalation and dermal exposure. The analysis of samples collected from workers' hands would be a valuable indicator of microbial exposure via the hand-to-mouth route. Furthermore, this approach would serve to reinforce the developed framework, which has been demonstrated to be effective in the assessment of human health risks associated with the production of a novel type of bio-composite material.

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ENVIRONMENTAL RISK ASSESSMENT RELATED TO USING RESOURCE RECOVERY-BASED BIO-COMPOSITE MATERIALS IN THE AQUATIC ENVIRONMENT WITH NEW LABORATORY LEACHING TESTS DATA

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4.1. ABSTRACT

The concept of circular economy, aiming at increasing the sustainability of products and services in the water and other sectors, is gaining momentum worldwide. Driven by this concept, novel bio-composite materials produced by recovering resources from different parts of the water cycle are now manufactured in the Netherlands. The new bio-composite materials are used for different products such as canal bank protection elements, as an alternative to similar elements made of hardwood. As much as these new materials are appealing from the sustainability point of view, they may leach toxic substances into the aquatic environment given some of their ingredients, e.g., cellulose recovered from wastewater treatment. Therefore, a methodology for the assessment of related environmental risks is needed and it does not exist currently. This chapter addresses this knowledge gap by presenting a framework for this. The framework is based on European environmental risk assessment guidelines, and it includes four key steps: (i) hazard identification, (ii) dose-response modelling, (iii) exposure assessment and (iv) risk characterization (i.e., assessment). As part of the first step, laboratory leaching tests were carried out to evaluate the potential release of specific chemical substances such as heavy metals and resin compounds into the aquatic environment. Laboratory test results were then used as input data to evaluate the risk of potential leaching from canal bank protection elements into surface water. A deterministic model was used first to identify the chemicals exceeding the guideline threshold. Subsequently, a stochastic model was applied to evaluate the environmental risks across a range of leaching concentrations and water velocities in the canal, thereby simulating a broader spectrum of possible situations. The risk analyses were conducted for four alternative bio-composite materials made of different ingredients, two different flow conditions (stagnant water and advective flow) in two types of canals (wide ditch and primary watercourse) and for two different water levels based on season conditions (summer and winter conditions). The results of the leaching tests indicated the presence of potentially problematic chemicals, including copper, manganese, zinc, styrene, and furfuryl alcohol. In the case of stagnant water, the absence of a flow rate increases the residence time of the chemicals in the surface water, resulting in a higher PEC/PNEC (i.e., risk) value. However, under stagnant case conditions, environmental risks for all chemicals considered turned out to be below the safety threshold. In the advective case, the existence of a flow rate, even at low velocities simulating the conditions of "almost no flow," contributes to increased dilution, resulting in lower PEC/PNEC ratio values. The results presented here, even though representing real-case scenarios, are only indicative as these are based on laboratory leaching tests and a number of assumptions made. Additional field tests involving collecting and analysing water and sediment samples from the canal where the

canal bank protection elements are located, over a prolonged period, are required to come up with more conclusive findings.

4.2. INTRODUCTION

The move towards circular economy solutions is desired and encouraged for several reasons, including the availability and low cost of up-cycled products and economic well-being. The world's population is growing and with it the demand for raw materials, while the availability of raw materials is limited. The use of up-cycled materials, according to European reports [2], may reduce the use of natural resources, reduce landscape and habitat disruption, and help limit biodiversity loss. Another reason for moving to a circular economy is the potential to reduce greenhouse gas emissions [2]. Creating sustainable products based on recovered and recycled materials helps to reduce energy and resource consumption.

In the Netherlands, novel bio-composite materials have been successfully developed by using various resources recovered from different parts of the water management cycle [3].

These bio-composite materials are potentially used to replace traditional materials such as hardwood in the manufacture of a range of products, including canal bank protection elements. As these materials and related products are produced by recovering resources from wastewater and other sources and using resins, there is a potential for toxic substances such as heavy metals (e.g., Co, Cu, Cr, Pb, V, Zn, As) and resin compounds to leach into the environment. Contamination with heavy metals is a pervasive phenomenon in nature, demonstrable by the prominent accumulation of aluminium in indoor environments as reported by Cetin and Abo Aisha [4]. Furthermore, a comprehensive investigation conducted by Cetin et al. [5] evaluated heavy metals pollution specifically focusing on the assessment of calcium, copper, and lithium contamination in blue spruce trees. Complementing this research, Cesur et al. [6] investigated the accumulation of heavy metals in plant organs. The trend of accumulation of heavy metals poses concern in terms of air and soil pollution. In line with the latter, bio-monitors, such as trees, soil and plants, commonly serve as effective tools for monitoring atmospheric heavy metal concentrations. Cetin et al. [7] conducted also an insightful study mapping the accumulation patterns of specific heavy metals, including nickel and cobalt, through topsoil sampling.

In the context of the current study, it is crucial to evaluate the applicability of novel materials as canal bank protection elements and the potential hazards associated with the water body contamination. The presence of heavy metals poses substantial concerns for both surface and groundwater quality, given their documented adverse effects on aquatic ecosystems, agriculture, and human health, as demonstrated in previous studies [8, 9]. Consequently, it is essential to evaluate the environmental risks related to the use of these new materials in aquatic environments.

Currently, there are no established industry standards for the environmental risk assessment of novel bio-composite materials, regardless of their application. We propose a methodology based on European environmental risk assessment guidelines [10–12] that uses an experimental approach applied under relevant conditions, taking into account the allowable environmental limits. For this purpose, the viability of laboratory leaching tests is evaluated based on published literature. The value of conducting leaching tests for environmental risk assessment has been demonstrated previously by van der Sloot et al. [13]. They described how leaching tests can be used to conduct an environmental risk assessment for construction materials. Leaching tests have been instrumental in characterizing soil contamination with potential implications for underground water quality, as highlighted by Amlal et al. [14]. These tests offer valuable insights into leaching rates, chemical accumulation, and associated risks. Kabiri et al. [15] conducted diverse leaching test methods to explore PFASs leaching behaviour from soil. Additionally, leaching tests were employed by Guleria and Chakma [16] for human health risk assessment, specifically evaluating heavy metals leaching to assess potential risks via dermal contact. Notably, all the mentioned studies in the literature employed leaching tests based on a simulation approach. The latter aims to replicate specific field scenarios in laboratory settings, ensuring the results are interchangeable and comparable.

The goal of carrying out the environmental leaching tests is to provide an estimation of the leaching potential of constituents from various materials across a range of potential scenarios. It is therefore of paramount importance to select an appropriate leaching test and testing protocol in order to ensure the reproducibility and downstream usability of the results. Four internationally recognized types of leaching tests are the pH-dependence test, the percolation test, the monolith test and the compacted granular test [13]. In the pH-dependence test, solid materials are submerged into eluent of different pH for fixed time intervals. Variation of a single parameter (pH) captures the response of the material to different environmental conditions (acidic/basic). The percolation test, or as often referred to in the literature as dynamic column leaching test, evaluates the leaching of the material as a function of eluent volume and dry weight of the material. The monolith test is used for the analysis of single solid pieces of material. From this method, information about the predominant release mechanism can be obtained. Leaching of the finely grounded clays is analysed with a compacted granular test. This test is performed in the same manner of as the monolith leaching test, but applicable only for fine-grained materials. In their study, van der Sloot and Kosson [17] performed a comparative analysis between the pH-dependence leaching test and percolation (column leaching test) test, for the leaching from hazardous waste and industrial sludge. At the same pH and L/S (liquid/solid) ratio the results from both tests are comparable. However, if the material is expected to be exposed to the eluent with the range of pH values, then the pH-dependence tests would provide a more comprehensive picture.

Above mentioned leaching tests and other tests documented in the literature [13, 17] show that tests can be conducted across a spectrum of scenarios involving different materials (waste, ash, construction materials, soil, sediments, etc.) and water samples [18]. The choice of the specific type of leaching test to be undertaken should be guided by the objectives of the study and the chemicals to be analysed [18]. In this study, the percolation dynamic column leaching test was utilized. This test was selected according to the scenario to be simulated. The aim of this study is to analyse the leaching of heavy metals and resin compounds such as styrene and furfuryl alcohol, from the novel bio-composite materials used as canal bank protection and their potential impact on the aquatic environment. The environmental scenario is therefore characterised by surface water with an almost constant pH, and continuous flow rate. This excludes the use of pH-dependence tests. The monolithic test is used to evaluate the mass transfer of monolithic construction materials such as concrete.

In this study, a new type of bio-composite material made from resources recovered from the water sector, was analysed. Thus, the percolation column leaching test (column leaching test) was selected as more appropriate for the purpose of this study and for the environmental conditions to be simulated.

The leaching of the chemicals depends on several factors. As demonstrated by van der Sloot and Kosson [17], chemical parameters such as pH of the eluent, redox potential, kinetics, adsorption, ion exchange and electrostatic attraction, affect the leaching behaviour. Cappuyns and Swennen [19] assessed the mobility of heavy metals within river soil sediments, depending on the eluent pH. The mobility of elements such as Zn, Cd, Ni and Mn increased at decreasing pH, for others such as Cu and Fe a higher leachability was observed at greater pH values. From these studies, it can be concluded that variations in the pH can greatly affect the results. As mentioned above, the environmental scenario consists of the application of these novel materials as canal bank protection in surface water canals. Therefore, no significant pH variations are expected. In order to remove the effects of pH changes on the results, in this study it was decided to use buffered ultra-pure water having a constant pH of 7.00 ± 0.2 as influent.

Oppel et al. [20] investigated the environmental impact of pharmaceutical leaching in soil and groundwater and the consequent toxicity to human health due to groundwater contamination. Their study highlights that examining the environmental impacts of a product in the aquatic environment may have implications for human health and safety, resulting in impacts on the entire ecosystem. In this study, only the environmental risk associated with the use of these materials in an aquatic environment was assessed. This was done because of the novelty of these new bio-composite materials. These materials have never been tested for environmental risk assessment and have never been used for canal bank protection or other applications yet.

The majority of the research reported in the above literature utilized soil and/or sediment samples for their studies. On-site samples were collected to assess potential leaching, after which laboratory leaching tests were employed to replicate leaching under controlled conditions. Subsequently, the obtained results were compared with chemical analyses of on-site leaching samples, serving as a baseline for environmental risk assessment. However, in the current study, collecting on-site samples as a baseline for laboratory leaching tests was not feasible, thus only laboratory leaching tests were performed to assess the environmental risks. On the basis of the above, a knowledge gap was identified: no environmental risk assessment of the leaching of toxic substances into the aquatic environment from these new bio-composite materials, particularly those used as canal bank protection elements and similar products, has been carried out. By conducting leaching tests under controlled laboratory conditions, it may be possible to obtain a more complete general picture of constituents leaching from different bio-composite materials. In the meantime, these data provide significant information, that could be used for environmental risk assessment. In the absence of a baseline, usually represented by on-site water and sediment samples, a number of assumptions had to be made, as described in section 4.3 of this chapter. This, in turn, has led to the selection of the existing Environmental Risk Assessment (ERA) framework [11] for environmental risk analysis.

In this study, the fate of chemicals once leached from the canal bank protection element, made of bio-composite material, into the surface water was not part of the scope of this research. However, it would be interesting to extend the framework with artificial neural network modelling to predict contaminant behaviour, and subsequent concentrations, in surface water. Moreover, artificial neural network modelling can be utilized to model the adsorption of heavy metals into the soil and monitor their fate within the groundwater cycle [21].

The chapter is structured as follows. The experimental setup and the methodology are described in Section 4.3. The results for both a deterministic and stochastic risk assessment approach are presented in Section 4.4. Conclusions are then presented in Section 4.5.

4.3. MATERIALS AND METHODS

The identified knowledge gap concerning the leaching test and the environmental impact assessment of these emerging bio-composite materials, particularly in water environments, have been addressed by proposing a framework. This framework is based on three building blocks: (i) the existing Environmental Risk Assessment (ERA) [11] and the corresponding Dutch guidelines published by the Dutch National Institute for Public Health and the Environment (RIVM) [12]; (ii) the database of European Chemicals Agency [10]; (iii) percolation column leaching tests [22] providing input data for the environmental risk assessment, and simulating the real case scenario in absence of detailed on-site data due to the novelty of these materials. Leaching test results were used and modelled to simulate the potential leaching in the real canal under various environmental conditions such as a stagnant case (absence of flow rate) and the presence of flow rate. Two types of canals were analysed. No other leaching tests were performed on this new type of bio-composite material up till now, while the corresponding environmental risk analysis was not conducted so far.

4.3.1. BIO-COMPOSITE MATERIALS AND THEIR USE FOR CANAL BANK PROTECTION ELEMENTS

This work assesses the environmental risks associated with potential leaching of heavy metals and resin compounds from canal bank protection elements made from new bio-composite materials. The purpose of canal bank protection elements is to protect the canal bank from soil collapse into the water. The canal bank elements are placed on both sides of the canal. Four different alternatives of new bio-composite materials (M1, M2, M3, M4), which characteristics are listed in Table 1.1, are considered to produce these elements. Table 1.1 presents the raw materials used in the four alternatives bio-composite materials. The four materials are all made of natural fibres and fillers (e.g., water reeds, wastewater cellulose, bio-filler from agricultural waste, etc.) with additives added for different purposes, and all bonded together using a resin (e.g., polyester resin, or furan resin, etc.).
The analysed water canal system consists of: (i) wide ditch and (ii) primary watercourse. To estimate the flow rate, the full operation of the nearby pumping station, located along the primary watercourse, was taken into account. Furthermore, the flow rate varies based on the water level, which varies according to the seasonal conditions (summer and winter conditions). The characteristics of the wide ditch and primary watercourse are as follows (see Figure 4.1 for the wide ditch and Figure 1 in the Supplementary Material B for the primary watercourse, respectively).

- Wide ditch: trapezoidal profile, bottom width of 4 m, top width of 8 m and effective depth of 1 m in the middle. The water cross section velocity was measured and found to have an average of 2.4 m/h. The flow rate based on water cross section area, was calculated to have an average value of 11.52 m^3/h under summer conditions (low water level due to the dry season). In contrast to an average value of 14.4 m^3/h, under the winter conditions (high water level due to the rainy season).

- Primary watercourse: similar profile as the wide ditch (trapezoidal profile) with a bottom width of 5 m and a top width of 10 m, and a depth of 1 m in the middle. The water cross section velocity was measured to be 270 m/h on average. The flow rate, based on the water cross sectional area, was estimated to be 1620 m^3/h under summer conditions (low water level due to the dry season), and 2025 m^3/h under the winter conditions (high water level due to the wet season).

The pumping station works approximately 800 hours per year.

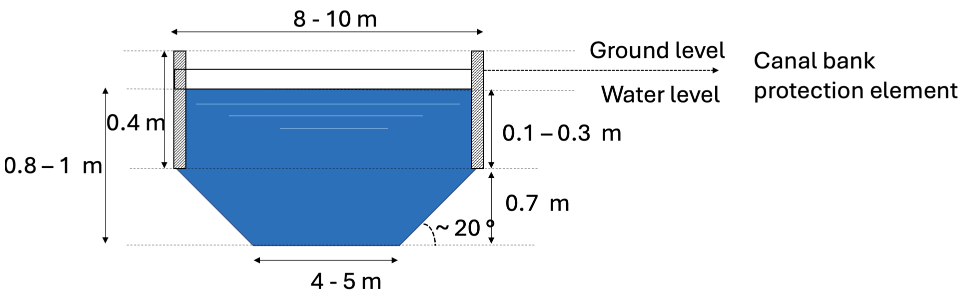

Figure 4.1.: Wide ditch profile

The canal bank protection elements, placed on both sides of the canal, are of conventional pile-bulkhead construction, using a combination of softwood where possible (always below the waterline), and bio-composite material where needed to extend the lifespan of the system (below and above the waterline, depending on the season). The water level changes with the seasons, as explained above. Based on expert knowledge, it was assumed that the water level varies by 0.2 m between the summer and winter seasons. The 0.4 m high bio-composite elements are then assumed to be submerged by a minimum of 0.1 m (low water level representing summer season conditions) to a maximum of 0.3 m (high water level representing winter season conditions). Only the submerged part of the bio-composite bank protection elements is considered in this study.
Table 4.1 lists the mass of the submerged bio-composite material over 1 m of length, during the summer and winter season conditions. The dimensions of the canal bank protection elements (e.g., width, length, and thickness) are the same for all four bio-composite alternatives. Each

bio-composite alternative has a specific density, which defines the actual submerged mass. Density data are not shown here for confidentiality reasons.

Table 4.1.: Mass of submerged bio-composite material during the summer and winter season conditions per 1 m of length of canal bank protection.

Material	Flow Regime	Mass of submerged material per 1 m length (kg/m)
M1	Summer	1.032
	Winter	3.096
M2	Summer	1.032
	Winter	3.096
M3	Summer	1.068
	Winter	3.204
M4	Summer	0.828
	Winter	2.484

4.3.2. COLUMN LEACHING TESTS

To analyse the potential leaching of heavy metals and resin compounds from bio-composite materials in an aquatic environment, percolation column leaching tests were carried out, following Dutch standard Guidelines [23] and U.S.E.P.A. Method 1314 [22]. Percolation test, called column leaching test in this study, is a dynamic leaching test method which requires the continuous renewal of the influent. Column leaching test method was selected based on the purpose of the study: evaluate the potential leaching from new bio-composite canal bank protection in surface water (canals at almost constant pH and various flow rates). As mentioned in section 4.2, Bridson et al. [18] suggested to select carefully the leaching test method based on the environmental conditions. In the present study, canal bank protection elements, submerged in surface water canals, were analysed in terms of their potential leaching. Thus, a test that took into account a constant renewal of the influent, by using a pump providing fresh influent continuously to the columns, was preferable. Figure 4.2 shows the experimental setup.
The bio-composite materials were ground to a particle size up to 4 mm and packed in sealed glass columns (0.3 kg of material in each column) to a height of 20 cm. Gauze and quartz sand ($20-30$ mesh) were used as filters at the bottom and the top of the columns. A buffered ultra-pure water at pH 7.00 ± 0.2 was used as influent for the experiments. The columns were operated at a specific liquid-solid ratio (L/S). The liquid to solid ratio is defined as the fraction of the total liquid volume (including the moisture contained in the "as-used" solid sample) to the dry mass

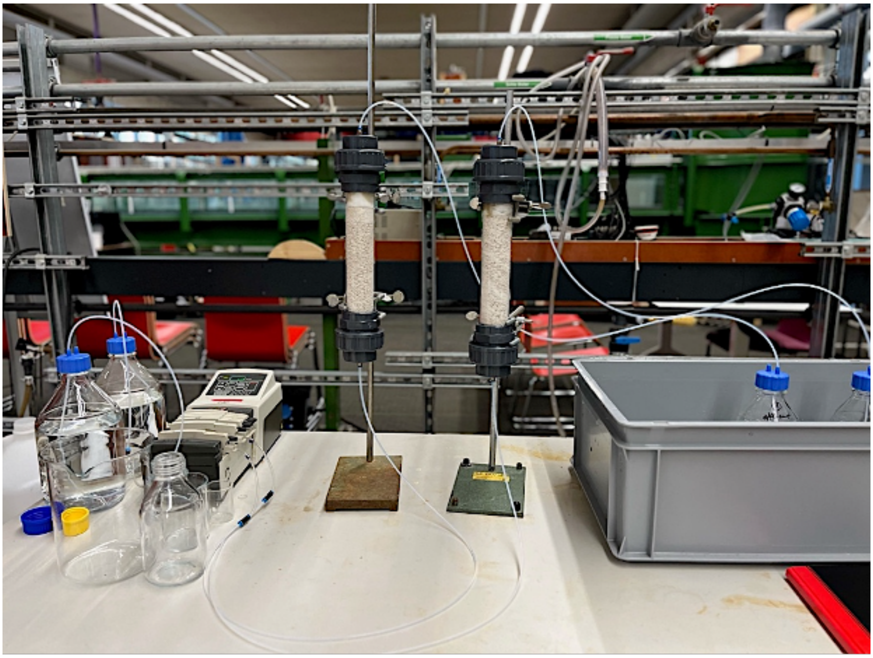

Figure 4.2.: Experimental setup for column leaching tests.

equivalent of the solid material. L/S is typically expressed in volume units of liquid per dry mass of solid material (ml/g-dry) [22]. A flow rate of 9 ml/h was chosen to maintain the liquid-solid ratio between $0.5 - 1.0$ l/kg per day, specifically about 0.72 l/kg in this case, to facilitate the higher probability of achieving local equilibrium between the solid and liquid phase [22]. The effluent samples to be analysed were selected on the basis of the liquid-solid ratio as specified in the leaching tests standard and guidelines [22, 23], as shown in Table 4.2. Four 24 h composite samples (shown in blue in Table 4.2) were collected on days 1, 2, 6, and 13 of the two-week periods for which the leaching tests lasted. The effluent samples were collected and stored in the fridge at 4°C, until further analysis. Analyses for resin compounds (styrene and furfuryl alcohol), were performed within one week of sampling as both styrene and furfuryl alcohol are VOCs (Volatile Organic Compounds). All leaching tests were carried out in duplicates. ICP-MS was used to measure the concentrations of heavy metals in water samples. The samples were homogenized and acidified (HNO_3), after which the analysis was performed from the liquid phase. GC-MS was used to measure styrene in water samples. HPLC-UV was used for measuring furfuryl alcohol in the samples.

Table 4.2.: Effluent fractions sampling based on NEN7373 [23], and USEPA Method 1314 [22] Guidelines.

Daily Sample [-]	V [l]	S [kg]	L/S [l/kg]
1	$2.2 \cdot 10^{-1}$	$3.0 \cdot 10^{-1}$	$7.2 \cdot 10^{-1}$
2	$4.3 \cdot 10^{-1}$	$3.0 \cdot 10^{-1}$	$1.44 \cdot 10^{0}$
3	$6.5 \cdot 10^{-1}$	$3.0 \cdot 10^{-1}$	$2.16\ 10^{0}$
4	$8.6 \cdot 10^{-1}$	$3.0 \cdot 10^{-1}$	$2.88 \cdot 10^{0}$
5	$1.08 \cdot 10^{0}$	$3.0 \cdot 10^{-1}$	$3.60 \cdot 10^{0}$
6	$1.30 \cdot 10^{0}$	$3.0 \cdot 10^{-1}$	$4.32 \cdot 10^{0}$
7	$1.51 \cdot 10^{0}$	$3.0 \cdot 10^{-1}$	$5.04 \cdot 10^{0}$
8	$1.73 \cdot 10^{0}$	$3.0 \cdot 10^{-1}$	$5.76 \cdot 10^{0}$
9	$1.94 \cdot 10^{0}$	$3.0 \cdot 10^{-1}$	$6.48 \cdot 10^{0}$
10	$2.16 \cdot 10^{0}$	$3.0 \cdot 10^{-1}$	$7.20 \cdot 10^{0}$
11	$2.38 \cdot 10^{0}$	$3.0 \cdot 10^{-1}$	$7.92 \cdot 10^{0}$
12	$2.59 \cdot 10^{0}$	$3.0 \cdot 10^{-1}$	$8.64 \cdot 10^{0}$
13	$2.81 \cdot 10^{0}$	$3.0 \cdot 10^{-1}$	$9.36 \cdot 10^{0}$

4.3.3. ENVIRONMENTAL RISK ASSESSMENT

The environmental risk assessment framework used in this study [11], is based on European guidelines and the RIVM Dutch guide lines [12], and shown in Figure 4.3.

Environmental risk assessment (ERA) is a method used to evaluate the environmental safety of manufactured products, focusing on the potential impacts of pollutants on ecosystems, including various species and the long-term consequences of contaminant releases. The ERA framework, based on European guidelines, categorizes environmental compartments such as seawater, freshwater, soil, and identifies affected species such as fish, algae, and microorganisms.

The ERA framework involves the following four main steps:

- Hazard identification: The leaching effluents exhibited the presence of heavy metals and resin compounds.

- Dose-response model: Freshwater (surface water in which the canal bank protection elements are applied) is selected as the receiving ecosystem. The Predicted No Effect Concentrations (PNEC) for freshwater were collected from European Chemical Agency (ECHA) database [10]. The PNEC represents the concentration of a substance below which adverse effects are unlikely to occur in both long-term and short-term exposure scenarios. Table 4.3 shows the PNEC values in [μg/l].

- Exposure assessment: The Predicted Effects Concentration (PEC) is

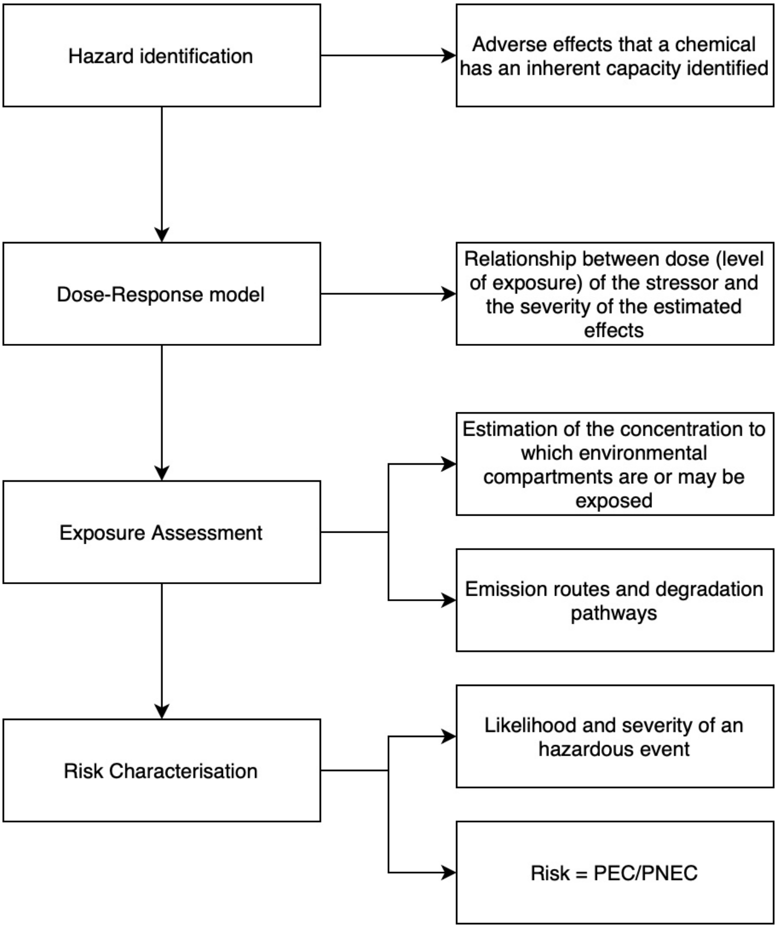

Figure 4.3.: Scheme of the environmental risk assessment based on the European and RIVM Dutch Guidelines.

the predicted environmental concentration of the contaminant. The next step is to assess whether the pollutant can pose a threat at this concentration. The PECs have been estimated for various environmental conditions, which are explained in section 4.3.4. The input data for this exposure assessment were derived from the laboratory leaching tests. These data were used to calculate the potential concentrations in the real case scenarios, taking into account key factors such as the dimensions of the bank protection and the canal, as well as the flow rates (section 4.3.4).

- Risk characterization: the environmental risk was calculated as follows:

$$Risk = \frac{PEC}{PNEC} \quad (4.1)$$

When the PEC/PNEC ratio is below the threshold of 1.00 set by the European and Dutch guidelines, the risk level is considered acceptable [11, 12]. A value exceeding the threshold of 1.00 indicates that the PEC is greater than the PNEC and is therefore not an acceptable outcome.

Table 4.3.: List of PNEC values from the ECHA database [10].

Chemical [-]	**PNEC [μg/l]**
Hg	$5.70 \cdot 10^{-2}$
Ba	$1.15 \cdot 10^{2}$
B	$2.90 \cdot 10^{3}$
Co	$1.06 \cdot 10^{0}$
Cu	$6.30 \cdot 10^{0}$
Li	$1.65 \cdot 10^{3}$
Mn	$3.40 \cdot 10^{1}$
Mo	$1.19 \cdot 10^{4}$
Sn	$3.70 \cdot 10^{1}$
V	$4.10 \cdot 10^{0}$
Zn	$1.44 \cdot 10^{1}$
Cd	$1.90 \cdot 10^{-1}$
Cr	$6.50 \cdot 10^{0}$
Ni	$2.00 \cdot 10^{1}$
Pb	$2.40 \cdot 10^{0}$
As	$5.60 \cdot 10^{0}$
C_8H_8	$2.80 \cdot 10^{1}$
$C_5H_6O_2$	$1.70 \cdot 10^{2}$

The above ERA methodology was conducted using the following assumptions:

1. No further degradation or transformation of the leached chemicals occurs in the canal.

2. Leached chemicals are instantaneously mixed with canal water and no Brownian motion occurs.

4.3.4. LEACHING SCENARIO

Two case studies, stagnant water and advective flow, were analysed to simulate different real-world flow conditions. These two cases were analysed each for two different types of canals (wide ditch and primary watercourse, described in subsection 4.3.1), and for winter and summer conditions resulting in a total of eight cases. The description of the case studies (stagnant water and advective flow) is given below.

1. Stagnant water case: When the pumping station is off, the scenario assumes instantaneous mixing and no Brownian motion. Both summer and winter conditions were evaluated for the wide ditch and the primary watercourse. Contaminant concentrations in the water, based on leaching from the canal bank protection elements were calculated for all four bio-composite materials.

2. Advective flow case: the pumping station operates 800 hours per year. Both the wide ditch and the primary watercourse were evaluated under summer and winter conditions. The contaminant concentrations in the water, based on leaching from the canal bank protection elements were calculated for all four bio-composite materials.

The environmental risk was assessed using both a deterministic approach and a stochastic approach (using the Monte Carlo method) in all 8 cases mentioned above. The deterministic approach was used to assess whether one or more chemicals exceeded the safety threshold. The stochastic approach was used to perform a sensitivity analysis. This was done by using the Monte Carlo method to evaluate how the environmental risk varies with different input data such as leaching concentration and water velocity. Two sensitivity cases were analysed:

1. Sensitivity case 1 (s1): simulation of leaching concentrations using a uniform distribution based on leaching test results. Two batches of data were collected from the duplicate tests: one from column 1 (effluent 1) and one from column 2 (effluent 2) for day 1. The objective of this sensitivity analysis was to assess how the environmental risk level varies with different leaching concentrations.

2. Sensitivity case 2 (s2): various water velocities and consequently various flow rates were considered, ranging from a minimum value of 0.2 m/h (representing the "almost no flow conditions") to a maximum value of 270 m/h corresponding to the pumping station in full operation on the primary watercourse. The water velocity was simulated using a normal distribution, with the mean and standard deviation calculated geometrically based on the generated vector. The objective of this scenario was to evaluate how the environmental level varies with flow rates and flow velocities.

To simulate the real-world conditions, leaching test data were used as input to predict the potential release of chemicals in the real case for both the wide ditch and primary watercourse and for both the stagnant and advective scenario, taking into account the seasonal variation in flow rate. First, the mass of contaminants released per day under laboratory leaching test conditions was calculated. The equivalent mass released from the submerged bio-composite canal bank protection elements was then calculated. These calculations considered both winter and summer conditions as shown in the following equations:

$$M1_s = C_L \cdot Vol_L \cdot \frac{M_{sub,s}}{M_L} \tag{4.2}$$

$$M1_w = C_L \cdot Vol_L \cdot \frac{M_{sub,w}}{M_L} \tag{4.3}$$

where:

- $M1_s$ and $M1_w$ are the masses released over 1 meter of canal bank from both sides in one day during the summer conditions ($M1_s$) and winter conditions ($M1_w$), respectively [mg].
- C_L is the concentration from the laboratory leaching test at day 1 [mg/l].
- V_L is the effluent volume of the leaching tests in 24 hours [l].
- $M_{sub,s}$ and $M_{sub,w}$ are the mass of the bio-composite submerged in the water [kg], over 1 meter of canal length, at both sides, during the summer conditions ($M_{sub,s}$) and winter conditions ($M_{sub,w}$), respectively, listed in Table 4.1.

$M1_s$ and $M1_w$ were then used as input to calculate the actual leaching concentrations firstly for the stagnant water scenario and then for the advective flow scenario. The concentrations for both summer and winter conditions for both stagnant and advective cases are given by Equations 4.4, 4.5, 4.6 and 4.7, respectively.

$$C1_{stagnant,s} = \frac{M1_{stagnant,s}}{Vol_{w,s}} \tag{4.4}$$

$$C1_{stagnant,w} = \frac{M1_{stagnant,w}}{Vol_{w,w}} \tag{4.5}$$

$$C1_{Q,s} = \frac{M1_{Q,s}}{Vol_{w,s} \cdot F_s} \tag{4.6}$$

$$C1_{Q,w} = \frac{M1_{Q,w}}{Vol_{w,w} \cdot F_w} \tag{4.7}$$

Where:

- $C1_{stagnant,s}$ and $C1_{stagnant,w}$, are the concentrations that will be present in the canal compartment of 1 m length due to the leaching under stagnant case, for summer conditions ($C1_{stagnant,s}$) and winter conditions ($C1_{stagnant,w}$), respectively [mg/m^3] [3].
- $M1_{stagnant,s}$ and $M1_{stagnant,w}$ are the released concentrations from the canal bank in one day calculated by using Eq. 4.2 and Eq. 4.3 [mg] under stagnant case for summer ($M1_{stagnant,s}$) and winter ($M1_{stagnant,w}$) conditions, respectively.
- $Vol_{w,s}$ and $Vol_{w,w}$ are the volumes of water per 1 m of canal length, dependent on the water level in summer conditions ($Vol_{w,s}$) and winter conditions ($Vol_{w,w}$), respectively [m^3].
- $C1_{Q,s}$ and $C1_{Q,w}$, are the concentrations that will be present in the canal compartment of 1 m length due to the leaching under adevctive flow conditions for both summer ($C1_{Q,s}$) and winter ($C1_{Q,w}$) conditions, respectively [mg/m^3].
- F_s and F_w are factors that represent the number of times the volume of water is renewed under summer (F_s) and winter (F_w) conditions in 1 m compartment per day. The factor F is calculated as follows:

$$F = \frac{Q}{V} \tag{4.8}$$

where Q is the flow rate in the canal in [m^3/day] and V is the volume of water [m^3] for 1 m length of canal.

4.4. RESULTS AND DISCUSSION

4.4.1. LEACHING TESTS

The leaching test results for four different bio-composite materials (M1-M4) are shown in Figure 4.4.
As can be seen from Figure 4.4, some heavy metals such as Co, Cu, Mn, Sn, Zn, Cd, Cr, Ni, and Pb leached from all four materials at significantly high concentrations ranging from 100 to $10,000$ μg/l. In addition, styrene (in M1, M2 and M3) and furfuryl alcohol (in M4) were identified as resin compounds leaching from the bio-composite materials with the highest leachate concentrations up to $10,000$ μg/l. In the column tests, the highest releases were observed at L/S ratio of 0.2 L/kg on day 1 and 0.5 L/kg on day 2, at a pH level 7.00 ± 0.2. These results are aligned with the findings reported by van der Sloot and Kosson [17].

[3]These concentrations are then expressed in μg/l for comparison with the PNEC values collected for the freshwater compartment.

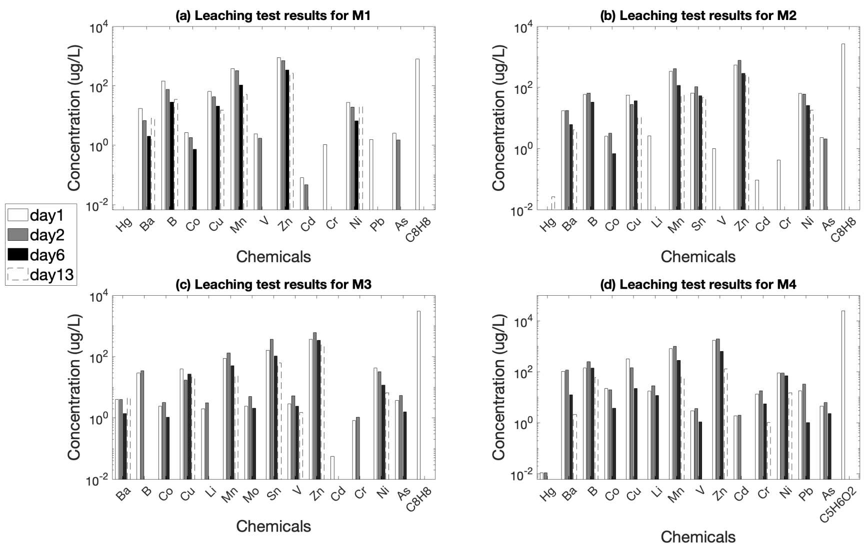

Figure 4.4.: Leaching test results for all four bio-composite materials.

As shown in Figure 4.4, the concentration of various heavy metals such as Ba, Cu, Mn, Zn, Cr, Ni, Pb, and As in the leaching effluent was higher on the second day than on the first day, for all four bio-composite materials. After 24 hours, heavy metals could potentially be released in higher amounts compared to the leaching concentrations observed on day 1. Several factors influence the leaching behaviour, such as variability of pH of the effluent or the intensity of the flow rate. Cappuyns and Swennen [19] conducted research on the mobility of heavy metals due to the leaching, as described in section 4.2 of this chapter. However, in the leaching tests performed here on new bio-composite materials, the pH remained constant due to the consistent influent characteristics (buffered ultra-pure water with a pH of 7.00 ± 0.2). No acidification of the samples was introduced to replicate various environmental conditions such as rainfall events. The collection of effluent samples, pH measurements were consistently monitored. The monitoring results obtained showed a near constant pH value between 6.8 and 7.2. Therefore, the observed leaching behaviour cannot be related to pH variation but is likely to be related to other factors such as slow flow rate, amount of contaminant in the bio-composite materials analysed and freshness of the materials. Details of the observed leaching behaviour are discussed below.

As it can be seen from Figure 4.4, the observed gradual dissolution of metal compounds is subject to a time delay. The delay may be attributed to the low infiltration rate resulting from a slow flow rate (set at 9 ml/h).

The reduced infiltration rate causes the water to move slowly through the solid material, resulting in a gradual release of the metals over time rather than an immediate response. The delay was observed only at day 2, then the leaching concentrations showed a gradual decrease until day 13, as expected.

Another factor that can influence leaching was observed to be the freshness of the samples tested. The bio-composite materials M1, M2 and M3, although containing a similar amount of polyester resin, showed a significant difference in styrene leaching, as shown in Figure 4.4 (a), (b) and (c) representing the leaching of M1, M2 and M3, respectively. This discrepancy in styrene leaching concentration could possibly be attributed to the freshness of the materials, knowing that styrene is a volatile organic compound. These observed results are in line with the findings of Dandautiya et al. [24], that in their study analysed a fresh and a weathered sample 30 days after its disposal of fly ash. The aged material was not representative of the long-term effects (weathered of 30 days), which observed a lower leaching in the weathered samples compared to the fresh samples even if the authors analysed a short-time age difference such as 30 days. In the present study, materials M2 and M3 were analysed shortly after their production while material M1 was produced several years before the leaching tests.

According to the safety data sheets and knowing the composition of the materials, it was possible to estimate the percentage of release of styrene for M1, M2 and M3 and furfuryl alcohol for M4. The percentage release, or release rate, indicates the mass of a substance, in this case styrene and furfuryl alcohol, released relative to the initial mass of these substances in the corresponding fresh material. Due to the confidentiality of material composition information, only the estimated (i.e., calculated) percentage release results obtained during leaching tests are presented in Table 4.4.

Table 4.4.: Estimated percentage of release of chemicals during leaching.

Chemicals	**M1**	**M2**	**M3**	**M4**
Styrene (C_8H_8)	0.0011%	0.0038%	0.0042%	Not present
Furfuryl Alcohol ($C_5H_6O_2$)	Not present	Not present	Not present	0.47%

As it can be seen from this table, the release of resin compounds is low compared to the total amount present in the original bio-composite. Furthermore, as styrene is a volatile compound, it is plausible that material M1, being the oldest of styrene-containing materials tested and having an initial amount of resin comparable to M2 and M3, showed a lower release of styrene in the water samples. Similarly, the bio-composite material M4 was subjected to analysis shortly after its manufacture. However, the lack of a second sample containing furfuryl alcohol precluded any conclusion regarding the effect of volatilisation.

The cumulative release curves for leached heavy metals from four analysed materials are shown in Figure 4.5. As it can be seen from this figure, leaching is mainly influenced by the content of heavy metal in the bio-composite material. A deeper analysis of the cumulative release curves reveals that certain metals such as Co, Cr, and V exhibit a pronounced slope across all four materials. This indicates a rapid release of the chemical (high leaching), driven by a strong dissolution force of the substance in the eluent. As time progresses (beyond one week), the curve levels out and reaches a plateau. This plateau indicates a significant slowdown in the leaching process, accompanied by a reduction in the driving force, resulting in the dissolution rate no longer being as rapid as in the initial stages. Analysing this plateau is crucial for understanding the leaching behaviour. In previous literature, van der Sloot and Kosson [17] and Cappuyns and Swennen[19], observed a similar trend in the release of heavy metals due to the leaching. In the first study [13, 17], the plateau suggested that the solution had become saturated with the solute, implying that the introduced liquid (influent) could no longer dissolve more of the substance as it had reached its maximum solubility under the prevailing conditions. In the second study [19], was observed the gradient concentration as influential parameter for the leaching behaviour. Thus, the driving force is the concentration gradient between the solution analysed for leaching and the fresh influent, reaching the chemical equilibrium at the observable plateau. In this study, concerning the leaching from the novel bio-composite materials, the influent was renewed without recirculation. Therefore, it would be inaccurate to describe the effluent solution as saturated; it probably depends only on the number of heavy metals in the bio-composite and the driving force driving the leaching is represented by the concentration gradient. More data and information are needed to perform more accurate analyses, i.e., to establish with larger accuracy why the plateau was observed in the cumulative release curves.
Figure 4.5 displays the cumulative release for Co in M1, As in M2, Cr in M3 and V in M4, respectively. Further details about cumulative release curve can be found in the Supplementary Material B.

4.4.2. ENVIRONMENTAL RISKS OF LEACHING FROM CANAL BANK PROTECTION ELEMENTS MADE OF BIO-COMPOSITE MATERIALS

The study evaluated the effectiveness of the methodological approach to assess the leaching of heavy metals and resin compounds from novel bio-composite materials in the aquatic environment, in the absence of on-site data. This section addresses the efficacy of the proposed methodology. The laboratory leaching tests demonstrated the suitability of this approach in simulating real-world conditions, providing a reliable basis for assessing leaching behaviour of novel bio-composite materials. The

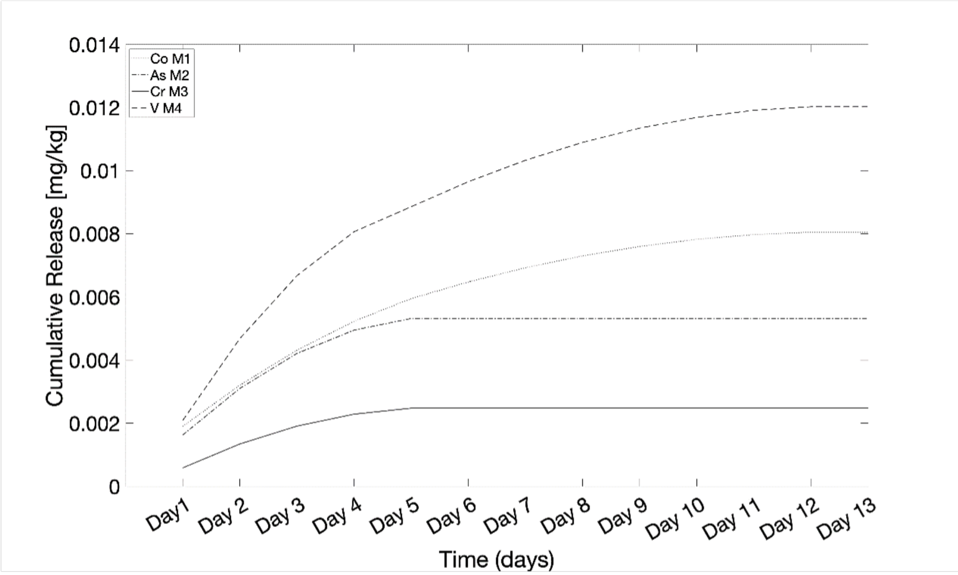

Figure 4.5.: Cumulative release of Co leached from M1, As released from M2, Cr leached from M3, and V released from M4.

tests were able to simulate two different real case scenarios: (i) stagnant conditions; and (ii) advective conditions. The cost-effectiveness of employing this proposed methodology in assessing the environmental impact of these novel materials is enhanced by the possibility of predicting leaching behaviour without on-site data.

To simulate the real conditions, all cases were evaluated by considering only the first day of leaching results as the worst-case scenario. Although certain metals exhibited higher leaching values on day 2, it was decided to consider the first day as the worst-case scenario. This decision takes into account the volatile nature of styrene and furfuryl alcohol, for which the leaching tests were limited to a 24-hour time range. For the heavy metals, the differences between the first day and second day were very limited. With regard to the winter and summer conditions only the results for winter season conditions are shown, representing the worst-case scenario with elevated water levels in the canal resulting in a greater fraction of bio-composite material below the water level. Consequently, higher quantities of heavy metals and resin compounds may leach into the water from the bio-composite material under these conditions. Additional information concerning the summer season conditions can be found in the Supplementary Material B.

4.4.3. DETERMINISTIC ENVIRONMENTAL RISK ASSESSMENT

Figure 4.6 shows the environmental risk assessment results on the day 1 (expressed as PEC/PNEC ratios) for all bio-composite materials, for stagnant and advective flow conditions for both wide ditch and primary watercourse type canals.

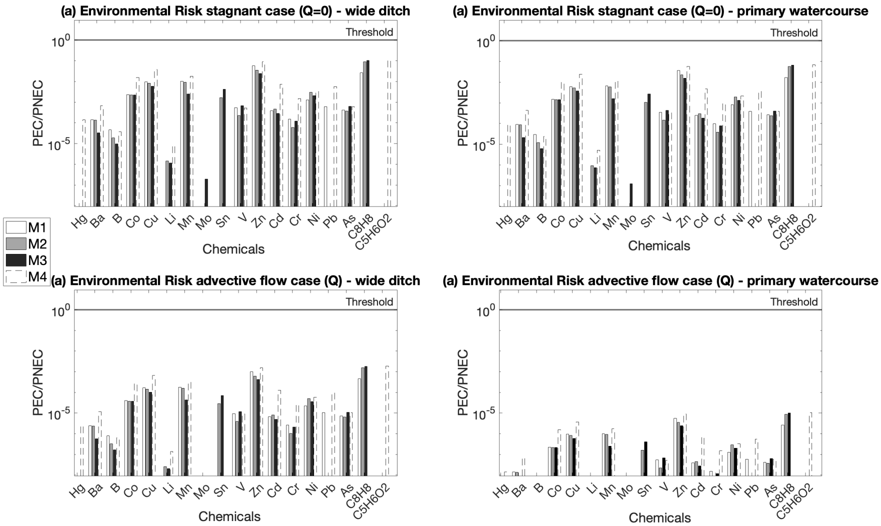

Figure 4.6.: Environmental risk expressed as PEC/PNEC ratio on day 1 for stagnant and advective flow conditions for both wide ditch and primary watercourse.

As it can be seen from Figure 4.6, all environmental risks under all conditions are below the threshold for all four bio-composite materials.
A comparison of the results of the stagnant water and advective flow cases reveals that the stagnant case, as illustrated in Figure 4.6 (a) and (b) for the wide ditch, and primary watercourse, respectively, yielded higher PEC/PNEC ratios for all the chemicals analysed. This is because in the stagnant case, where there is no flow, the assumed instantaneous mixing resulted in retention of chemicals in the water without transport. Unlike this, in the advective flow case, shown in Figure 4.6 (c) for a wide ditch and Figure 4.6 (d) for a primary watercourse, the presence of a flow rate allows the transportation of chemicals, leading to further dilution. This results in lower PEC/PNEC ratios for the advective case for both the wide ditch and primary watercourse. Further, when comparing the wide ditch results with the primary watercourse results lower PEC/PNEC ratios were observed for the primary watercourse in both stagnant and advective cases. This can be attributed to the larger dimensions of the primary watercourse, resulting in a greater volume of water and, consequently

increased dilution in the primary watercourse.
The environmental risk assessment carried out in this study does not take into account the fate of chemicals released and subsequent effects, due to the lack of onsite data. For example, certain metals such as Pb, Zn and Cu exhibit significant bio-accumulative properties, while some metals can react with oxygen, leading to the formation of toxic substances [25]. Furthermore, leaching behaviour is strongly influenced by the factors that represent environmental conditions, such as the pH, eluent temperature, and redox conditions [19]. Given the aforementioned lack of on-site information, this study employs laboratory leaching tests to simulate real-world scenarios, focusing solely on assessing the environmental impact of using these new bio-composite materials in aquatic environments. The availability of on-site data, such as chemical analysis of water and/or sediment samples, would have provided a more complete picture of the leaching behaviour of these materials in a surface water canal. This data would have been useful for assessing not only the level of leaching but also the potential chemical reactions of leached elements with the oxygen present in the water. This includes analysing the likelihood of the formation of toxic compounds such as oxidates, which provides critical insight into the overall environmental impact. Furthermore, on-site data is also valuable in defining the reliability of the laboratory tests carried out by comparing the results obtained with the chemical analyses carried out in the field.

4.4.4. STOCHASTIC ENVIRONMENTAL RISK ASSESSMENT

The limitations associated with an environmental risk assessment based only on laboratory data were mitigated by implementing a stochastic approach. In this approach, variables such as leaching concentrations and water flow velocities were assumed uncertain. The aim was to analyse the potential impact of realistic variations in these values that could exist in real world conditions and could be obtained through field testing rather than controlled laboratory experiments. The purpose of this analysis was to determine whether such variations could affect the overall environmental risk levels, increasing the PEC/PNEC values above the threshold of 1.00.
The stochastic approach is based on the Monte Carlo method with $10,000$ trials. The selection of $10,000$ trials was based on the observation that no significant changes were observed when the number of iterations was increased beyond this value (not shown here). Two sensitivity cases were modelled, s1 with uncertain leaching concentrations and s2 with uncertain water velocity, both using pre-specified probability density functions, as described in section 4.3.4. The eight cases mentioned in the previous section were also analysed here. Regarding the stagnant water case, only the variations in leaching concentrations were considered, as there

is no flow in that scenario. Materials M3 and M4 were chosen as representative worst-case materials as they showed the highest leaching in terms of styrene (M3) and furfuryl alcohol (M4), as can be observed from Table 4.4.
The results obtained for the wide ditch, stagnant water, winter condition and materials M3 and M4 are shown in Figure 4.7 and Figure 4.8, respectively. As it can be seen from this figure, the environmental risk levels, expressed by the PEC/PNEC ratios, are all below the threshold of 1.00. The primary watercourse is characterized by a larger volume of water resulting with a higher dilution for the stagnant scenario, which significantly reduces the PEC concentrations. Consequently, the environmental risk levels expressed as PEC/PNEC ratios are even lower for the primary watercourse (results not shown).

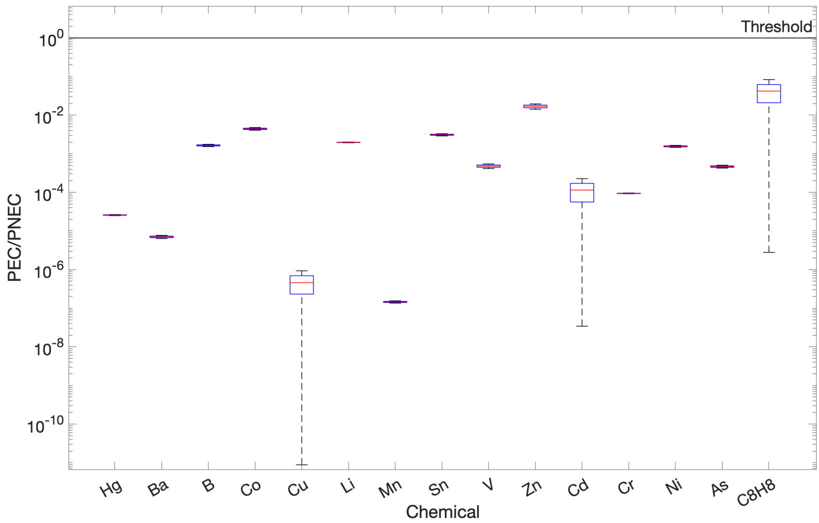

Figure 4.7.: Environmental risk expressed as PEC/PNEC ratio on day 1 for the wide ditch, stagnant case: sensitivity s1 case, for M3.

The results obtained for the sensitivity case s1 for the wide ditch, which represents the stagnant case for M3 and M4 on day 1 (Figure 4.7 and Figure 4.8), showed minimal deviation from the deterministic approach (Figure 4.6(a)). This is because the leaching concentrations were modelled using a narrow uniform distribution, aligning well with experimental data. The range of values used to simulate the uniform distribution was based on the analyses of the effluent 1 (1^{st} column) and effluent 2 (2^{nd} column) from the conducted leaching tests. These results of both columns demonstrated a high level of concordance and showed minimal discrepancies. Consequently, the results observed from this s1 sensi-

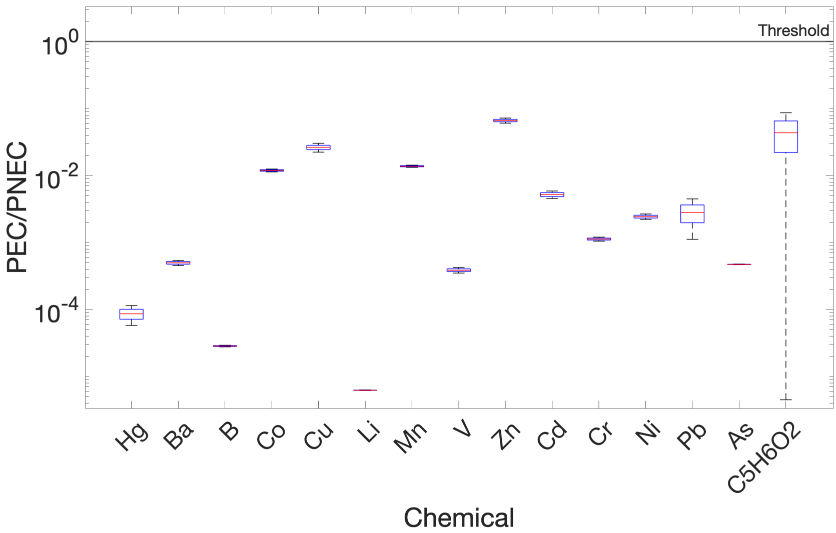

Figure 4.8.: Environmental risk expressed as PEC/PNEC ratio on day 1 for wide ditch, stagnant case: sensitivity s1 case, for M4.

tivity case matched well with the deterministic obtained results. The inclusion of field data would have further improved the sensitivity analysis, providing the chance to consider a wider range of values and thus a more complete evaluation of potential variations in the results.

The results for sensitivity case s2 (different water velocities at fixed leaching concentrations) in the advective flow scenario for wide ditch and are shown in Figures 4.9 and Figure 4.10, for M3 and M4, respectively. The water velocity was modelled by using normal distributions as described in section 4.3.4.

As it can be seen from Figures 4.9 and Figure 4.10, the results obtained indicate a significant variation in the PEC/PNEC values over a range of 10^{-09} to 10^{-02} and precisely a PEC/PNEC ratio about 0.108 for furfuryl alcohol in M4, as observed in Figure 4.10. This can be attributed to the changes in the water velocities. The maximum values of PEC/PNEC ratios were obtained at minimum water velocity, for the reasons mentioned before.

The sensitivity analysis indicates that water velocity, and therefore flow rate, is the most influential input environmental parameter affecting the outputs. As expected, higher flow rates increase dilution, and lead to lower PEC values. This is consistent with the results of the deterministic approach and further confirms that stagnant conditions (no flow) combined with varying leachate concentrations represent the worst-case scenario.

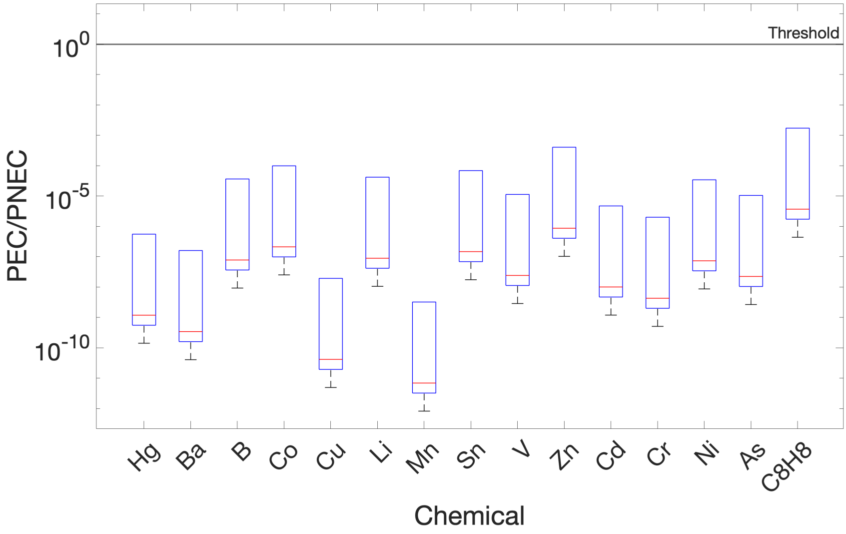

Figure 4.9.: Environmental risk expressed as PEC/PNEC ratio, for advective flow on day 1, wide ditch: sensitivity s2 case for M3.

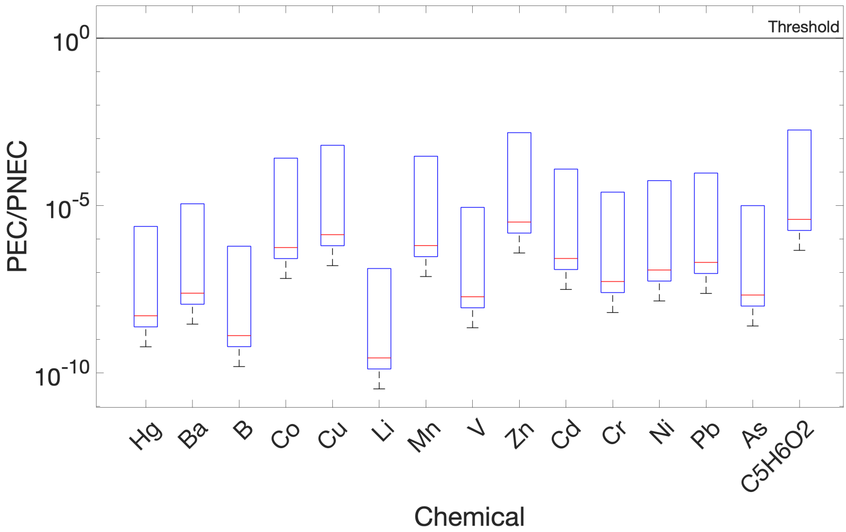

Figure 4.10.: Environmental risk expressed as PEC/PNEC ratio, for advective flow on day 1, wide ditch: sensitivity s2 case for M4.

4.5. CONCLUSIONS

The objective of this study was to develop a methodology and present associated results obtained for the environmental risk assessment associated with the potential leaching of toxic substances from four new types of bio-composite materials used in the production of canal bank protection elements. A comprehensive set of laboratories leaching tests were carried out to generate input data for this assessment. Eight cases of potential leaching were analysed by performing the risk analyses for two flow conditions (stagnant water and advective flow) in two types of canals (wide ditch and primary watercourse) and for two flow rates (low and high, corresponding to summer and winter conditions respectively). Both deterministic and stochastic environmental risk assessment approaches were used, the former to assess the environmental risks and the latter to assess the sensitivity of the results obtained in the deterministic case due to uncertainties in leaching concentrations and water velocities (i.e., flow rates).

The leaching tests yielded results that could be used as input for the environmental risk assessment. The results indicated that the release of toxic substances remains within acceptable limits, as the PEC/PNEC ratios did not exceed the environmental threshold of 1.00 in all cases analysed. However, under stagnant conditions in the wide ditch, certain chemicals showed slightly higher PEC/PNEC ratios compared to the other cases. Specifically, furfuryl alcohol for material M4 had the highest PEC/PNEC ratio of 0.108, which was closest to the threshold of 1.00. Zn was the second chemical for material M4, approaching the threshold of 1.00 under stagnant conditions with a PEC/PNEC ratio of 0.00898. For materials M1, M2, and M3, Zn and styrene showed the highest PEC/PNEC values in stagnant scenarios. The sensitivity analysis performed in this study indicated that water velocity and thus flow rate is the most influential input parameter affecting the outputs.

Overall, the findings obtained show the importance of monitoring and managing aforementioned chemicals, especially under specific environmental conditions, to ensure the protection of the ecosystem. It would also be interesting to assess the potential risks to human health from the use of these new bio-composite materials, for example by analysing human contact with water during recreational activities such as swimming in the canals. However, this assessment is out of the scope of this study, i.e., this remains to be done as part of future work.

The obtained results are only indicative at this stage, as these are based on laboratory leaching tests and a number of assumptions mentioned in section 4.3.3. To further validate the accuracy of the approach of combining laboratory leaching tests with environmental risk assessment, additional field tests are required to collect water and sediment samples from the canal where the bank protection elements are located over a longer period of time. Analysis of these field samples will provide an overview of the water quality and also the actual leaching of toxic substances. Furthermore, these field tests would provide valuable information on the effects of dilution in the real-case scenarios, which is a significant parameter in determining whether the leaching concentration of a specific chemical is within the environmental risk limits. In addition to field tests, simulation of flow rate conditions, particularly “almost no flow” conditions, could be improved by using more detailed mixing models rather than the assumed instantaneous mixing used in this work.

Despite the above considerations, the integration of leaching tests with the environmental risk assessment methodology, as outlined in this study, has proven its effectiveness in assessing the risks associated with the use of new bio-composite materials. This combined approach is significant for its applicability to various other implementations of bio-composite materials, ranging from building façade elements to water level scales installed in canals.

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RISK OF RAINFALL CAUSED LEACHING FROM BIO-COMPOSITE MATERIAL BASED BUILDING FAÇADES INTO THE AQUATIC ENVIRONMENT

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This chapter is based on: Nativio, A., Jovanovic, O., van der Hoek, J.P., & Kapelan, Z., Risk of Rainfall Caused Leaching from Bio-Composite Material based Building Façades into the Aquatic Environment (submitted for publication)

5.1. ABSTRACT

The increasing focus on sustainability and circularity is driving the global production of environmentally friendly products. The Netherlands has emerged to produce new bio-composite materials, which are created by reclaiming resources from various sectors of the water industry. These innovative materials are being used in various applications, including façade elements in buildings, providing a sustainable alternative to traditional materials such as aluminium, ceramic, glass and wood. Although these new materials have ecological appeal, it is important to investigate the impact on the natural environment. To address this issue, a systematic methodology to assess environmental risks is crucial, yet such a methodology is notably lacking. This paper introduces such a methodology based on comprehensive experimental work. The proposed methodology is based on the following key stages: (i) existing environmental risk assessment framework; (ii) collection of data from database of European Chemical Agency; (iii) laboratory work: sample preparation and leaching tests. Because the novelty of the bio-composite materials, onsite leaching data were not available. Two new bio-composite materials were analysed. Each material was tested in its new and weathered forms, the latter being subject to cyclic UV irradiation and high humidity to simulate weather conditions. First, two rainfall intensities were selected using the Koninklijk Nederlands Meteorologisch Instituut (KNMI) database, followed by laboratory work including the preparation of synthetic rainwater and leaching tests to determine the potential release of specific chemical substances, such as heavy metals and resin compounds, under different rainfall conditions, The leaching concentrations obtained from these tests were then assessed for their potential impact on surface water quality. Using laboratory test outcomes as a basis, the risk assessment for potential leaching from façade elements into surface waters was conducted. Two scenarios of leaching were analysed, a single rain event of intensity 5 mm/h and duration of 1 hour, and a single rain event of intensity 15 mm/h and duration of 1 hour. The results obtained reveal disparate leaching behaviour among the new and weathered samples, as well as between the two material types, depending on the rain intensity. in order to overcome the uncertainties caused by the limited input data available, a sensitivity analysis was carried out by first varying the leaching concentrations and then the rainfall intensity. The aim was to evaluate the changes in the PEC/PNEC ratio as a function of these two input parameters and to gain a better understanding of the leaching behaviour as a function of these two parameters. Still, the environmental risk associated with both materials and for both sample types remained below the safety threshold for all rainfall conditions studied. While these findings are representative of real-case scenarios, they should be considered indicative only due to their reliance on laboratory tests and conditions and the assumptions inherent in such a setting.

To obtain more definitive conclusions, further laboratory studies and especially field tests should be conducted, particularly those evaluating leaching dynamics over time.

5.2. INTRODUCTION

The climate crisis is becoming a priority for most of the industries in the world, specifically in Europe. Affinity towards the use of green solutions, renewable resources, and materials with a lower environmental impact is increasing and resulting in an added value in the market reducing the greenhouses gas emission [1].
Sustainable and green materials are increasingly used in various applications such as packaging, automotive industries, agriculture, and medicine [2]. A new type of bio-composite material made from water resources is now being produced in the Netherlands. However, the use of these novel materials, even though made from natural resources, may pose a concern in terms of environmental risk due to the potential chemical contaminants of the new materials, introduced by the raw materials used. Extended exposure to environmental factors such as sunlight, rain, snow, and wind, may degrade material quality, leading to environmental concerns due to the potential release of pollutants or the increased need for environmentally intensive replacement.
New bio-composite materials, that are subject of this study, are made from resources recovered from the water cycle as described by [3]. The aforementioned water sources are likely to be contaminated with heavy metals, including Ba, B, Mn, and Zn [4], which may pose a risk to both human health and the environment. Furthermore, bio-composite materials, like other composite materials, use resins such as polyester-based or furan resins, which contain hazardous substances such as styrene and furfuryl alcohol. The new type of bio-composites is mostly being used in applications in aquatic environments as water level scales, and canal bank protection elements. However, they are also finding applications as building façade elements.
Based on the scientific literature, referred to this section, and industry regulations [5], the main concern regarding traditional façades is the leaching of biocides from the façade during rain events. Biocides are substances designed to inactivate or inhibit the growth of algae, fungi and other microorganisms via chemical or biological reactions as described in the European Directive 98/8/CE [5, 6]. Plasters, mortars, and coatings used for external thermal insulation and finishing protection frequently contain water-soluble biocides that migrate within the coating and leach into the environment over time. In order to evaluate the biocides leaching from façade building elements, both outdoor and indoor tests were performed. Schiopua et al. [7], with the aim to meet the standards in the European Directive concerning the placing of biocidal products on

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the market [5], developed a chemical transport model of the leached chemicals during rain events. Laboratory tests were carried out by using a mathematical model and software to reproduce the precipitation scenarios. The chemical-transport model developed at laboratory scale was implemented by adding external parameters regarding natural exposure conditions. The laboratory scale indoor tests were then compared to the outdoor tests, which consisted of exposing samples to the outdoor environmental conditions. The simulation conducted in this study was satisfactory in demonstrating the feasibility of modelling leaching behaviour [7]. T.P. Wangler et al. [8] observed that biocide release from building façade elements, under controlled wetting and temperature conditions, was diffusion controlled, accelerated by cyclic wetting, and drying. Additionally, increase in ambient temperature directly corresponded with the increase in emissions rate. Façade orientation was identified as important factor that affects leaching, as investigated by Vega-Garcia et al. [9]. In their study authors investigated the correlation between leaching of biocides and the Wind Driven Rain (DWR), which was identified as the main parameter that influenced the leaching load.

In addition to biocides, potential leaching of dangerous substances such as heavy metals is of concern too. Islam et al. [10] conducted column leaching tests to investigate the leaching and mobility of copper and lead due to simulated road runoff. In accordance with this, runoff may be responsible for the leaching of heavy metals and could also lead to groundwater contamination by transferring heavy metals leached in the soil to the groundwater. Heavy metals accumulation is a major consequence of toxic pollution, resulting in the aggregation of elements in the ecosystem, such as through plant roots. The accumulation of heavy metals can have adverse effects on the food chain, leading to acute and chronic health issues in humans [11]. Weiler and Vollpracht [12] investigated the potential leaching of heavy metals and hazardous substances from concrete carbon composite façade elements. The evaluation was conducted through the implementation of both outdoor and indoor tests, with the objective of assessing the validity of laboratory experiments and their potential transferability to outdoor behaviour. There was no observed correlation between laboratory leaching data and outdoor emissions. This lack of correlation was mainly dependent on the substance leached and the method used. Additionally, the wetting cycle of the laboratory tests needs to be optimized to better simulate outdoor conditions and represent outdoor leaching behaviour more accurately. However, laboratory leaching tests could be used to vary single factors and better understand outdoor leaching behaviour.

It is clear from above that leaching tests for building facades should be ideally conducted in field/outdoor conditions. Having said this, this would be difficult and expensive to achieve, for obvious reasons. An alternative is to conduct lab/indoor tests where rainfall events are simulated under more controlled conditions. However, it is not easy to do this as replicating the complexities of outdoor weather conditions in a lab setting poses significant challenges on its own. For example, raindrop size is one of the crucial parameter since it has an effect on the drop velocity and consequently on the kinetic energy which affects the detachment process [13]. To simulate indoor precipitation events and evaluate droplet size, rainfall events were simulated both using pressurized nozzles (which employ a gravity-based flow rate) and no-pressurized nozzles (which utilize an upstream pressure-based flow rate) [14, 15]. Weiler and Vollpracht [12] refer to the common mean diameter of raindrops in Western Europe, specifically in Germany, which is approximately 2.4 mm in their study, to replicate a precipitation intensity within the range of $1-5$ mm/h. It was also observed that in order to simulate realistic rain intensities, the droplet size simulated in the experiments (in terms of droplet diameter) was smaller than the actual size that the drops would have in reality, due to the limitations of the kinetic energy representation [16]. Various factors like water head, velocity, and shape of droplets during indoor experiments make it impossible to achieve accurate representation [16]. It is clear from all this that lab based leaching tests with simulated rainfall are not easy to conduct and that these cannot fully substitute for outdoor leaching tests. Still, indoor leaching tests can serve as valuable means for preliminary assessment of environmental risk potential, providing initial insights before moving the experiments outdoor.

The new bio-composite materials used in this work have been analysed previously in terms of environmental risk but in a different application, as canal bank protection elements [17]. However, the environmental risk assessment was never conducted for the façade elements analysed here which has its own specifics and challenges. To address this knowledge gap, this work aims to develop and present the approach for risk assessment based on rainfall caused leaching from façade elements (made of new bio-composite materials) into the aquatic environment. The environmental risk assessment is conducted using the established methodology for this [18] with newly collected input data obtained by simulating the rainfall events under laboratory conditions and conducting the corresponding leaching tests. Even though the leached hazardous substances from façade elements can potentially pollute the air, surface water, soil, and groundwater, in this work, only the risk of surface water pollution is analysed.

The paper is structured as follows. Section 5.3 presents the methodology used to perform the leaching analysis, including the related experimental design. Section 5.4 presents the obtained results with relevant discussions. Conclusions are presented in section 5.5.

5.3. MATERIALS AND METHODS

5.3.1. OVERVIEW

In this study the framework developed and tested in a previous study by Nativio et al., (2024) [17] was used to assess the leaching of components from bio-composite materials used as façade elements. The framework consists of three blocks: (i) existing Environmental Risk Assessment (ERA) [18] and the corresponding Dutch guidelines published by the Dutch National Institute for Public Health and the Environment (RIVM) [19]; (ii) the database of European Chemical Agency [20]; (iii) laboratory work: sample preparation and leaching tests. Because of the novelty of the bio-composite materials, on-site leaching data were not available. Therefore, laboratory leaching tests were used to simulate the real case scenario and to predict the potential leaching over time. Application of bio-composites as façade building elements leads to the evaluation of the potential leaching after adverse weather conditions such as rainfall events. In line with this, two precipitation events, each lasting 1 hour, were selected from Koninklijk Nederlands Meteorologisch Instituut (KNMI) database [21] to evaluate the leaching behaviour in relation of the rain intensity.

5.3.2. BIO-COMPOSITE MATERIALS USED AS FAÇADE BUILDING ELEMENTS

The study assesses the environmental risks associated with the potential leaching of heavy metals and resin compounds from façade building elements made from new bio-composite materials. The utilisation of bio-composites as façade building elements is solely for aesthetic purposes. A total of four distinct bio-composite alternatives have been produced in the Netherlands, and their characteristics are presented in Table 1.1. The precise compositions and percentages of each raw materials are not presented in this study due to the confidential nature of the data. For the purpose of this study, two new bio-composite materials (M3 and M4) were selected for analysis. Both materials are made of natural fibres (reeds and grass clippings from the canal maintenance, wastewater cellulose) and fillers (calcite from the drinking water softening process and bio-filler from agricultural waste) with the addition of additives. They are bonded together using a resin (polyester-based resin, or furan resin), as listed in Table 1.1. The novel bio-composite materials are manufactured through the process, as outlined in section 3.3.1 of this dissertation [4]. Two bio-composite types of samples of façade elements were analysed for each material. The first type was the new sample. These samples were used to evaluate the leaching behaviour of new façade panels. The samples were produced approximately three months before being tested and were stored under dry conditions and without sun exposure and are defined as 'new' in this manuscript. The second type analysed were

samples that after production underwent cyclic exposure to simulated solar irradiation and extreme humidity, 100% Relativity Humidity (RH), to accelerate weathering/aging effects. These samples (treated samples) were labelled as "weathered" in this study.
The use of additives, in particular of the release agent, enhances the presence of chemical contamination in terms of zinc for M3 (where zinc stearate was used as release agent). Furthermore, based on the study conducted by Quero et al. [22], olive pomeate, used as release agent for M4, can be contaminated with chemicals such as calcium, potassium, magnesium, sodium, manganese, and zinc.

5.3.3. WEATHERING TREATMENT OF SAMPLES

In total four samples were analysed, two new samples for M3 and M4, and two weathered samples for M3 and M4. For the preparation of weathered samples, new materials were placed in an accelerated weathering tester, QUV/se by Q-LAB-UVA for a period of 1372 hours (i.e., just over 57 days), where they were subjected to cycles of UVA irradiation (0.89 $W/m^{-2}s$ at 340 nm for a period of 8 h at 60°C) and humidity (100% RH for a period of 4 h at 50°C), following ASTM-G1545 Standard [23, 24]. Following the Guidebook of the weathering machine [25] and using annual solar irradiation data for the Rotterdam area obtained from the Netherlands Meteorological Service database [21], it was possible to estimate the corresponding age of the weathered samples to be 2.6 years. It should be noted that only a short band of solar irradiation spectrum in the range 280 − 390 nm was taken into account as shown in Figure 5.1, as most of the material damage occurs in that range. Detailed calculations can be found in the Supplementary Material C.

5.3.4. LEACHING EXPERIMENTS

For the leaching experiments, rainfalls intensities of 5 mm/h (i1) and 15 mm/h (i2) were selected to simulate 1-hour rainfall events. The data for these intensities were obtained from the KNMI database [21]. The volume of water required to cover the 78 x 99 mm bio-composite sample surface for these intensities are 39 ml for i1 and 116 ml for i2.

RAINWATER SIMULATION

Composition of the simulated rainwater, shown in Table 5.1 is based on the recommendations of the European Commission [26].
The rainwater solution was left for a week to stabilize, and pH was measured daily. Final pH was adjusted to the desired value of 6.5 with 1M HCl (35%) and 2M NaOH solutions. Further details can be found in the Supplementary Material file C.

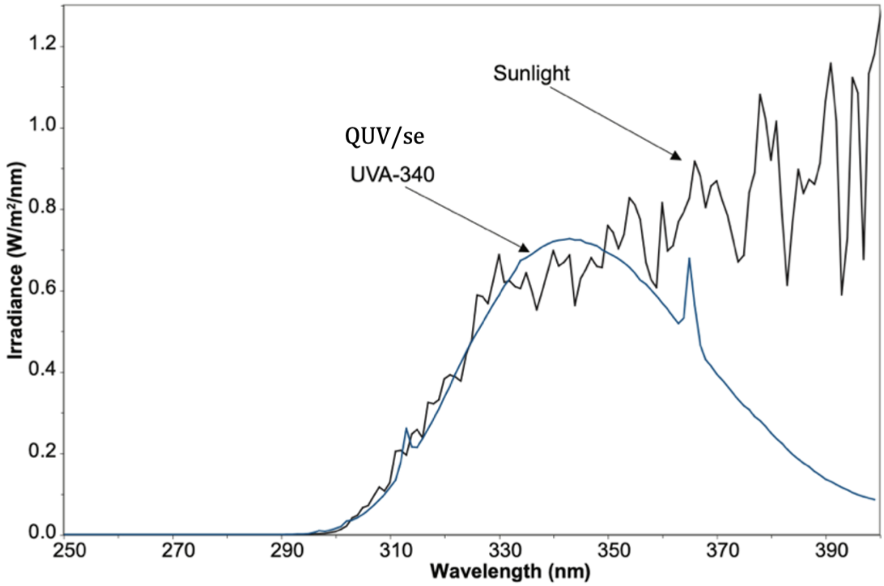

Figure 5.1.: Irradiation spectrum of the QUV/se weathering machine (blue line) and solar spectrum (black line) [24].

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Table 5.1.: Simulated rainwater composition.

Ions	**Concentration [mg/l]**
NH_4^+	$9.1 \cdot 10^{-1}$
Cl^-	$1.96 \cdot 10^{0}$
Mg^{2+}	$1.45 \cdot 10^{-1}$
NO_3^-	$2.010 \cdot 10^{0}$
PO_4^{3-}	$1.000 \cdot 10^{0}$
SO_4^{2-}	$1.460 \cdot 10^{0}$

EXPERIMENTAL SETUP

Leaching test experiments were performed in order to evaluate the potential leaching of metals and resin compounds from new bio-composite materials under precipitation exposures. All façade sample surfaces both new and weathered, were dusted, rinsed with the ultra-pure water, and dried prior to the start of the experiment. Bio-composite samples of size 78 x 99 mm were placed on a fixture inclined at 45°, as shown in Figure 5.2, to ensure proper exposure of the surface to the simulated rainwater and adequate residence time of the droplets on the bio-composite surface [12]. A 45°angle was maintained by utilising a stand device to support the façade sample. The surface of the support was covered with inert para-film to avoid leaching from the support and placed in a glass box. The rainwater was collected in the channel, placed underneath the sample. The façade sample surface was evenly covered with simulated rainwater using a multichannel pipette. Each channel had a volume of 125 μl, with a total of 8 channels used to deliver approximately 1.0 ml of water per load. The rain delivery was performed manually for an hour to simulate the duration of selected rainfall events at the specific rain intensity. To determine the number of loads for the multichannel pipette, the volume required, to cover the surface sample, was divided by the volume of water delivered per load. For the first intensity (i1, 5 mm/h), 39 loads were required, resulting in the delivery of approximately 39 ml of water over the course of one hour. For the second intensity (i2, 15 mm/h), 116 loads were required, with a total delivery of approximately 116 ml of water over the same period. The tests were performed in replicates - four for intensity i1 and two for intensity i2. Following the replicates, composite samples, which were mixtures of the effluent from each test, were collected, stored at 4°C and sent for analysis. The composite samples were analysed by using ICP-MS method to detect the heavy metals. The samples were homogenised and acidified (HNO_3), after which the analysis was performed from the liquid phase. GC–MS was used to measure styrene in water samples. In the end, HPLC–UV was used for measuring furfuryl alcohol in the composite samples.

The aforementioned leaching tests are not regulated by standards, but these tests follow the principle of Dynamic Surface Leaching Test (DSLT) regulated by the European harmonized technical specification CEN/TS $16637-2$ [27]. For the horizontal exposure of the façade samples to rainfall, there are two scenarios: ’run-off’ and ’stagnation’. The ’run-off’ scenario involves quick draining of the rainwater, while the ’stagnation’ scenario (normal Dynamic Surface Leaching Test) involves the rainwater remaining in contact with the samples for longer periods of time. Construction elements that are exposed to intermittent wet-dry stress may exhibit different leaching behaviour compared to those in permanent contact with water, with either increased or decreased release. In this study only the ‘run-off’ scenario has been selected to conduct leaching tests with the aim of evaluating the leaching after a one-hour rainfall event. It is important to note that the samples were initially subjected to testing for i1, following which they were rinsed with deionised (DI) water and dried. They were then tested for i2 on the same samples.

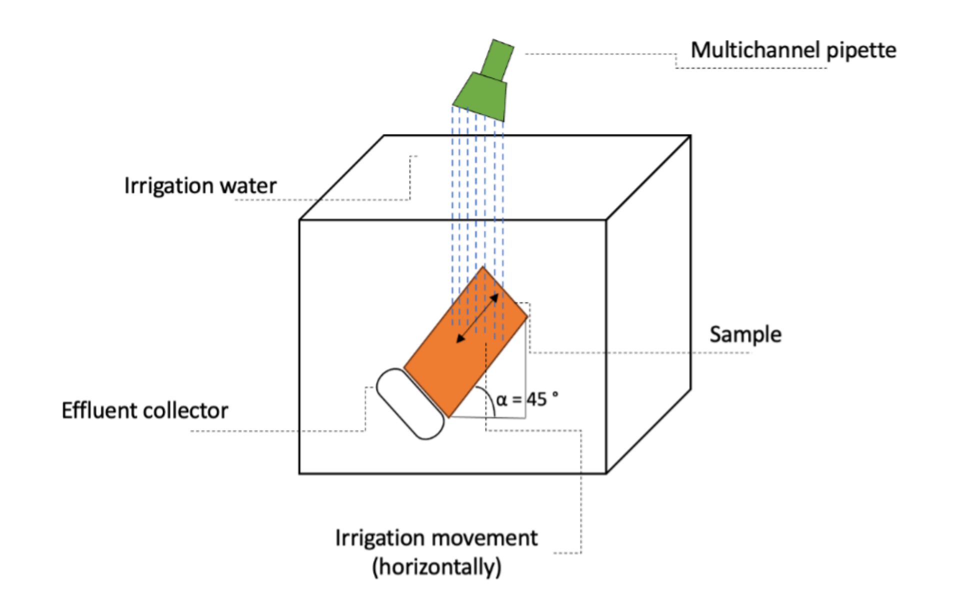


Figure 5.2.: Scheme of experimental setup of leaching tests using multi-channel pipette.

5.3.5. ENVIRONMENTAL RISK ASSESSMENT

The Environmental Risk Assessment (ERA) was carried out in accordance with established guidelines [18], the methodology is described below. This assessment considered a real-case scenario regarding a pumping station with façade elements made from the bio-composite material, a receiving pond for the rain water running off from the pumping station, and operating hours of the pumping station, as outlined in section 5.3.6, accounting for a single rain event of duration of 1 hour at intensity i1 (5 mm/h) and at intensity i2 (15 mm/h).

ERA methodology. The Environmental Risk Assessment (ERA) conducted in this study solely considers the effects of chemical leaching from façade panels, which result in a certain concentration in the pond beneath. The background concentrations of the chemicals that were already present in the pond, as well as the chemical composition of rainwater, were not included in the study. The reasons for this are the lack of on-site data concerning the background concentrations of chemicals in the pond, and the use of rainwater composition recommendations of the European Commission which lack geographical specificity of rainwater and its chemical composition in the Netherlands. When these two factors would have been taken into account, the results of the risk assessment may have been different. The leaching of chemicals, in addition to the background concentrations that are already present in the pond

and in the rainwater, could have resulted in the safety threshold being exceeded at an earlier stage.
To carry out the ERA, it is essential to follow the steps of the framework and define the risk objective, which in this case relates to the leaching of chemical such as heavy metals and resin compounds (VOCs) into surface water. The ERA methodology involves the following four main steps:

1. Hazard identification: Presence of heavy metals, styrene and furfuryl alcohol in the leaching effluent.

2. Dose-response model: Freshwater (where the façade elements considered in this study as real case scenario are placed in) is selected as the receiving ecosystem. The Predicted No Effect Concentrations (PNEC) for freshwater were obtained from European Chemical Agency (ECHA) database [20]. The PNEC represents the concentration of a substance below which adverse effects are unlikely to occur in both long-term and short-term exposure scenarios [20]. Table 5.2 shows the PNEC values of tested chemicals in freshwater in μg/l.

3. Exposure assessment: The Predicted Effects Concentration (PEC) is the predicted environmental concentration of the contaminant, which was calculated based on the leaching test results, as described in section 5.3.6 The next step is to assess whether the pollutant can pose a threat at this concentration.

4. Risk characterization: In order to evaluate the actual environmental risk, based on the ERA guidelines [18], the environmental risk was calculated as follows:

$$Risk = \frac{PEC}{PNEC} \tag{5.1}$$

The PEC/PNEC ratio must be below the threshold of 1.00, for the risk to be considered acceptable [18, 19].

5.3.6. LEACHING SCENARIO

The facade elements examined in this study are applied to an existing pumping station in the Netherlands which has a façade made of biocomposite panels, as displayed in Figure 5.3. These panels cover a total area of 54 m^2 and are 6 mm thick. The pumping station is situated above a pond with dimensions of 12.5 m wide, 50 m long and 1.25 m deep. This pond is located in the Amsterdam Dune Area (Amsterdamse Waterleidingduinen), a managed aquifer recharge system that is a nature reserve, part of the Natura 2000 network, a protected environmental area [28].

Table 5.2.: List of PNEC values for freshwater, [20].

Chemical [-]	**PNEC [μg/l]**
B	$2.90 \cdot 10^{3}$
Ba	$1.15 \cdot 10^{2}$
Cd	$1.90 \cdot 10^{-1}$
Cu	$6.30 \cdot 10^{0}$
Mg	$4.10 \cdot 10^{2}$
Mn	$3.40 \cdot 10^{1}$
Sb	$1.13 \cdot 10^{2}$
Zn	$1.44 \cdot 10^{1}$

Figure 5.3.: Façade panels applied at the pumping station in a natural reserve [picture from D1.9 WIDER UPTAKE report].

The ERA was conducted by examining the leaching process from façade elements. Figure 5.3 illustrates the vertical walls as a leaching surface for just one side of the construction. It should be noted that roof is not constructed from bio-composite materials. The experimental leaching test evaluated the impact of rain hitting a vertical wall at an angle of 45°. This angle was selected based on the findings of Weiler and Vollpracht [12], which indicated that this angle should result in the highest leaching

and represents the worst case.
The present study was conducted to investigate the release of substances into surface water following a single rainfall event. The pump station is operational for only three days per year, resulting in the renewal of water three times per year. This prolonged stagnation of water, in the absence of a flow rate, enhances the accumulation of heavy metals. However, due to the lack of consistent input data about leaching behaviour over time, in this study only the environmental impact due to the potential leaching after one rain event from the bio-composite façade from one side of the pumping station building was considered.
The potential environmental risk was evaluated using both deterministic and stochastic approaches. The deterministic approach was employed to ascertain whether any of the chemicals exceeded the safety threshold. Subsequently, the stochastic approach was implemented in order to mitigate the limitations associated with the availability of some input data for the deterministic approach. in the end, a sensitivity analysis was conducted to gain a more comprehensive understanding of leaching behaviour by assessing the PEC/PNEC ratio in response to varying input data, including leaching concentrations and rainfall intensities. Three sensitivity cases were analysed.

1. Sensitivity case 1 (s1): The objective of this sensitivity analysis was to assess the impact of varying leaching concentrations on the environmental risk (i.e., PEC/PNEC ratio). Furthermore, this sensitivity analysis was conducted to assess the reliability of the deterministic approach employed with limited input data. The samples collected from the leaching tests (representative of composite samples), were collected after four days (for rainfall intensity i1) and after two days (for rainfall intensity i2) of a wet-dry cycle. This was done in order to obtain a sufficient volume of effluent water for chemical analysis. Consequently, the observed leaching concentrations were interpreted as the cumulative leaching following one or more additional rainfall events. The cumulative leaching rate typically exhibits a rapid initial increase, followed by a constant rate [17]. Consequently, the leaching concentrations have been simulated in this sensitivity case using an exponential distribution.

2. Sensitivity case 2 (s2): The objective of this sensitivity case was to evaluate the impact of various rain intensities and to gain a deeper understanding of the leaching behaviour exhibited at varying rain intensities. A uniform distribution was employed to simulate rainfall intensities, with a minimum value of 5 mm/h (equivalent to intensity i1) and a maximum value of 15 mm/h (equivalent to intensity i2).

3. Sensitivity case 3 (s3): In this sensitivity analysis, both leaching concentrations and rainfall intensities have been simulated simulta-

neously. This case study proved to be a valuable tool in identifying the primary critical parameters that influence leaching behaviour. Further details concerning the sensitivity analysis can be found in the Supplementary material (C).

To simulate a real-life scenario, the leaching test data were used to predict the potential release in the actual case. The concentration based on the surface area of the façade elements (the actual PEC value) was calculated using Eq. 5.2, as follows.

$$C_{L,real} = \frac{C_L * H_i * A_{1side}}{V_{pond}} \tag{5.2}$$

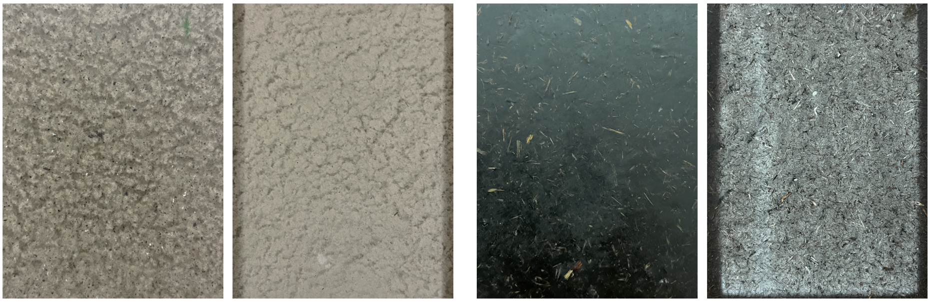
Where:

- $C_{L,real}$ [μg/L] represents the leaching concentration in the pond due to the leaching from the actual surface (A_{1side}) of façade elements into the pond with a volume V_{pond}. This value represents the Predicted Effects Concentration (PEC)
- C_L [μg/L] is the leaching concentration based on the leaching test results.
- H_i [m] is the height of the rain column (mm of rain in 1-hour duration converted in meter).
- A_{1side} [m^2] is the actual surface area of the one side of the vertical wall of pumping station construction.
- V_{pond} [m^3] is the volume of water in the pond estimated to be 781.250 [m^3].

Two distinct scenarios were employed to analyse the environmental risk, each characterised by different precipitation intensities and a duration of one hour. The first scenario evaluated the risk associated with a single rainfall event, with an intensity of 5 mm/h (i1), while the second scenario assessed the risk after a single rainfall event, with an intensity of 15 mm/h (i2).

5.4. RESULTS AND DISCUSSION

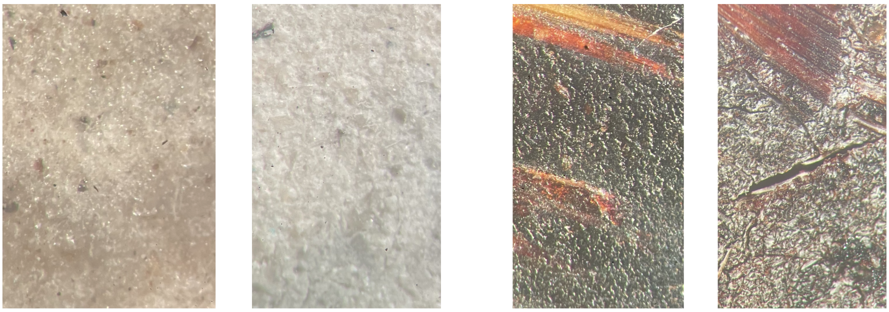
The weathering treatment leads to substantial change in the façade elements sample in terms of colour and texture of the surface, as displayed in Figure 5.4.
Figure 5.4 shows the two bio-composite materials M3 and M4, both new and weathered. The weathering treatment had an effect on the aesthetics of the materials, particularly in terms of colour and surface texture. The weathered samples, M4 in particular (Figure 5.4 (d)), appeared



(a) M3 New (b) M3 Weathered (c) M4 New (d) M4 Weathered

Figure 5.4.: (a) Material M3 New; (b) Material M3 Weathered; (c) Material M4 New; (d) Material M4 Weathered.

rougher and less water-resistant. The surface fibres, tightly pressed and glued together in fresh M4, were easily detached in weathered sample. The bio-composite samples before and after weathering were visually examined using an MBS-10 stereoscopic microscope equipped with an 8x eyepiece magnification and a 23 mm linear field of vision diameter. The selected objective magnification was 4x, resulting in a total magnification of 32x. This setup provided a field of vision in the object plane of 5.6 mm. The visual inspection of the weathered and not weathered samples using the MBS-10 stereoscopic microscope is presented in Figure 5.5.



(a) M3 New (b) M3 Weathered (c) M4 New (d) M4 Weathered

Figure 5.5.: MBS-10 Microscope images (32X magnification) of (a) Material M3 New; (b) Material M3 Weathered; (c) Material M4 New; (d) Material M4 Weathered.

Looking at both Figure 5.4 and Figure 5.5, it is evident that both weathered samples exhibit alterations primarily in the surface colour. The surface texture seems slightly rougher for both weathered materials, with noticeable wrinkles visible at the microscopic imagine for M4, as displayed in Figure 5.5 (d). In line with the aforementioned observations, it can be seen in Figure 5.4 (d) that the fibres are clearly distinguishable. Furthermore, the microscope image illustrated in Figure 5.5 (d) clearly indicated the presence of wrinkles, providing further evidence of weathering. The different weathering degradation of the two materials is probably due to the different composition of the materials and the different resin used.

5.4.1. LEACHING TEST RESULTS

The leaching test results for the analysed bio-composite material samples simulating two precipitation intensities (i1 = 5 mm/h and i2 = 15 mm/h) for one hour of rainfall, are shown in Figure 5.6. It should be noted that leaching results represent actual leaching of the material, as background concentration of ions, added by simulated rainwater, was subtracted. The samples were tested for the presence of heavy metals and for the presence of the resin compounds styrene and furfuryl alcohol. Both styrene and furfuryl alcohol were not detected.

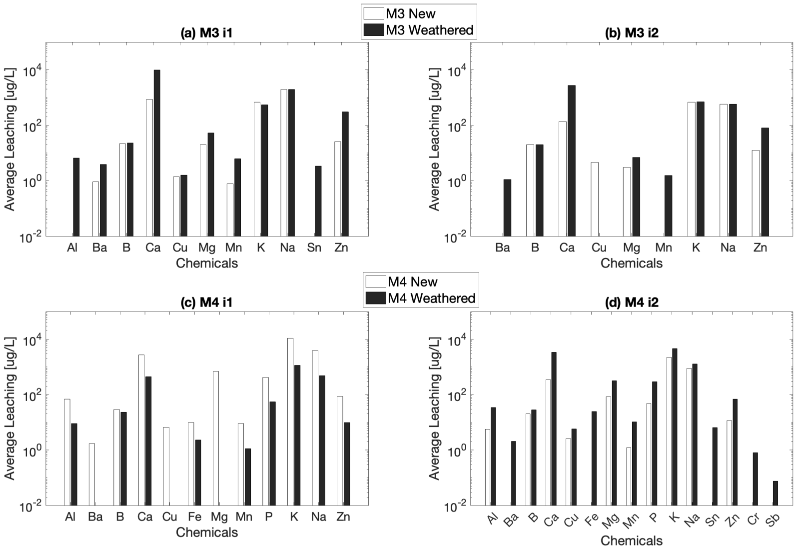


Figure 5.6.: Leaching test results after 1 hour of rain event, comparison between new and weathered samples: (a) M3 new and weathered samples at intensity i1 = 5 mm/h; (b) M3 new and weathered samples at intensity i2 = 15 mm/h; (c) M4 new and weathered samples at intensity i1 = 5 mm/h; (d) M4 new and weathered samples at intensity i2 = 15 mm/h.

Figure 5.6 illustrates the leaching behaviour of new samples compared to the leaching of weathered samples for each material, differentiated by the tested precipitation intensities. The results show distinct leaching patterns between materials M3 and M4, as well as between new and weathered samples, particularly for M4. Starting with M3 and referring to Figure 5.6 (a) and Figure 5.6 (b), both new and weathered samples exhibit similar leaching rates at rain intensities i1 (5 mm/h) and i2 (15 mm/h), with the exceptions of barium (Ba) at intensity i1, and calcium (Ca) and zinc (Zn) at both intensities. The elevated Zn release observed in M3 is probably due to the presence of zinc stearate, a release agent that resides on the surface, as mentioned in the footnote of Table 1.1. The weathered sample of M3, leads to a visible alteration in the colour surface as depicted in Figure 5.4 (b) and more detailed in Figure 5.5 (b). This exposure is likely to increase water penetration, which was also observed during testing. As a result, it enhances the leaching of water-soluble chemicals.

Regarding M4, as shown in Figure 5.6 (c, d), there is a noticeable difference in leaching behaviour between the new and the weathered samples. Specifically, at rain intensity i1 (5 mm/h), the new sample exhibits greater leaching compared to the weathered sample. Conversely, at rain intensity i2 (15 mm/h), the weathered sample demonstrates increased leaching relative to the new sample. Notably, the leaching of metals such as chromium, iron, tin, and antimony is exclusive to the weathered sample of M4. This observation implies that the weathering process may have inflicted more significant surface degradation on M4 than on M3. Surface degradation can be seen in in Figure 5.4 (c, d) and in more details in Figure 5.5 (c, d).

The alteration in the surface texture of the weathered M4 sample exposes the fibres within the bio-composite material, which, as already observed for M3, increases water penetration and activates the leaching of heavy metals present in the material at lower levels. Furthermore, findings of Quero et al. [22] indicated that olive pamoate, which is used as a release agent for this material, may be contaminated with metals such as boron, calcium, potassium, magnesium, sodium, manganese, and zinc. Similar to the findings for material M3, where the elevated release of zinc was linked to the use of zinc stearate as a release agent, the significant leaching of aforementioned heavy metals in the weathered samples of material M4 can likely be related to the use of olive pamoate as a release agent.

Another important comparison can be done between the bio-composite samples tested under different precipitation intensities. It is important to note that the samples were first tested for i1 (5 mm/h), then rinsed with ultra-pure water and dried before testing for i2 (15 mm/h) on the same samples. This sequence of actions may have affected the leaching results at intensity i2. However, the impact of this is uncertain, given the observed variations in leaching patterns between both M3 and M4, as well as between new and weathered materials. Figure 5.7 displays a comparison for two rain intensities analysed.

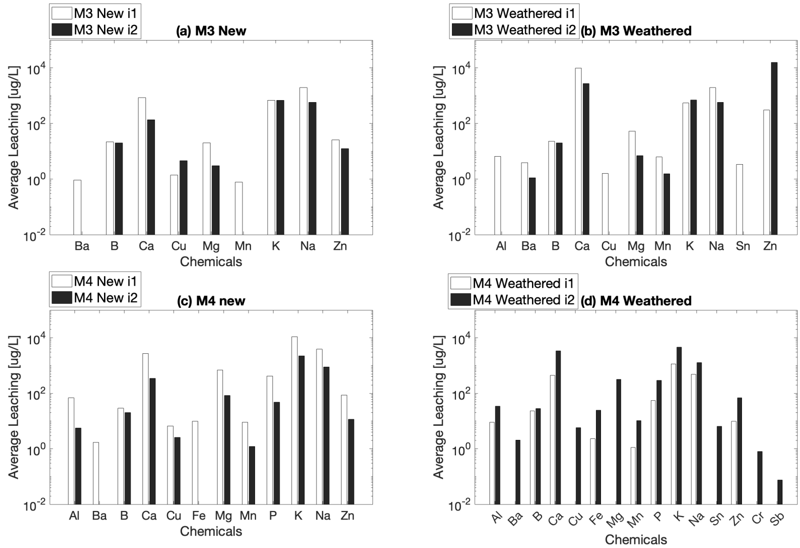


Figure 5.7.: Leaching test results, comparison between precipitation intensity i1 (5 mm/h) and precipitation intensity i2 (15 mm/h): (a) M3 new sample at both precipitation intensities; (b) M3 weathered sample at both precipitation intensities; (c) M4 new sample at both precipitation intensities; (d) M4 weathered sample at both precipitation intensities.

Figure 5.7 illustrates the variations in leaching patterns under subsequent precipitation intensities: intensity i1 (5 mm/h) and intensity i2 (15 mm/h) for the new and weathered bio-composite façade samples M3 and M4. As in the previous case (Figure 5.6), a notable distinction in leaching behaviours between M3 and M4 can be observed.

Figure 5.7 (a,b) illustrate the leaching concentrations of new and weathered samples of M3, respectively. In both cases, higher leaching concentrations are observed at intensity i1, except for zinc in the weathered sample, which may be due to the zinc stearate used as agent release, as mentioned above. This pattern can be explained by the dilution effect observed during an hour of rainfall intensity i2, where a larger volume of water dilutes the concentration of leached substances. Furthermore, as previously stated, the samples were initially tested for i1, and then, following rinsing with ultra-pure water and drying, the same sample was tested for i2. This sequence of actions may have affected the leaching results at intensity i2.

Zinc leaching is more pronounced in the weathered sample at higher precipitation intensity, indicating possible internal accumulation of zinc beyond surface deposition from the release agent. This behaviour suggests that in weathered samples, zinc is more easily mobilised under higher water volumes, highlighting the impact of rainfall intensity on leaching dynamics.

Regarding material M3, a completely opposite pattern is noticeable between the new and weathered materials. Figure 5.7 (c) shows that the highest leaching concentrations occur after one hour of precipitation at rain intensity of 5 mm/h (i1), which aligns the observation made for M3 about the dilution effects and the sequence of the experiments followed, resulting in lower leaching concentrations associated with the rain intensity of 15 mm/h (i2). Turning to Figure 5.7 (d), the weathered sample exhibits the opposite behaviour in terms of leaching, resulting in higher concentrations after intensity i2. This includes the leaching of chemicals which are only observed in the weathered sample under these conditions. This is in line with the previous consideration that the altering of the surface of the weathered M4 sample, which changes both its colour and texture, exposes the fibres, and increases leaching, particularly under higher precipitation intensity.

Percentage leaching release was calculated based on the total chemical mass of substances leached from materials M3 and M4 and chemical mass of these substances in the bio-composite materials. The chemical analysis of raw ingredients was described in our previous study [4] and additional details can be found in the Supplemental Material (C). The calculated percentage leaching release for M3 and M4, both "New" (N) and "Weathered" (W) samples, are listed in Table 5.3 and Table 5.4, respectively.

Table 5.3.: Percentage leaching releases based on the initial chemical contamination of M3.

% leaching	**Rainfall intensity i1**		**Rainfall intensity i2**	
	M3 N	**M3 W**	**M3 N**	**M3 W**
Al	0.00	$6.00 \cdot 10^{-2}$	0.00	0.00
Ba	$9.00 \cdot 10^{-2}$	$4.00 \cdot 10^{-1}$	0.00	$3.40 \cdot 10^{-1}$
B	$1.16 \cdot 10^{1}$	$1.22 \cdot 10^{1}$	$3.16 \cdot 10^{1}$	$3.16 \cdot 10^{1}$
Ca	0.00	$1.00 \cdot 10^{-2}$	0.00	$1.00 \cdot 10^{-2}$
Mg	0.00	$1.00 \cdot 10^{-2}$	0.00	0.00
Mn	$1.00 \cdot 10^{-2}$	$5.00 \cdot 10^{-2}$	0.00	$4.00 \cdot 10^{-2}$
P	0.00	0.00	0.00	0.00
K	$4.80 \cdot 10^{-1}$	$3.90 \cdot 10^{-1}$	$1.42 \cdot 10^{0}$	$1.44 \cdot 10^{0}$
Na	$2.10 \cdot 10^{0}$	$2.11 \cdot 10^{0}$	$1.84 \cdot 10^{0}$	$1.84 \cdot 10^{0}$
Zn	$9.80 \cdot 10^{-1}$	$1.17 \cdot 10^{1}$	$1.43 \cdot 10^{0}$	$9.21 \cdot 10^{0}$

The data in Table 5.3 indicate a significant release of boron ($\approx$ 31%) and

Table 5.4.: Percentage leaching release based on the initial chemical contamination of M4.

% leaching	Rainfall intensity i1		Rainfall intensity i2	
	M4 N	M4 W	M4 N	M4 W
Al	$9.00 \cdot 10^{-2}$	$1.00 \cdot 10^{-2}$	$2.00 \cdot 10^{-2}$	$1.40 \cdot 10^{-1}$
Ba	$1.00 \cdot 10^{-2}$	0.00	0.00	$2.00 \cdot 10^{-2}$
B	$9.80 \cdot 10^{0}$	$8.59 \cdot 10^{0}$	$2.01 \cdot 10^{1}$	$3.11 \cdot 10^{1}$
Ca	0.00	0.00	0.00	$1.00 \cdot 10^{-2}$
Cu	$1.00 \cdot 10^{-1}$	0.00	$1.10 \cdot 10^{-1}$	$2.80 \cdot 10^{-1}$
Fe	0.00	0.00	0.00	$3.00 \cdot 10^{-2}$
Mg	$1.10 \cdot 10^{-1}$	0.00	$1.10 \cdot 10^{-1}$	$1.70 \cdot 10^{-1}$
Mn	$1.40 \cdot 10^{-1}$	$2.00 \cdot 10^{-2}$	$6.00 \cdot 10^{-2}$	$5.50 \cdot 10^{-1}$
P	$1.40 \cdot 10^{-1}$	$2.00 \cdot 10^{-2}$	$3.70 \cdot 10^{-1}$	$3.20 \cdot 10^{-1}$
K	$5.01 \cdot 10^{1}$	$5.69 \cdot 10^{0}$	$4.67 \cdot 10^{1}$	$6.83 \cdot 10^{]1}$
Na	$1.53 \cdot 10^{0}$	$2.10 \cdot 10^{-1}$	$1.82 \cdot 10^{1}$	$1.66 \cdot 10^{0}$
Sn	0.00	0.00	0.00	$6.64 \cdot 10^{0}$
Zn	$5.20 \cdot 10^{-1}$	$7.00 \cdot 10^{-2}$	$2.10 \cdot 10^{-1}$	$1.36 \cdot 10^{0}$
Cr	0.00	0.00	0.00	$4.50 \cdot 10^{-1}$

zinc (≈ 10%), for the weathered sample of M3, following various precipitation events at both rain intensities (i1 = 5 mm/h and i2 = 15 mm/h). Similarly, Table 5.4 reveals that for M4, the leaching of potassium from the weathered sample can reach the maximum approximately 68.3% after two precipitation events at rain intensity of 15 mm/h (i2). Additionally, boron in both new and weathered samples exhibit leaching percentages between 10% and 32% approximately for both precipitation intensities. The pronounced leaching observed is related to the water solubility of these chemicals, which allows their release during the one-hour precipitation event mentioned above. Although long-term leaching trend data are lacking, the findings of the previous study by Nativio et al. [17] suggest that the leaching of substances initially found at elevated concentrations is likely to decrease over time. The observed decline can be attributed to the gradual exhaustion of the leachable chemical reserve within the material, which has resulted in the stabilisation of leaching patterns over time.

A comparison of the percentage leaching for both M3 and M4 (Table 5.3 and Table 5.4) with the leaching results (Figure 5.6, as well as Figure 5.7) reveals a discrepancy in calcium leaching for both new and weathered façade samples for both M3 and M4, respectively. It can be reasonably concluded that most of the calcium leaching cannot be attributed to the original contamination of the raw materials. It is likely that a portion of the calcium leaching originated from other contaminants, such as additives and resins, which were not verified for this study.

5.4.2. ENVIRONMENTAL RISK ASSESSMENT

The Environmental Risk Assessment evaluated the impact of leaching from new and weathered materials (both M3 and M4) for rain intensities of 5 mm/h (i1) and 15 mm/h (i2). The assessment aimed to determine whether the leached concentrations exceeded the PEC/PNEC threshold of 1.00 [18]. The evaluation of the environmental risk assessment has been done by considering only the chemicals for which the PNEC values are available in European Environmental Agency database [20]. Thus, chemicals such as Al, Ca, Fe, K, Sn, and Na were not considered in the assessment. The obtained results are shown in Figure 5.8.

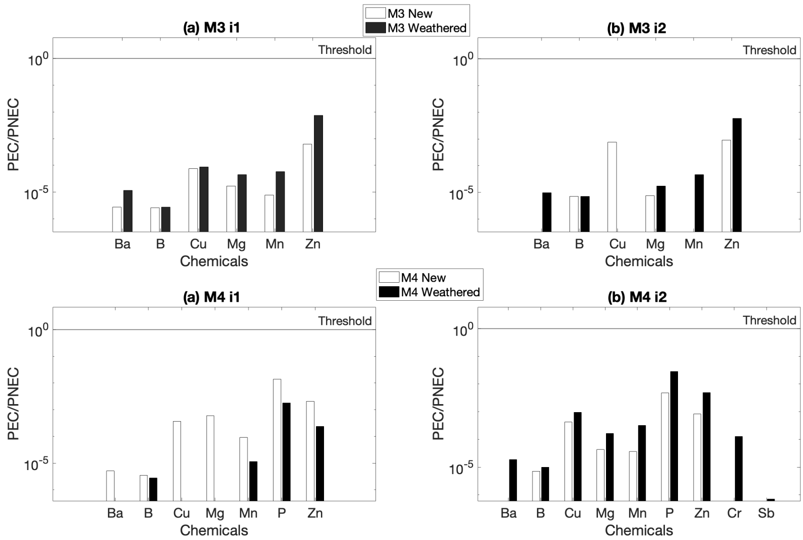


Figure 5.8.: Environmental Risk Assessment for M3 at one single rain event: (a) M3 new and weathered material at precipitation i1 (5 mm/h); (b) M3 new and weathered material at precipitation i2 (15 mm/h); (c) M4 new and weathered material at precipitation i1 (5 mm/h); (d) M4 new and weathered material at precipitation i2 (15 mm/h).

As it can be seen from Figure 5.8, the environmental risk assessment indicated that the risk levels for both materials M3 and M4 remained below the safety threshold of 1.00 for both rain intensities.
In the laboratory, the leaching tests on M3 and M4 bio-composites showed significant leaching of certain components, as shown in Figure 5.6 and Figure 5.7. However, even at these high levels of leaching, the results

remained below established thresholds for both new and weathered samples under a range of environmental conditions, including normal (i1) and high (i2) rainfall intensities. This consistency across different test conditions suggests that leaching does not pose a risk of exceeding safety or environmental standards. Therefore, it can be stated that the use of these bio-composite materials as façade elements is acceptable from the environmental risk perspective. These results support the suitability of M3 and M4 bio-composites for exterior applications, ensuring compliance with safety regulations and maintaining environmental integrity. However, background concentrations of both rainwater and surface water need to be considered for a comprehensive risk assessment.

The limitations of an environmental risk assessment based solely on laboratory data were addressed by employing a stochastic approach. In this approach, variables such as leaching concentration and rainfall intensity were treated as uncertain. The objective was to analyze the potential impact of realistic variations in these values, which could occur in real-world conditions. The objective was not only to ascertain whether such variations could elevate the overall environmental risk levels potentially increasing the PEC/PNEC values above the threshold of 1.00, but also to gain insight into the leaching behavior under varying input parameters.

The stochastic approach is based on the Monte Carlo method with $10,000$ - trials. The selection of $10,000$ trials was based on the observation that no significant changes were observed when the number of iterations was increased beyond this value (analysis not shown here). Two sensitivity cases were modelled, s1 with uncertain leaching concentrations, and s2 with uncertain rainfall intensity, both using pre-specified probability density functions, as described in section 5.3.6.

Figure 5.9 and Figure 5.10 illustrate the influence of the aforementioned input parameters on the PEC/PNEC ratio for both M3 and M4. The results presented in this study pertain solely to the “new” samples at fixed rain intensity i1 = 5 mm/h for sensitivity case s1.

As illustrated in Figure 5.9 and Figure 5.10, there was no significant increase in the PEC/PNEC ratios and the values remained below the safety threshold for all heavy metals and across all three sensitivity cases.

A comparison of Figure 5.9 (a) and Figure 5.9 (b) for M3, as well as Figure 5.10 (a) and Figure 5.10 (b) for M4, reveals that the sensitivity s1 case is distinguished by a wider boxplot in comparison to the sensitivity s2 case. Furthermore, the impact of varying the leaching concentrations is evident in the sensitivity s3 case Figure 5.9 (c) and Figure 5.10 (c), for M3 and M4 respectively, a distinguishably wider boxplot shape is also exhibited. This indicates that the leaching concentration is the factor that exerts the greatest influence on the PEC/PNEC ratio, rather than rainfall intensity.

A further significant outcome of this sensitivity analysis was the observation that, in this specific case study, the deterministic approach, due to

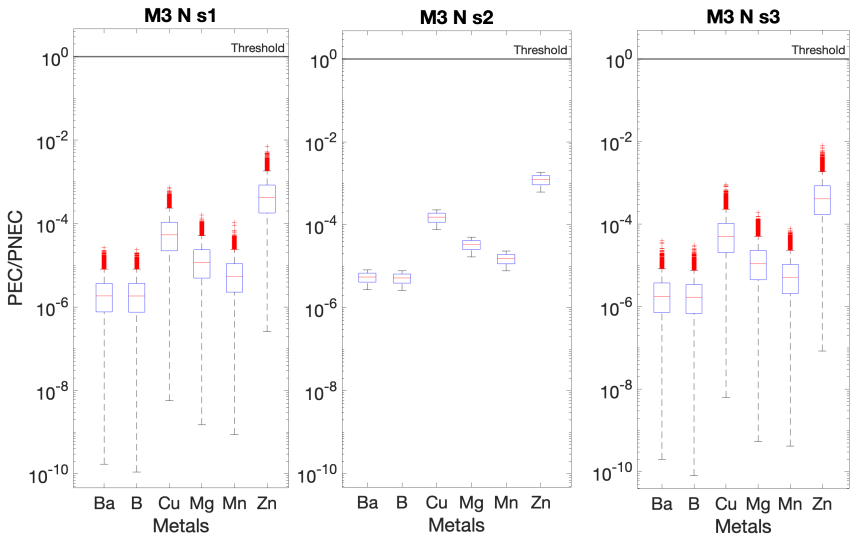


Figure 5.9.: Comparison sensitivity cases for M3 New sample: (a) case s1; (b) case s2; (c) case s3.

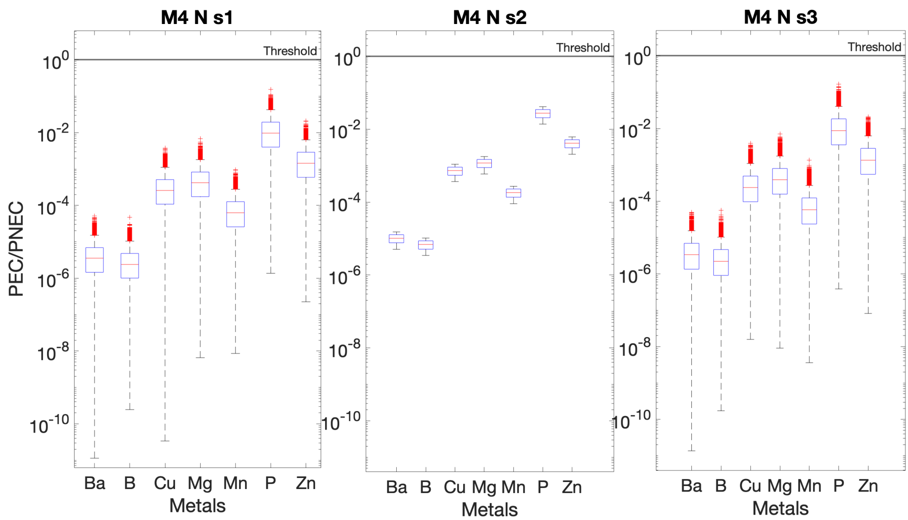


Figure 5.10.: Comparison sensitivity cases for M4 New sample: (a) case s1; (b) case s2; (c) case s3.

the limited availability of input data (including on-site data that is lacking, as well as composite samples representing leaching under various rainfall intensities and composite samples representing leaching behavior over time), tends to overestimate the overall risk. This can be seen by comparing the deterministic results to the stochastic (i.e. Monte Carlo simulation) results for sensitivity case s1, as shown in Figure 5.11 for material M4 at intensity i1 (new sample).

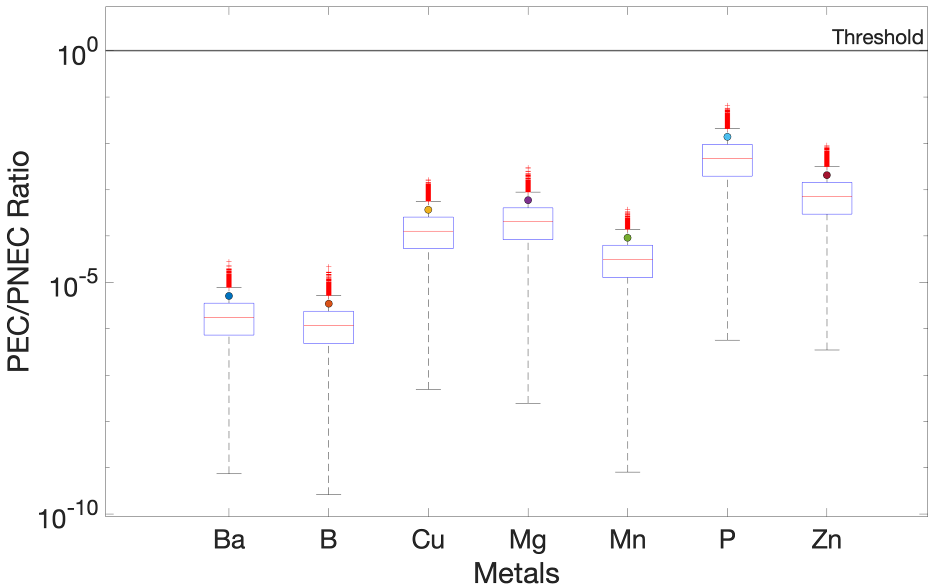


Figure 5.11.: Comparison deterministic approach and sensitivity case s1 for M4 - New sample at intensity i1 (5 mm/h).

Looking at Figure 5.11 as introduced above, the boxplot is representative of the results obtained from sensitivity s1 case for M4 at intensity i1, then the scatter points are representative of the deterministic results. As shown, the scatter points exceed the boundaries of the boxplot, indicating that the deterministic approach tends to overestimate the overall PEC/PNEC ratio. To confirm this, the probability density function (PDF) used to simulate the leaching concentrations was analyzed by comparing the average values obtained from the sensitivity analysis with the results obtained from the deterministic approach. The comparative results are presented in Figure 5.12.

Figure 5.12 shows the histogram of the simulated PEC/PNEC ratios based on the exponential probability density function used for simulating leaching concentrations. The y-axis represents the probability density, which indicates the frequency with which different PEC/PNEC ratios (represented on x-axis) are likely to occur according to the sensitivity analysis results.

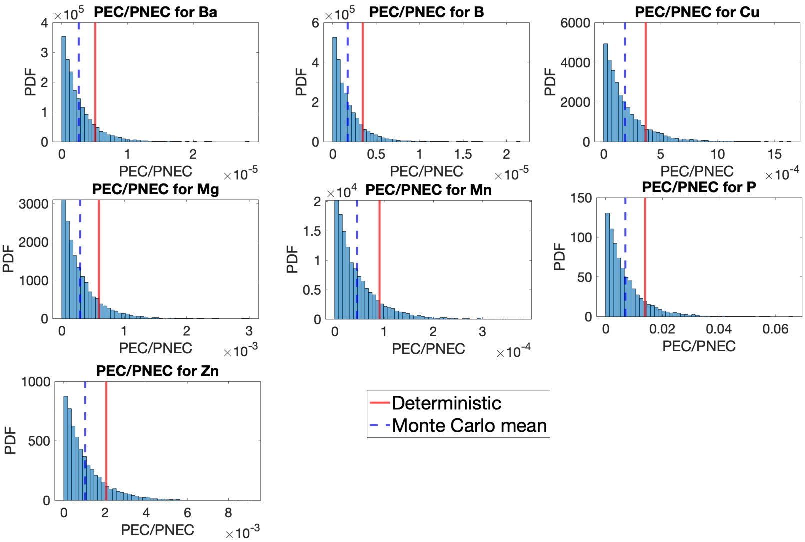


Figure 5.12.: Comparison deterministic approach and sensitivity case s1 for M4 - New sample at intensity i1 (5 mm/h).

The vertical blue dashed line represents the average PEC/PNEC ratio values obtained from the sensitivity analysis, while the red vertical line represents the deterministic PEC/PNEC ratio results. As it can be seen from the plots, the deterministic values yield a higher PEC/PNEC ratio, which is characterized by a lower frequency of occurrence, in comparison to the values obtained from the sensitivity analysis. This observation is consistent with the findings presented in Figure 5.11.

A comparison between the deterministic results and sensitivity s2 case has been conducted, revealing a significantly different outcomes from those of the earlier comparison between the deterministic approach and sensitivity case s1. Upon varying the rainfall intensities, the average values estimated by the Monte Carlo analysis and the deterministic approach exhibited minimal discrepancy, as illustrated in Figure 5.13. Further examination of Figure 5.13 reveals a histogram representative of the uniform distribution employed to simulate the rainfall analysis. The vertical lines representing the Monte Carlo average value (dashed blue vertical line) and the deterministic results (red vertical line) are in close proximity and frequently overlap. This demonstrates that variability in rain intensity has a predictable influence on the PEC/PNEC ratios, effectively captured by the deterministic approach. Overall, the environmental risk (PEC/PNEC) is more sensitive to variations in leaching concentration than to variation in rainfall intensity. The deterministic approach overestimates risk when leaching concentration varies (as stated above) but aligns with the stochastic approach when rainfall intensity varies. In conclusion, efforts to mitigate environmental risk should focus more on controlling leaching concentrations rather than rainfall intensities.

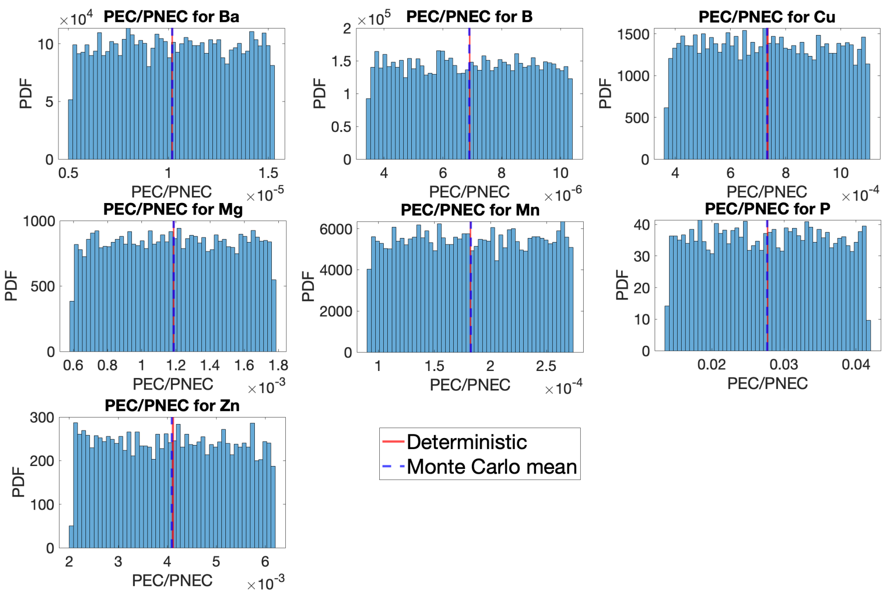


Figure 5.13.: Comparison deterministic approach and sensitivity case s1 for M4 - New sample at intensity i1 (5 mm/h).

In light of these findings, it would be both significant and interesting to replicate the laboratory leaching tests by evaluating more than two rainfall intensities and assessing the potential leaching over time. This would assist in identifying the distribution that most closely aligns with the cumulative leaching release for each chemical. In accordance with the aforementioned, it is of considerable significance to gather on-site data with the objective of validating the results of the laboratory tests and to gain a deeper comprehension of the leaching behavior in a real-world context.

5.5. CONCLUSIONS

This study proposed a methodology for assessing environmental risks associated with potential leaching from building façade into a nearby surface water. The façade panels were made of two new bio-composite materials (M3 and M4). Each material was tested in its new and weathered form, the latter being subjected to cyclic UV irradiation and high humidity. In addition, laboratory based leaching tests using simulated

rainfall were conducted to assess the amount of heavy metals, resins and other potentially harmful substances leaching back into the natural aquatic environment. Leaching tests were performed using two different rainfall intensities analysed, everyday rainfall of 5 mm/h (i1) and the less frequent rainfall of 15 mm/h (i2). The data generated by lab leaching tests was, at the end, used to perform the environmental risk analysis for a real-life pumping station in the Netherlands, located in a nature reserve. The European ERA framework was used for assessing both isolated rainfall events.
Based on the results obtained following key findings are reported:

1. Regarding the environmental risk assessment, the results obtained showed that the risk levels associated with potential leaching from the two analysed bio-composite materials M3 and M4, both for new and weathered samples and for both rainfall intensities analysed, remained below the safety threshold, as defined by the European Risk Assessment framework.

2. The deterministic approach was found to be overly conservative in the risk assessment for this particular bio-composite application, when leaching concentrations were analyzed stochastically (sensitivity case s1), resulting in a higher PEC/PNEC ratio characterized by a lower frequency of occurrence based on the sensitivity analysis results.

3. The leaching concentration, as determined by the sensitivity analysis, appears to have the greatest influence on the PEC/PNEC ratio, greater than the rainfall intensity. Indeed, the variability in rain intensity does not significantly contribute to the uncertainty in the PEC/PNEC ratios. This is also in accordance with the observed results of the leaching tests, which indicated a lower leaching concentration at higher rainfall intensities. This was observed to be the case for all bio-composite materials tested except for material M4 weathered samples, which exhibited a significantly altered leaching behavior due to the impact of the weathering treatment, which led to a notable surface degradation.

4. The leaching test results obtained for material M3 showed that the leaching concentrations between new and weathered samples were generally comparable, with notable exceptions being calcium and zinc for both tested rain intensities. Interestingly, M3 displayed a higher leaching concentration at a lower precipitation intensity (5 mm/h) compared to the higher intensity (15 mm/h), with zinc exhibiting increased leaching at the higher intensity. The highest leaching percentage observed for material M3 was approximately 31% for boron at rain intensity 15 mm/h, affecting both new and weathered materials.

5. The leaching test results obtained for material M4 indicated a higher leaching from the new sample compared to the weathered sample at intensity 5 mm/h. This trend was reversed at intensity 15 mm/h, where the weathered sample of M4 demonstrated a greater leaching effect, including the leaching of chromium, tin, and antimony exclusively under these conditions. The leaching of barium, potassium, and sodium was also significant when assessed against the initial chemical concentrations in M4. Furthermore, the leaching rate of potassium for material M4 reached a peak of approximately 69%, indicating a higher propensity for leaching. This increased leaching could be linked to the release agent employed, which has not undergone chemical analysis, only the raw materials has been tested.

6. The effect of the weathering treatment varied considerably between the different materials, mainly due to their composition, particularly the type of resin used. For example, material M3, which is made of polyester resin, exhibited aesthetic changes because of weathering, particularly in terms of colour and surface texture. In contrast, the weathered sample of material M4, made of furan resin, showed increased roughness, and reduced water resistance. Originally, the surface fibres of new M4 sample were tightly compressed and firmly bonded, but in the weathered sample these fibres tended to detach. In addition, microscopic examination (Figure 5.5), revealed significant wrinkling on the weathered M4, further illustrating the significant effects of the weathering process.

For future research, it would be interesting and valuable to replicate the leaching tests with a temporal focus to investigate the leaching patterns of various materials over time. Conducting these tests over extended periods would provide more data on the leaching behaviours of different materials, resulting in a more comprehensive dataset for statistical analysis. This would allow a comprehensive evaluation of leaching patterns over time and facilitate the assessment of uncertainties. Furthermore, conducting outdoor leaching tests would be significant in validating the consistency of laboratory leaching tests, particularly when on-site data is limited. This approach would strengthen the connection between controlled laboratory conditions and the variable conditions of natural environments, thereby enhancing the reliability of leaching data for environmental risk assessments. Furthermore, it would be valuable to carry out an environmental risk assessment analysing the potential impact of leaching of heavy metals from the façade elements into the soil and consequently into the groundwater. Finally, for an environmental risk assessment in a real case also the background concentration in the rainwater and in the receiving water should be taken into account, as these can affect reaching or exceeding the threshold value.

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6

CONCLUSIONS

6.1. THESIS SUMMARY

This dissertation developed and applied methods for the assessment of potential human health risks and environmental risks associated with the production and application of new bio-composite materials made by recovering water-based resources. The overall aim of this work was to develop an overall approach, i.e., framework for the assessment of these risks. The specific objectives of this study, based on the corresponding research questions shown in the next section, were as follows:

- To identify the key hazards and related risks associated with novel bio-composite materials based on resource recovery;
- To develop and integrate a framework for assessing human health risks related to the production of these materials;
- To develop an environmental risk assessment framework to assess potential leaching risks from bio-composite materials used in various applications;
- To adapt and apply the developed framework to investigate additional potential application of these materials.

The literature review shown is Chapter 2 was conducted first with the aim to address the first thesis specific objective shown above. It focused on two main topics: (i) identification of key hazards and related risks and the risk assessment methods used in drinking water and wastewater treatment plants; (ii) the main hazards and related risks and the risk assessment methods used for water/wastewater reuse and resource recovery. This entailed identifying the principal hazards and related risks associated with the novel resource recovery-based bio-composite materials and determining the most appropriate methodology for addressing these issues.

The framework presented in Chapter 3 was developed to address the second specific objective mentioned above. The framework was developed by integrating a number of existing risk assessment methodologies, in order to identify, map and assess the primary hazards and associated risks of the new bio-composite materials. The obtained result was the creation of a risk map. This map links the identified hazards to potential health consequences through cause-and-effect type events, facilitating the selection of the various human health risks needed to be quantified based on the purpose of the risk assessment.

To address the third specific objective of this study, an environmental risk assessment framework was developed as detailed in Chapter 4. This entailed developing a methodology that effectively assesses the environmental risks associated with the potential leaching of toxic substances from new bio-composite materials into the aquatic environment. The focus here was on leaching from canal bank protection elements made of new bio-composite materials. A significant challenge was the lack of consistent input data due to the novelty of the bio-composite materials. To address this, comprehensive set of leaching tests were conducted in the laboratory, yielding results that could be used as input for the environmental risk assessment. The corresponding assessment framework integrated the leaching tests results with an existing environmental risk assessment methodology based on EU guidelines.

In Chapter 5, another potential application for the new bio-composite materials has been investigated in terms of environmental risk, with a view to addressing the last thesis specific objective. The framework developed in Chapter 4 was adapted for assess environmental risk of leaching from building façade elements (made using new materials) exposed to rainfall of different intensity. The effects of weathering on the materials have been considered in this context too. The combination of laboratory experimental work with the existing Environmental Risk Assessment (ERA) methodology, in accordance with EU guidelines, was used.

The next section presents the key findings and scientific contributions of the research conducted.

6.2. THESIS findINGS

6.2.1. THESIS CONCLUSIONS

The main thesis conclusions are summarised for each research question.

Research question 1: *What are the main hazards and related risks associated with the production of the new resource recovery-based bio-composite materials and their applications and how are these interlinked? What existing methods can be potentially used (and with what modifications) and which new ones need to be developed to assess these risks?*

The findings related to the above research question are as follows:

- A review of the literature revealed that the primary risks associated with the production and application of new bio-composite materials are related to human health and the environment.
- No specialised risk assessment methodology currently exists for the assessment of above risks associated with the production and application of new, water resource recovery based bio-composite materials. The existing risk assessment methodologies are focused on the assessment of human health risks associated with water treatment and water-based resource recovery (in terms of microbial and chemical risks), water quality, environmental risk for wastewater reuse, and operational risks. Therefore, a comprehensive new assessment framework is required to evaluate above risks.
- Existing risk assessment methods such as HAZOP and ETA, as well as QCRA and QMRA, seem to have a potential to be used for haz-

ards identification and assessment of human health and environmental risks associated with the production and applications of new bio-composite materials. In particular, HAZOP can be used for the hazard identification, starting from the main hazards involved in the resource recovery processes. Furthermore, the ETA, when employed in a qualitative manner, can be an effective tool for creating a risk map linking hazards to different causes. The ETA method has the potential to be applied quantitatively, to assess relevant risks associated with the production and application of new bio-composite materials.

- The efficacy of established risk assessment methods, including Failure Modes and Effects Analysis (FMEA), Failure Modes, Effects, and Criticality Analysis (FMECA), and the Risk Matrix, has been demonstrated in the evaluation of human health risks and operational risks associated with failure modes in known processes, provided that sufficient input data is available. However, the applicability of these methods to the production and application of the new bio-composite material is not straightforward given the specifics of risks associated with the new bio-composite materials.

Research question 2: *What is the best approach to define and quantify the human health risks involved in the production of bio-composite materials?*
The findings related to the above research question are as follows:

- A novel human health risk assessment framework presented in Chapter 3 has been demonstrated to be effective for assessing human health risk associated with the production of new water resource recovery-based bio-composite materials.

- The quantitative chemical risk assessment (QCRA) results obtained lead to the following findings:
  - Regarding the non-cancer risk, the relevant hazard index is below the safety threshold for all four bio-composite materials tested. The highest hazard index for non-cancer risk was observed under dermal exposure conditions. The production process of the bio-composites involves the manipulation of the raw materials, including resins. The raw materials used tend to generate dust, which may result in dermal contact exposure during the mixing stage. In line with this, dust can potentially settle on hair, clothing, hands, and pose a risk of dermal contact after the mixing stage.
  - Regarding the cancer risk, the Cancer Risk Index has been found to exceed the threshold for exposure to styrene and furfuryl alcohol (resin compounds). Furthermore, in this case, dermal

contact was identified as the primary contributor to the risk level above the threshold.

- The chemical contamination of the raw materials has a greatest impact on the overall chemical risk level of the bio-composite materials. More specifically, the presence of chromium, manganese, and vanadium has been identified as a significant factor in the non-cancer risk level, particularly in relation to materials M1 and M4. The use of mined calcite as a filler for M1 and the incorporation of grass as natural fibres in M4 are two key sources of these heavy metals. In terms of cancer risk, chromium is the primary contributor, as evidenced by its presence in elevated quantities in both mined calcite and grass.
- The sensitivity analysis revealed that the parameter representing chemical concentration was the most influential factor affecting risk levels for both non-cancerous and carcinogenic risks. This conclusion is supported by the observation that varying the chemical concentration input parameter resulted in the widest box plot, in comparison to varying other exposure parameters, including ingestion rate, inhalation rate, available skin surface area, and frequency of exposure. It can thus be concluded that chemical concentration exerts the most significant influence on the outcome of the risk assessment.

- The quantitative microbial risk assessment (QMRA) conducted on material M3 (the only one that is exposed to potential microbial contamination of cellulose fibres) resulted in the following findings:
  - The presence of *E. coli* in cellulose fibres resulted in a risk level above the safety threshold.
  - The data collected about microbial contamination of cellulose fibres is relative to the untreated cellulose fibres recovered from untreated wastewater. This was done due to the lack of relevant information about which disinfection treatments the fibres underwent to produce the bio-composite materials. Typically, cellulose fibres are dried after their recovery and before reuse, which already contributes to the pathogen removal. However, since the pathogen removal treatments are unknown, the most pessimistic scenario was considered by using the data of untreated cellulose fibres, which resulted in an overestimation of the overall microbial risk level.
  - The results of the sensitivity analysis indicated that the parameter that most influences the results in terms of human health risk level is represented by the number of pathogens rather than the exposure factors such as ingestion rate.

- It is important to note that above human health this risk assessment was conducted under the most unfavourable conditions, assuming no use of personal protective equipment (PPE) or safety protocols. Consequently, due to the limited input data, it was assumed that the workers were exposed to the maximum possible levels of chemical and microbial contamination, which resulted in an overestimation of the overall risk level. In practice, obviously, this would not be the case and the associated human health risks would be lower.

Research question 3: *What is the environmental risk associated with the utilisation of novel bio-composite materials in aquatic environments? In particular, what is the associated risk in the context of the use of canal bank protection elements made from these new materials?*
The proposed environmental risk assessment framework seems to work well delivering logical results. The findings from the application of this framework to the analysis of leaching of potentially harmful substances from canal bank protection elements (made of new bio-composite materials) to the aquatic environment are as follows:

- The leaching tests provided a reliable basis for the assessment of the leaching behaviour of the novel bio-composite materials and the simulation of real-world case conditions.
- The leaching of chemicals including Co, Cu, Mn, Sn, Zn, Cd, Cr, Ni, and Pb, was observed for all four bio-composite materials analysed, as well as the leaching of resin compounds such as styrene (from M1, M2 and M3) and furfuryl alcohol (from M4). Still, in the analysed case study, the release of above-mentioned toxic substances from the bio-composite materials to the aquatic environment always remained within the acceptable limits. The only potential concerns identified were the presence of styrene and furfuryl alcohol, which exhibited the highest PEC/PNEC ratios in all scenarios (but all values still below the safety threshold of 1.00).
- The release of chemicals such as Cr, V, and Co is rapid at the outset, likely due to a strong dissolution force exerted by the substance in the eluent. Over time (beyond a week), the curve levels out and reaches a plateau, indicating a significant slowdown in the leaching process accompanied by a reduction in the driving force. This phenomenon may be attributed to the saturation of the eluent, but this is not the case since the influent water during the leaching tests was renewed continuously without recirculation. Therefore, this is due to the quantity of the heavy metals in the bio-composite materials and the related leaching, which is driven by the concentration gradient.
- The highest release of certain heavy metals including As, B, Mn, Pb, Sn, V, and Zn was observed on day 2, with an L/S ratio of approx-

imately 0.5 L/kg. This time delay may be attributed to a number of factors including: (i) the observed delay was not dependent on the pH variation, given that the pH was monitored on a daily basis and remained within the narrow range of 6.8˘7.2; (ii) The observed low infiltration rate, resulting from the slow flow rate of the influent water (approximately 9 mL/h), causes the water to move at a slow pace through the ground material, thereby facilitating a gradual rather than immediate release of the material. As anticipated, the leaching behaviour exhibited a gradual decline from day 2 to day 13; (iii) The age of the material has an impact on the release of styrene. The M1 sample, tested several years after production, exhibited a lower level of styrene release compared to the M2 and M3 samples, which were tested shortly after production. Despite the similar polyester resin content, the older M1 released less styrene, a volatile organic compound (VOC), than the newer M2 and M3.

- The dilution of contaminants in the aquatic environment plays a significant role in the assessment of environmental risk. A comparison of the results obtained for the stagnant water case of the wide ditch and the primary water course reveals a higher PEC/PNEC ratio for the wide ditch. This is due to the lower volume of water, which results in a smaller dilution factor. The primary watercourse, characterised by a greater volume of water, increases the dilution, thereby reducing the level of risk (i.e., PEC/PNEC ratio).

- It is crucial to acknowledge that the analysis conducted in this work did not incorporate diffusion or Brownian motion and assumed instantaneous mixing of leached chemicals in the aquatic environment (i.e., surface water). Consequently, the fate of chemicals was not considered in this study, resulting in a slight underestimation of the actual environmental risk. In alignment with this, the fate of chemicals in terms of degradation, redox reaction, may lead to the formation of by-products such as oxides, which may be toxic for the environment.

- The background concentrations of surface water, which will contribute alongside leaching concentrations from the bio-composites used as canal bank protection elements, were not incorporated in the analysis. This may have resulted in an underestimation of the actual risk levels. When background concentrations of surface water are taken into account, along with leaching concentrations from the bio-composite materials, it may lead to the PEC/PNEC ratio reaching or exceeding the safety threshold.

- A sensitivity analysis was conducted to assess the impact of realistic variations in parameters such as water flow velocity and leaching concentrations, which could potentially occur in real-world settings.

This was achieved by analysing on-site data rather than relying on controlled laboratory conditions. The findings of the sensitivity analysis are as follows:

- The velocity of water flow was identified as a significant factor influencing the risk levels. Altering the velocity of water flow resulted in a range of PEC/PNEC ratios between 10^{-9} and 10^{-2}, indicating the highest leaching concentration for furfuryl alcohol with a maximum ratio of $1.08 \cdot 10^{-1}$ at a water flow velocity approaching zero.
- The variation in leaching concentrations was achieved by simulating a narrow uniform distribution, with the minimum and maximum values taken from the observed leaching test results for both columns 1 and 2. This may have affected the PEC/PNEC ratio results for this sensitivity case.

Research question 4: *What is the environmental risk associated with using new bio-composite materials as building façade elements and how does the weathering of these elements affect this risk?*
The findings related to the above research question are as follows:

- The leaching tests provided a reliable basis for the assessment of the leaching behaviour of the novel bio-composite materials used as façade building elements and the simulation of real-world case conditions.
- The potential environmental risks associated with the use of new bio-composite materials as building façade elements have been subjected to a comprehensive analysis in the context of rainfall-induced leaching and weathering effects. The results of this study confirm that all associated risks remain below the established safety threshold.
- A sensitivity analysis employing the Monte Carlo method with an exponential distribution indicated that leaching concentration exerted a more pronounced influence on the PEC/PNEC ratio than rainfall intensity. This observation was consistent across all bio-composites, with the exception of M4 weathered samples, which exhibited disparate leaching behaviour, potentially attributable to surface degradation.
- Upon varying rainfall intensity using a uniform distribution, the deterministic and Monte Carlo results exhibited near-overlap, suggesting that the deterministic approach did not result in any significant overestimation for this variable.
- The resin compounds, i.e., styrene and furfuryl alcohol, were not detected, leaving the primary concern regarding the release of chemicals, such as Ba, B, Cu, Mg, Mn, Na, P, and Zn. In this case, it was

not possible to evaluate the leaching behaviour over time. Consequently, it was only possible to consider the leaching after a single rain event. Furthermore, the absence of consistent on-site data precludes the consideration of background concentrations of both rainwater and surface water, thereby also resulting in an underestimation of the actual risk levels.

- The leaching test results obtained for material M3 (made from cellulose, drinking water calcite and bio-based polyester resin) showed no significant differences in the leaching concentrations between the new and weathered samples, with notable exceptions being Ca and Zn for both tested rain intensities. Interestingly, material M3 displayed a higher leaching concentration at a lower precipitation intensity (5 mm/h) compared to the higher intensity (15 mm/h), with Zn exhibiting increased leaching at the higher intensity. This may be due to the use of zinc stearate as release agent in M3 composition. The highest leaching percentage observed for material M3 was approximately 31% for B at rain intensity 15 mm/h, affecting both new and weathered materials.

- The leaching test results obtained for material M4 (made from grass, bio-filler from agricultural waste and furan resin) indicated a higher leaching from the new sample compared to the weathered sample at intensity i1 (5 mm/h). This trend was reversed at intensity i2 (15 mm/h), where the weathered sample demonstrated a greater leaching effect, including the leaching of Cr, Sn, and Sb exclusively under these conditions. The leaching rate of K for material M4 reached a peak of approximately 69%, indicating a higher propensity for leaching. This increased leaching could be linked to the release agent employed, which has not undergone chemical analysis, but only the raw materials has been tested.

- The effect of the weathering treatment varied considerably between the different materials, mainly due to their composition, particularly the type of resin used. For example, material M3, which is made of polyester resin, exhibited aesthetic changes because of weathering, particularly in terms of colour and surface texture. In contrast, the weathered sample of material M4, made of furan resin, showed increased roughness, and reduced water resistance. Originally, the surface fibres of new M4 sample were tightly compressed and firmly bonded, but in the weathered sample these fibres tended to detach. In addition, microscopic examination revealed significant wrinkling on the weathered M4, further illustrating the significant effects of the weathering process.

The overarching objective of this research was to develop a comprehensive approach for evaluating potential risks to human health and the

environment associated with the production and application of new bio-composite materials. Based on the findings of Chapters 2 to 5, which are summarized above, it can be concluded that both microbial and chemical risks are inherent in the production processes and applications of these materials. These risks originate from the utilization of specific raw materials, including calcite from drinking water, cellulose derived from wastewater, reed and grass sourced from water boards, as well as the resins and additives employed.
Given these identified risks, it is evident that a risk assessment is always necessary. This assessment must be adapted to the specific conditions of the work environment during production and the environment during application. The framework developed in this research, which includes laboratory testing, modelling, and risk assessment methods, has been validated as applicable to the case studies and shows potential for further applications. By adopting and adapting this framework, it is possible to ensure that the production and application of new bio-composite materials are conducted safely, thus mitigating risks to human health and the environment.

6.2.2. THESIS SCIENTIFIC CONTRIBUTION

The scientific contributions of this dissertation can be summarized as follows:

- **Development of comprehensive risk assessment frameworks**: This research has introduced two novel frameworks for both human health and environmental risk assessment, specifically designed for bio-composite materials. These frameworks integrate laboratory testing, modelling, and risk assessment, and are adaptable for various bio-composite materials production and application cases, making it a valuable tool for future research and industry use.

- **New experimental data collection**: The principal challenge encountered in conducting this research was the novelty of the new bio-composite materials which, in turn, resulted in a lack of certain data required for human health and environmental risk assessments. To address this issue, laboratory leaching tests were conducted with samples of different bio-composite materials resulting in the collection of new data. The data was employed for a variety of applications in real-world scenarios, including canal bank protection and building façade elements. Furthermore, chemical analyses of the raw materials were conducted to identify potential contaminants and address potential human health risks

- **A novel approach to risk assessment and new insights into the use of bio-composite materials**: This research conducted novel risk assessments for two applications of bio-composite materials: canal bank protection and building facades. By integrating empirical laboratory data with sophisticated modelling techniques, the study yielded novel insights into the environmental and health implications of these materials. The findings emphasise the necessity for comprehensive safety assessments in the development of sustainable materials and underscore the importance of using detailed laboratory data as a reliable basis for risk evaluation. Furthermore, the research identified areas for improvement, including the necessity for on-site data collection and the implementation of advanced modelling techniques, such as human exposure modelling and chemical transport in surface water, for future studies.

6.3. IMPLICATIONS FOR PRACTICE

The comprehensive risk assessment conducted in this study provides a deeper understanding of the safety and impact of water resource recovery based bio-composite materials. The novel risk assessment framework developed in this study can be adopted and adapted by industries working with bio-composites and by the research sector for further implementation, with the aim of using the framework for risk assessment analysis for a broad application of water resource recovery-based bio-composite materials. This framework, which effectively integrates various risk assessment methodologies, can guide in identifying, mapping, and quantifying risks associated with the use of bio-composite materials in different applications.

Enhancing Risk Assessment in Industry Settings: The novel risk assessment framework developed in this thesis integrates various risk assessment methodologies to address the unique challenges posed by bio-composite materials. It is recommended that industries utilising these materials adopt and further adapt this framework in order to enhance their capability to identify, map and quantify risks. This will ensure a comprehensive approach to the management of health and environmental risks associated with the production and application of bio-composites.

Safety Protocols and Worker Protection: The identification of the volatile organic compounds such as styrene and furfuryl alcohol serves to highlight the necessity for the implementation of rigorous safety measures within the context of manufacturing processes. It is recommended that industries implement enhanced safety protocols, including improved ventilation and the mandatory use of personal protective equipment. This will reduce the risk of exposure to workers, particularly from dust and chemical emissions during mixing and moulding processes.

Quality Control and Monitoring: The implementation of regular quality control checks and monitoring of raw materials and finished products is a fundamental aspect to prevent chemical and microbial contamination. Consequently, it is recommended that industries producing or using these bio-composite materials apply the developed framework in their quality control and monitoring protocols as standard practice. Such measures will assist in maintaining product safety, ensuring compliance with environmental standards, and ultimately protecting human health and the natural environment.

Utilizing On-site Data for Accurate Risk Assessments: The incorporation of on-site data is recommended in order to validate the reliability of laboratory experiments and provide a more accurate prediction of the materials' behaviour in real environmental conditions. Adoption of this practice will enable industries to enhance their environmental risk assessments and gain a clearer understanding of the materials' impacts under operational conditions. This approach will enhance the overall accuracy of risk assessments, thereby facilitating more informed decision-making and more effective risk management strategies.

Continuous Improvement and Industry Collaboration: It is recommended to implement feedback loops which integrate data from field tests and laboratory results in order to facilitate the continuous improvement of materials and methodologies. Furthermore, it is crucial to foster collaborative efforts between research institutions and industry. Such collaboration will facilitate innovation of new bio-composite materials and enhances the safety and sustainability of bio-composite materials.

Education and Training: It is recommended to develop educational and training programs to increase awareness of the risks associated with bio-composite materials. These programs should extend to emergency response and risk management strategies, equipping professionals with the knowledge to effectively manage potential risks in the bio-composite sector.

6.4. FUTURE RESEARCH RECOMMENDATIONS

The findings of this dissertation are largely influenced by various uncertainties, with the results being derived from laboratory-scale experiments that were subsequently adapted to simulate real-world conditions. This adaptation and the assumptions made were necessary to overcome the lack of consistent input data and on-site measurements, such as air pollution levels during the bio-composite production process and the quality of surface water into which bio-composite chemicals might leach. The study has yielded insights regarding both human health and environmental risk assessments for the production and application of these new bio-composite materials. However, further validation and implementation of the risk assessment methodology is required. This section presents future research directions aimed at optimising the framework's implementation.

Human health risk assessment. The human health risk assessment framework, as detailed in Chapter 3, considers dust from raw materials to be the primary medium for exposure through ingestion, inhalation, and dermal contact.

Future research should extend to validating the proposed human health risk assessment framework for other exposure routes, such as assessing potential ingestion rates and dermal contact exposure, particularly with the use of personal protective equipment, in order to better gauge actual worker exposure. Furthermore, in order to enhance the evaluation of inhalation exposure, it is crucial to analyse the quality of the air within the laboratory where bio-composites are produced. The Quantitative Microbial Risk Assessment (QMRA) model currently focuses solely on ingestion exposure, utilising pathogen concentrations sourced from existing literature. In order to refine the QMRA model further, it is essential to collect additional microbial data and include other pathogens and exposure routes, such as inhalation and dermal exposure. The analysis of samples from workers' hands could provide valuable insights into microbial exposure via the hand-to-mouth route, thereby enhancing the comprehensiveness of the risk assessment framework.

There is considerable scope for expanding the scope of human health risk assessment by analysing the different applications of bio-composites, in addition to the health risks related to their production.

For instance, the utilisation of bio-composite materials as canal bank protection in recreational contexts, such as swimming, may give rise to concerns regarding human health. Such risks are due to the potential for accidental ingestion and dermal contact with contaminated water. An additional example pertains to a distinct application of the novel bio-composite materials as plates and/or pots. The leaching of chemical substances may be initiated when the material comes into contact with heated food and food-related liquids, which could give rise to concerns regarding human health. Furthermore, concerns regarding human health may emerge as a consequences of the pollution in the natural environment. The potential accumulation of heavy metals in the soil may result in the contamination of groundwater, which often serves as a primary drinking water source. Such expansions in research would not only reinforce the current framework's effectiveness in assessing risks during the production of new bio-composite materials but also extend its applicability to real-world environmental and public health scenarios.

Environmental risk assessment. The results of the environmental risk assessment for both applications of the bio-composites analysed in this work are based on laboratory leaching tests and assumptions made for both canal bank protection and façade building elements, as outlined in Chapters 4 and 5, respectively. To further validate the accuracy of the approach of combining laboratory leaching tests with the environmental risk assessment, on-site tests are required.

With regard to the assessment of environmental risk in the case of canal bank protection elements, it would be beneficial to analyse water and sediment samples from the canal over an extended period. This would provide a more comprehensive overview of the water quality and the actual leaching of toxic substances. In accordance with aforementioned, the water quality data may provide a significant evaluation of various factors, including the effects of heavy metal accumulation in surface water, adsorption in soil sediment, and the effects of dilution in real-world scenarios. Modelling these parameters has a crucial role in determining whether leaching concentration of a specific chemical is within the environmental risk limit. Collection of water quality data, and the use of models for transport of chemicals in water rather than the assumed instantaneous mixing, will strengthen the use of the framework.

In order to enhance the assessment of environmental risk in the case of bio-composite materials based building façade elements, it is recommended that comprehensive leaching tests be conducted over an extended period of time. Investigating leaching patterns over time will yield a more detailed understanding of the materials' long-term behaviour. Consequently, the extended testing period will provide a richer data set for statistical analysis, leading to more accurate and reliable risk assessments.

It is recommended to conduct field leaching tests with diverse meteorological parameters, such as wind direction and varying precipitation intensities over different duration. These tests will permit the examination of a spectrum of leaching scenarios and assist the validation of the consistency of laboratory leaching tests, particularly when on-site specific data are limited, as observed in this study. By aligning controlled laboratory conditions with the variable conditions of natural environment, this approach will enhance the reliability of leaching data for environmental risk assessment. The implementation of this method will facilitate the acquisition of a more robust and accurate understanding of the environmental impacts of bio-composite materials.

Finally, it would be beneficial for future research to conduct an environmental risk assessment that examines the potential impact of leaching of heavy metals from façade elements into the soil and subsequently into groundwater. For the purposes of an environmental risk assessment in a real case, it is necessary to consider the background concentration of the relevant substances in the rainwater and the receiving water. These factors may potentially influence the achievement or exceedance of the threshold value.

Further applications of new bio-composite materials. The framework developed in this study is applicable to a range of contexts beyond the specific context of canal bank protection and building façade elements, such as water level scale and indoor furniture (i.e., lamp, plates, pots). It is recommended that a comprehensive risk assessment be conducted for any new application of bio-composite materials using the developed method. In the case of new applications, it is of the utmost importance to:

- The collection of valuable input data for risk assessments necessitates the acquisition of on-site samples of bio-composite materials from natural environments for further applications such as water level scale.
- In the case of alimentary applications, such as plates and pots, migration tests should be conducted to evaluate the potential leaching of toxic substances. These tests are performed under elevated temperature and pressure conditions, which replicate the scenarios in which the plates and pots may come into contact with heated food.

The implementation of these practices will enable industries to extend the benefits of bio-composite materials to a wider range of applications while maintaining high standards of safety and environmental protection. The developed framework serves as a robust tool for the management of risks associated with innovative materials, thereby promoting their safe and sustainable use across different sectors.

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APPENDIX A

Human health risk assessment framework for new water resource recovery-based bio-composite materials - Supplementary File

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A.1. QUANTITATIVE CHEMICAL RISK ASSESSMENT

HAZARD IDENTIFICATION

The ICP-MS was carried out on the external lab, in order to detect the presence of heavy metals in the raw materials. The obtained results are shown in Table A.1.

Table A.1.: ICP-MS results for heavy metals detection on raw materials.

Element	Reed [mg/kg]	Cellulose [mg/kg]	Grass [mg/kg]	Mined calcite [mg/kg]	DW Calcite [mg/kg]	Bio-filler [mg/kg]
Si	$<5.00\cdot10^{-2}$	$7.77\cdot10^{2}$	$3.42\cdot10^{2}$	$1.22\cdot10^{3}$	$<5.00\cdot10^{1}$	$<5.00\cdot10^{1}$
Al	$<1.00\cdot10^{0}$	$3.12\cdot10^{0}$	$4.10\cdot10^{2}$	$3.18\cdot10^{2}$	$1.34\cdot10^{1}$	$2.78\cdot10^{0}$
Fe	$<1.00\cdot10^{1}$	$1.39\cdot10^{1}$	$1.35\cdot10^{3}$	$6.36\cdot10^{2}$	$<1.00\cdot10^{1}$	$<1.00\cdot10^{1}$
Ca	$<5.00\cdot10^{1}$	$6.98\cdot10^{2}$	$3.15\cdot10^{3}$	$7.36\cdot10^{3}$	$1.74\cdot10^{5}$	$1.81\cdot10^{5}$
Mg	$<5.00\cdot10^{0}$	$3.83\cdot10^{2}$	$3.05\cdot10^{2}$	$2.05\cdot10^{3}$	$5.47\cdot10^{2}$	$1.33\cdot10^{3}$
Na	$<1.50\cdot10^{1}$	$6.15\cdot10^{2}$	$3.42\cdot10^{2}$	$4.79\cdot10^{3}$	$2.40\cdot10^{1}$	$4.43\cdot10^{2}$
Ti	$<2.00\cdot10^{-1}$	$<2.00\cdot10^{-1}$	$4.29\cdot10^{0}$	$3.80\cdot10^{-1}$	$<2.00\cdot10^{-1}$	$<2.00\cdot10^{-1}$
K	$<5.00\cdot10^{0}$	$9.71\cdot10^{2}$	$8.76\cdot10^{1}$	$1.52\cdot10^{4}$	$3.02\cdot10^{1}$	$1.25\cdot10^{1}$
P	$<5.00\cdot10^{0}$	$1.76\cdot10^{2}$	$1.53\cdot10^{3}$	$1.62\cdot10^{3}$	$<5.00\cdot10^{0}$	$1.49\cdot10^{1}$
Be	$<1.00\cdot10^{-2}$	$<1.00\cdot10^{-2}$	$2.02\cdot10^{-2}$	$2.94\cdot10^{-2}$	$<1.00\cdot10^{-2}$	$<1.00\cdot10^{-2}$
Cr	$<5.00\cdot10^{-1}$	$<5.00\cdot10^{-1}$	$3.07\cdot10^{0}$	$9.96\cdot10^{-1}$	$<5.00\cdot10^{-1}$	$<5.00\cdot10^{-1}$
Co	$<2.00\cdot10^{-1}$	$<2.00\cdot10^{-1}$	$2.47\cdot10^{-1}$	$2.72\cdot10^{-1}$	$<2.00\cdot10^{-1}$	$<2.00\cdot10^{-1}$
Cu	$<1.00\cdot10^{0}$	$<1.00\cdot10^{0}$	$3.57\cdot10^{1}$	$<1.00\cdot10^{0}$	$<1.00\cdot10^{0}$	$<1.00\cdot10^{0}$
Pb	$<1.00\cdot10^{0}$	$<1.00\cdot10^{0}$	$1.29\cdot10^{1}$	$2.72\cdot10^{0}$	$<1.00\cdot10^{0}$	$<1.00\cdot10^{0}$
Mn	$<5.00\cdot10^{-1}$	$2.78\cdot10^{1}$	$3.09\cdot10^{1}$	$3.63\cdot10^{1}$	$1.16\cdot10^{1}$	$1.02\cdot10^{0}$
Ni	$<1.00\cdot10^{0}$	$<1.00\cdot10^{0}$	$3.18\cdot10^{0}$	$<1.00\cdot10^{0}$	$<1.00\cdot10^{0}$	$<1.00\cdot10^{0}$
V	$<1.00\cdot10^{-1}$	$<1.00\cdot10^{-1}$	$3.38\cdot10^{0}$	$9.09\cdot10^{-1}$	$<1.00\cdot10^{-1}$	$<1.00\cdot10^{-1}$
Zn	$<3.00\cdot10^{0}$	$2.11\cdot10^{1}$	$8.71\cdot10^{1}$	$5.74\cdot10^{1}$	$<3.00\cdot10^{0}$	$<3.00\cdot10^{0}$
Ba	$<2.00\cdot10^{-1}$	4.19	$1.56\cdot10^{1}$	$1.09\cdot10^{1}$	$6.00\cdot10^{-1}$	$5.87\cdot10^{1}$
B	$<1.00\cdot10^{0}$	$1.52\cdot10^{0}$	$1.56\cdot10^{0}$	$7.80\cdot10^{0}$	$<1.00\cdot10^{0}$	$<1.00\cdot10^{0}$
Li	$<1.00\cdot10^{0}$	$<1.00\cdot10^{0}$	$<1.00\cdot10^{0}$	$1.28\cdot10^{0}$	$<1.00\cdot10^{0}$	$<1.00\cdot10^{0}$
Sn	$<1.00\cdot10^{0}$	$<1.00\cdot10^{0}$	$1.67\cdot10^{0}$	$<1.00\cdot10^{0}$	$<1.00\cdot10^{0}$	$<1.00\cdot10^{0}$
Bi	$<1.00\cdot10^{0}$	$<1.00\cdot10^{0}$	$1.54\cdot10^{0}$	<1.00	$<1.00\cdot10^{0}$	$<1.00\cdot10^{0}$
S	$<3.00\cdot10^{1}$	$5.81\cdot10^{2}$	$1.32\cdot10^{3}$	$1.42\cdot10^{3}$	$<3.00\cdot10^{1}$	$<3.00\cdot10^{1}$
Sr	$<1.00\cdot10^{-1}$	$6.00\cdot10^{0}$	$1.06\cdot10^{1}$	$2.33\cdot10^{1}$	$2.71\cdot10^{1}$	$6.15\cdot10^{2}$

EXPOSURE ASSESSMENT

Non-cancer risk: The exposure assessment have been calculated by assuming the human exposure through the dust formed from the raw materials during the mixing process. The dust may be contaminated with chemicals such as heavy metals.

It is important to distinguish the effects of chemical exposure. For this case study, heavy metals and resin components were selected as potential chemicals to which workers are exposed during the bio-composite production process. The human exposure to these substances can lead to negative effects on human health in short term-effects (non-cancer risk) and long term-effects (cancer risk).

In this study, the non-cancer risk includes all potential effects such as eye irritating, breathing difficulties, allergic reaction and dermal rush. The exposure routes taken into account in this study are: accidental ingestion, inhalation and dermal contact. The exposure doses were calculated as reported in Eq. A.1, Eq. A.2 and Eq. A.3 respectively, published by U.S.E.P.A. [1, 2].

$$D_{ing} = \frac{C_{metal} \cdot IngR \cdot E_f \cdot E_d}{BW \cdot AT} \tag{A.1}$$

$$D_{inh} = \frac{C_{metal} \cdot InhR \cdot E_f \cdot E_d \cdot E_t}{PEF \cdot BW \cdot AT} \tag{A.2}$$

$$D_{derm} = \frac{DA_{dermal} \cdot SA \cdot E_f \cdot E_d}{BW \cdot AT} \tag{A.3}$$

Where:

- D_{ing} is the ingestion dose [mg/kg/day].
- C_{metal} is the concentration of heavy metals [mg/kg] for ingestion exposure and [g/kg] for inhalation exposure, respectively.
- E_d is the exposure duration [years].
- E_t is the exposure time [hrs].
- E_f is the exposure frequency [days/years].
- BW is the body weight [kg].
- AT is the averaging time calculated by multiply the exposure duration of 25 years in days [days].
- IngR is the ingestion rate [g/day].
- D_{inh} is the inhalation dose [mg/kg/day].
- PEF is the particle emission factor [$1.316 \cdot 10^{-09}$ m^3/kg [1]].
- InhR is the inhalation rate [m^3/h].
- SA is the available skin surface [cm^2].
- DA_{derm} is the absorbed dose [mg/cm^2-event].

The absorbed dose for dermal contact exposure (Eq. A.3) was calculated by using Eq. A.4.

$$DA_{dermal} = K_p \cdot C \cdot t \tag{A.4}$$

Where K_p is the permeability coefficient (cm/hr), C is the concentration of chemical in vehicle contacting skin (mg/cm^3) and t is the time of contact (hrs/event). In this study, the dermal contact was through the contaminated dust formed from the raw materials to the skin. As U.S.E.P.A. [3]

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indicates, for dermal contact with solids (e.g., sediments, soil), the concentration of contaminant contacting the skin is a function of the concentration of the contaminant in the solid material (e.g., soil or dust). Thus, it is possible to calculate the absorbed dose by multiplying the concentration of contaminant in soil (mg/g) to the adherence factor rate (Adh) of soil to skin (g/cm^2-event) to estimate the concentration of contaminant on the skin (g/cm^2-event).
The exposure frequency was calculated by using the probability value of the exposure given by Eq. A.5.

$$E_f = \frac{250}{365} \tag{A.5}$$

The ingestion and inhalation rates, skin surface available and adherence factors were calculated by selecting values for adult exposure ($21-61$ years old) for both female and male. Then, the average value was calculated and used for the deterministic approach. The obtained values are listed in Table A.2.

Table A.2.: Obtained input data values to be used for chemical risk assessment for the bio-composite production case study.

Parameter	Value obtained
Ingestion rate (mg/day)	$3.00 \cdot 10^{-2}$
Inhalation rate (m^3/day)	$1.55 \cdot 10^{1}$
Skin surface available: hands (cm^2)	$9.80 \cdot 10^{2}$
Skin surface available: head (cm^2)	$1.25 \cdot 10^{3}$
Adherence factor: hands (g/cm^2-event)	$2.76 \cdot 10^{-4}$
Adherence factor: head (g/cm2-event)	$9.82 \cdot 10^{-5}$
Body weight (kg)	$7.56 \cdot 10^{1}$
Exposure frequency (days/year))	$6.85 \cdot 10^{-1}$

Cancer risk: With regards for cancer risk, the exposure assessment was calculated for the same exposure routes taken into account for non-cancer risk. The exposure doses were calculated using Eq. A.6, Eq. A.7, and Eq. A.8 reported below [2, 4].

$$LADD_{ing} = \frac{C_{metal} \cdot IngR \cdot E_f \cdot E_d}{BW \cdot AT_{carc}} \tag{A.6}$$

$$LADD_{inh} = \frac{C_{metal} \cdot InhR \cdot E_f \cdot E_d \cdot E_t}{PEF \cdot BW \cdot AT_{carc}} \tag{A.7}$$

$$LADD_{derm} = \frac{DA_{dermal} \cdot SA \cdot E_f \cdot E_d}{BW \cdot AT_{carc}} \tag{A.8}$$

Where LADD is the lifetime average daily dose [mg/kg-day] and in this case AT_{carc} [days] is the average exposure time for the cancer risk estimated as the lifetime, so in this case it is assumed to be equal to 70 years in days ($2.56 \cdot 10^{+04}$). The other parameters are the same explained for Eq. A.1, A.2, and A.3 concerning the non-cancer risk.

DOSE-RESPONSE MODEL

Non-cancer risk: The dose response model provides the level of the Hazard Quotient (HQ) as a probability of toxicological effects on human health after the exposure. The HQs were calculated by using Eq. A.9, Eq. A.10 and Eq. A.11, as reported below.

$$HQ_{ing} = \frac{D_{ing}}{RfD_{ing}} \tag{A.9}$$

$$HQ_{inh} = \frac{D_{inh}}{RfD_{inh}} \tag{A.10}$$

$$HQ_{derm} = \frac{D_{derm}}{RfD_{derm}} \tag{A.11}$$

Cancer risk: Cancer risk is calculated by using Eq. A.12, Eq. A.13 and Eq. A.14 for ingestion, inhalation and dermal exposure respectively.

$$Risk_{carc,ing} = LADD_{ing} \cdot SF_{ing} \tag{A.12}$$

$$Risk_{carc,inh} = LADD_{inh} \cdot SF_{inh} \tag{A.13}$$

$$Risk_{carc,derm} = LADD_{derm} \cdot SF_{derm} \tag{A.14}$$

RISK CHARACTERIZATION

Non-cancer risk: To estimate the non-cancer risk, the Hazard Index (HI) was calculated for each chemical (heavy metals and resin components) as the sum of the HQi calculated for each chemical for all exposure route, using Eq. A.15 as follows.

$$HI = \sum_i HQ_i \tag{A.15}$$

Cancer risk: To estimate the cancer risk, the Cancer Risk Index (CRI) was calculated by using Eq. A.16, as follows.

$$CRI = \sum_i Risk_{cancer(i)} \tag{A.16}$$

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Also, in this case the index represents the i-th exposure routes taken into account. The threshold value settled for cancer risk is 10^{-06} by standard guidelines [4].

SENSITIVITY ANALYSIS

As explained in the manuscript, five cases were assessed for sensitivity analysis. Matlab codes were used to perform the sensitivity analysis by using Monte Carlo method (10, 000 trials). Below parts of the script for the simulations performed are provided. The following examples regard material M1 and M3 for QCRA and QMRA, respectively. For the other materials, the same code was used.

1. **Sensitivity case 0 (s0)**: the concentrations of chemicals (QCRA) and pathogens (QMRA) detected in raw materials, are simulated using a uniform distribution:

```
Heavy_Metal_1_raw1_M1_s0 = (max-min)*
   rand(n,1)+min;

Pathogen_raw2_s0 = (max-min)*rand(n,1)
   + min;
```

   Where:

   - The name of variable is composed from: name of chemical + code for used raw material (i.e., "raw1" is for calcite), concerning QCRA. The same code was applied for QMRA.
   - "Max" is the detected value from ICP-MS analysis.
   - "Min" is assumed as zero (not contamination) in order to perform the analysis with a wide range of values per chemical.
   - *n* is the number of trials.
   - s0 is the sensitivity case 0.
   - 1 is the liberty grade (1 dimension).

2. **Sensitivity case 1 (s1)**: exposure rate parameters such as ingestion rate, inhalation rates, and skin area are simulated using a lognormal distribution, following the USEPA Handbook guidelines [5]. Different values were chosen for each parameter depending on the age and gender groups. The geometric mean and standard deviation values were calculated for the inhalation rate and the available skin area for the head and hands. Concerning the ingestion rate, only a single value for dust ingestion is available in the literature, therefore the 96% confidence interval was used as standard deviation. With regards to the QMRA model, only the ingestion route was considered, as described in section 3.5.1 Therefore, only the ingestion rate was simulated as done for the QCRA.

```
InhR_s1 = lognrnd(mu,sigma,n,1);
IngR_s1 = lognrnd(mu,sigma,n,1);
Adh_face_s1 = lognrnd(mu,sigma,n,1);
Adh_hand_s1 = lognrnd(mu,sigma,n,1);
```

Where:

- The name of the variable is composed from: parameter to simulate + sensitivity case.
- σ ("sigma") is the standard deviation.
- μ ("mu") is the average value.
- n is the number of trials.
- s1 is the sensitivity case.
- 1 is the liberty grade (1 dimension).
- σ and μ are the logarithmic parameters that were calculated as follows:

$$\mu = log \frac{(m^2)}{\sqrt{v + m^2}} \tag{A.17}$$

$$\sigma = \sqrt{(log(v/(m^2) + 1))}; \tag{A.18}$$

  where m and v are the geometric mean and standard deviation data based on the collected values from the Handbooks, shown in Table 3.2 of the manuscript.

3. **Sensitivity case 3 (s3)**: In order to simulate the QCRA body weight, a lognormal distribution was employed, as previously described. The parameters of the distribution are based on gender. Subsequently, the geometric mean and standard deviation were calculated. For QMRA, body weight was not an input parameter; therefore, this case of sensitivity analysis is not included in the QMRA stochastic approach model.

   ```
   BW_s3 = lognrnd(mu_bw, sigma_bw, n,1);
   ```

   The above script follows the same model of the scripts shown above.

4. **Sensitivity case 4 (s4)**: All input parameters were subjected to simultaneous simulation as uncertain variables in order to ascertain the maximum tolerable risk. This case is represented as “s3” for QMRA.

The average value was calculated by collecting a vector of values from the U.S.E.P.A. handbook [5] that cover different age range such as 21−31 years old, 31−41 years old, 41−51 years and 51−61 years old for male and female combined. Then, the geometric mean and standard deviation were estimated. The collected values are shown in the Table A.3 below.

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Table A.3.: Collected input data from literature by taking into account age range of 21-61 for both male and female combined.

Parameter	Value	Mean	Std	Ref.
Ingestion rate [mg/day]	[34; 30; 29.9; 25.9]	30	1.44	[5]
Inhalation rate [m^3/day]	[15.7; 16; 15.7; 14.2]	15.52	0.567	[5]
Skin area (face) [cm^2]	[754.96; 1241.80; 1927.10]	1250	155.56	[5]
Skin area (hands) [cm^2]	[608.53; 973.75; 1504.9]	980	127.3	
Frequency exposure [d/y]	[200/365; 250/365; 300/365]	250/365	0.0274	[5]
Body Weight [kg]	[71.3; 75.61; 79.96]	75.6	5.94	[5]

A.2. QUANTITATIVE MICROBIAL RISK ASSESSMENT

1. **Exposure Assessment**: Human exposure to microbial contamination was assessed by taking into account only the accidental ingestion exposure route due to the lack of indicative input data. The exposure dose was calculated by using Eq. A.19, as follows.

$$Dose = C_{pathogen} \cdot Ing_{dose} \tag{A.19}$$

   Where:

   - "Dose" is exposure dose by ingestion [No.];
   - Ing_{dose} is the ingestion dose as the amount of dust ingested [mg];
   - $C_{pathogen}$ is concentration of pathogens (No./mg).

   The input data utilised for the determination of pathogen concentration consists of data regarding untreated cellulose flakes and fibres collected from wastewater. The ingestion rate used for this calculation was assumed to be 0.03 mg/day of the dust through accidental ingestion.

2. **Dose-response model**: Dose-response model was used to define the probability of infection, and it is specific for each pathogen. In Equation A.20 and A.21 are shown the dose-response model for *E.coli* and *Clostridium* by using a β-Poisson and Exponential distribution, respectively [6].

$$P_{inf} = 1 - [1 + \frac{D}{N_{50}} \cdot (2^{\frac{1}{\alpha}} - 1)]^{-\alpha} \tag{A.20}$$

$$P_{inf} = 1 - [1 - exp((\lambda_{crypt} \cdot D)] \tag{A.21}$$

   Where:

   - P_{inf} is the probability of infection after the exposure [-].

- *D* is the exposure dose ("Dose") by ingestion (No.), see Eq. A.19 above.
- N_{50} is the median infectious effective/mean dose level equal to $2.11 \cdot 10^{+06}$[-] for *E.coli*.
- α is the on-negative parameters of the beta distribution equal to $1.55 \cdot 10^{-01}$ [-] for *E.coli*.
- λ_{crypt} is is the rate parameters. The distribution is supported on the interval [0, inf). If a random variable X has this distribution, it is usually written $X \approx \text{Exp}(\lambda)$.

3. **Risk characterization**: Once the dose-response model was defined, the final risk was calculated by using risk characterization formula as indicated by the Eq. A.22, which defines the probability of illness given the infection:

$$P_{ill|inf} = 1 - (1 - P_{inf})^n \quad \text{(A.22)}$$

Where:

- $P_{ill|inf}$ is the probability of illness having got the infection [-].
- P_{inf} is the probability of infection after exposure;
- n is the exposure frequency [day/year], assumed to be equal to 0.68 day/year (250 worked day on 1 year, as it was done for QCRA exposure time).

The results obtained were then compared with the safety thresholds established by the World Health Organization (W.H.O.) [7], which are set at 10^{-04}.

The results $P_{ill|inf}$ must be below the threshold value to be considered acceptable, otherwise measures to mitigate the risks are required.

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B

APPENDIX B

Environmental risk assessment related to using resource recovery-based bio-composite materials in the aquatic environment with new laboratory leaching test data - Supplementary File

B.1. PRIMARY WATERCOURSE

The primary watercourse exhibits a comparable profile to the wide ditch, with a trapezoidal geometry. Its dimensions are notably larger, exhibiting variation in cross-section and side slope. The profile of the primary watercourse is presented in Figure B.1.

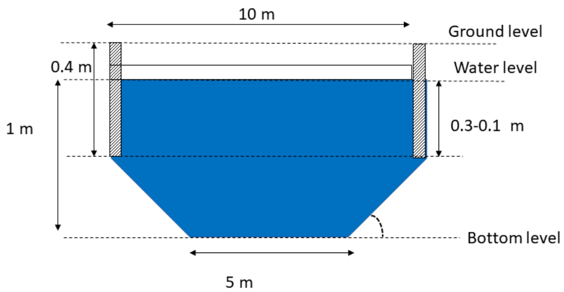

Figure B.1.: Primary water course profile.

B.2. SUMMER SEASON CONDITIONS RESULTS

The summer season was distinguished by a lower water level (0.1 m) due to the dry season. Consequently, the cross-sectional area of the water was diminished, resulting in a reduction in volume and low flow rate. Furthermore, the bio-composite canal bank protection element was partially submerged in the water, leading to a decrease in the release of chemicals into the surface water. In the context of summer conditions, the PEC/PNEC ratio is observed to decrease, thereby reducing the environmental risk.

The obtained results for the summer season conditions are presented in this supplementary material for both deterministic and stochastic approaches.

B.2.1. DETERMINISTIC APPROACH

STAGNANT CASE

The stagnant case is characterised by the absence of flow rate, which extends the residence time of chemicals in surface water, and limits their transport. Under these conditions, the observed PEC/PNEC ratios are higher and indicate a high environmental risk. However, as mentioned above, under summer conditions the PEC/PNEC ratios are reduced compared to the winter conditions (characterised by higher flow and water level).

The obtained results for all four bio-composite alternatives for both wide ditch and primary watercourse are shown in Figure B.2 and Figure B.3 for wide ditch and primary watercourse, respectively.

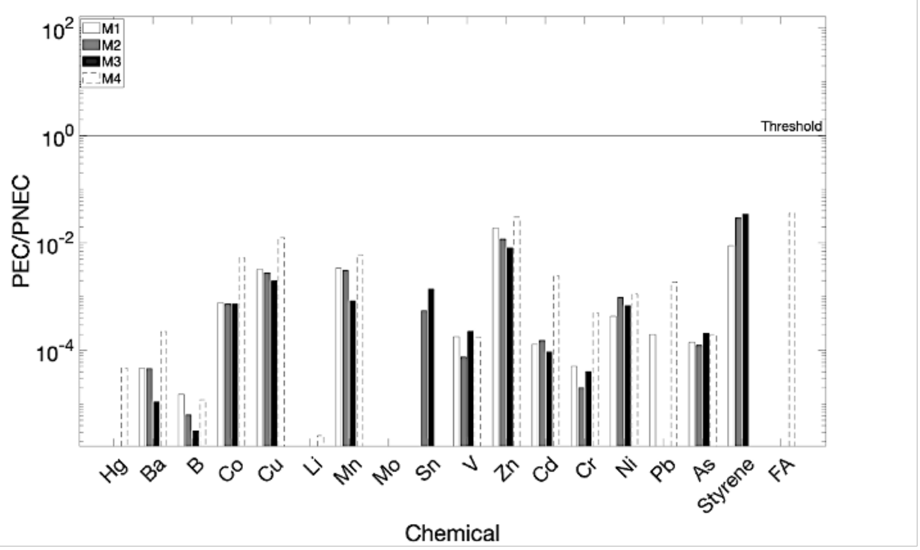

Figure B.2.: Stagnant case, wide ditch under summer season conditions.

ADVECTIVE FLOW CASE

The presence of flow rate (advective flow case) increases the dilution due to the periodic renewal of the water volume per day. This results in a lower PEC/PNEC ratio, especially under summer season conditions, for the reasons explained above. Results for the advective flow case for all four bio-composite materials, for both the wide ditch and the primary watercourse under summer conditions, are shown in Figure B.4 and Figure B.5 for wide ditch and primary watercourse, respectively.

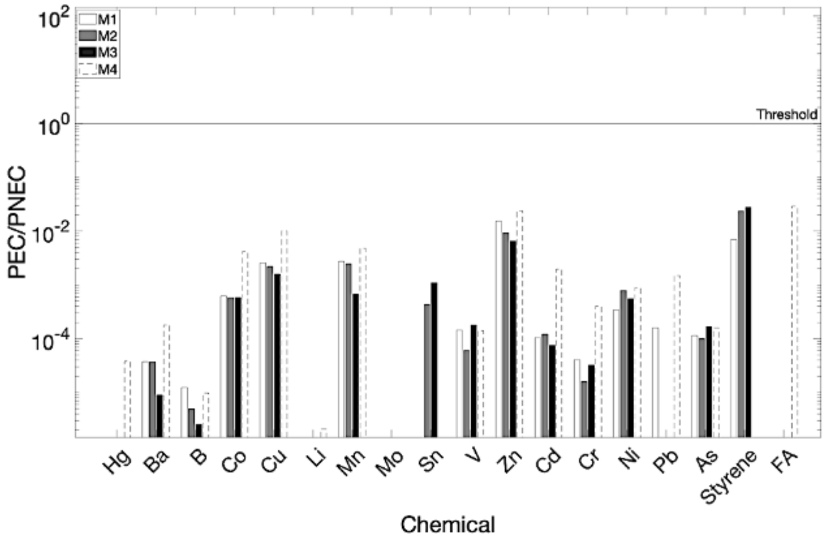

Figure B.3.: Stagnant case, primary watercourse under summer season conditions.

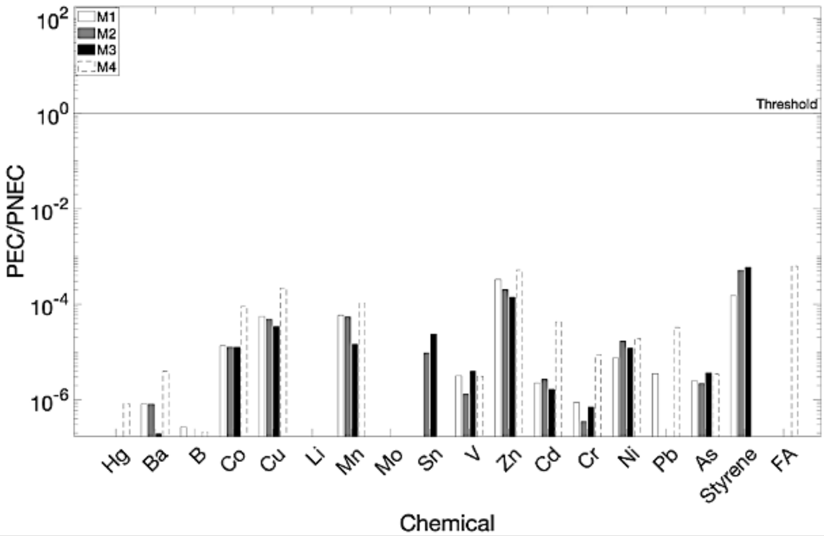

Figure B.4.: Advective flow case, wide ditch under summer season conditions.

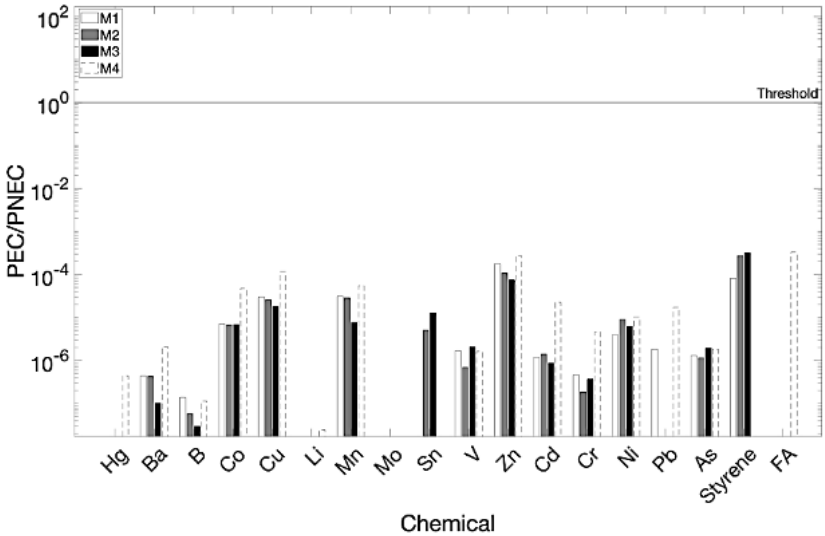

Figure B.5.: Advective flow case, primary watercourse under summer season conditions.

B.2.2. STOCHASTIC APPROACH

STAGNANT CASE: SENSITIVITY ANALYSIS S0 (VARIATION OF FLOW RATE) FOR M3 AND M4 FOR BOTH WIDE DITCH AND PRIMARY WATERCOURSE

The sensitivity analysis used a stochastic approach, specifically using the Monte Carlo method with 10, 000 trials. In the first sensitivity case (s1), the concentrations from the laboratory leaching tests were simulated using the uniform distribution under stagnant conditions (no flow). For this analysis, M3 and M4 were chosen as relevant materials due to the high release of styrene and furfuryl alcohol, respectively.
Results for both wide ditch and primary watercourse under summer conditions for M3 and M4 are displayed below. Specifically, Figure B.6 and Figure B.7 shown the sensitivity case s1 with regards of both wide ditch and primary watercourse for material M3, respectively. Figure B.8 and B.9 with regards of M4 for both wide ditch and primary watercourse, respectively.

IN THE CONTEXT OF THE ADVECTIVE CASE, A SENSITIVITY ANALYSIS (S2 CASE) WAS CONDUCTED TO ASSESS THE IMPACT OF VARYING THE FLOW RATE ON BOTH M3 AND M4, WITH A FOCUS ON BOTH THE WIDE DITCH AND PRIMARY WATERCOURSE

Results for material M3 are shown in Figure B.10 and Figure B.11, for both wide ditch and primary watercourse, respectively. With regards of material M4, the results for the sensitivity s2 case are shown in Figure

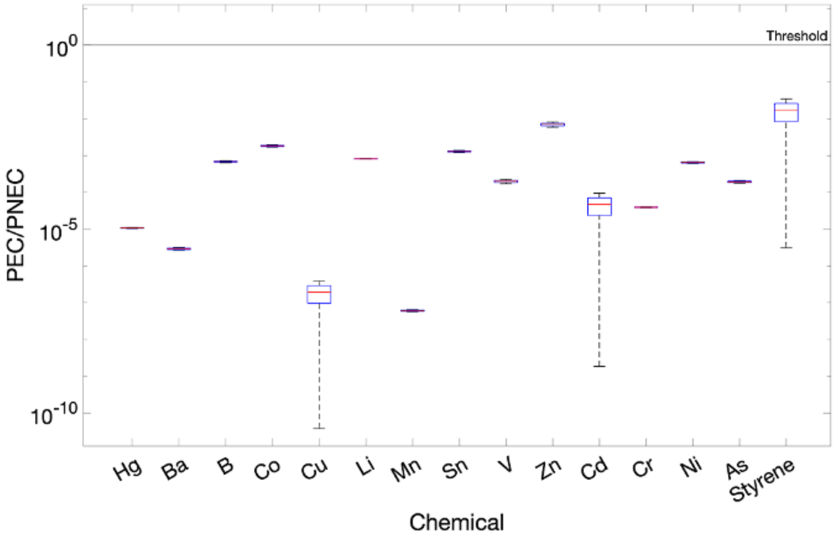

Figure B.6.: Stagnant case conditions, M3 wide ditch under summer conditions - s1 case.

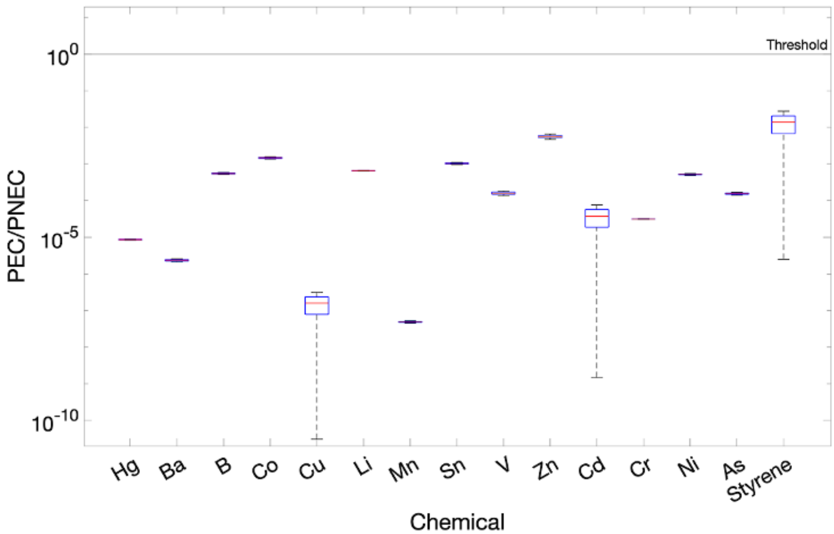

Figure B.7.: Stagnant case conditions, M3 primary watercourse under summer conditions - s1 case.

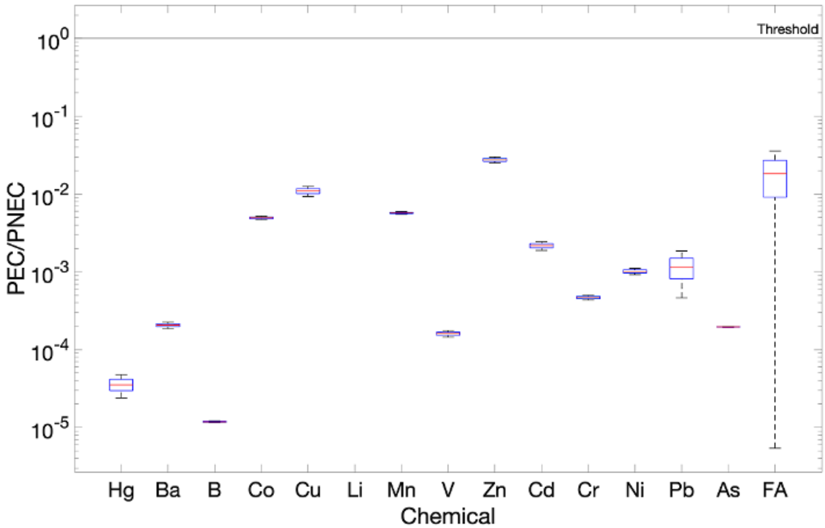

Figure B.8.: Stagnant case conditions, M4 wide ditch under summer conditions - s1 case.

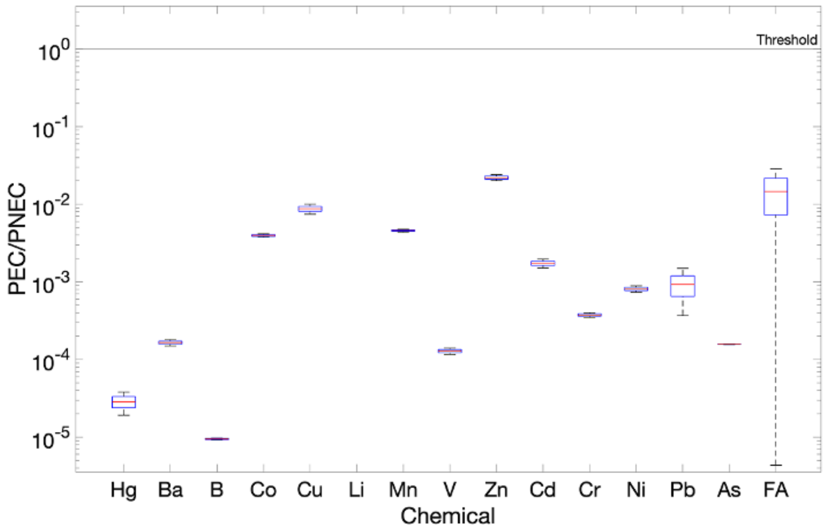

Figure B.9.: Stagnant case conditions, M4 primary watercourse under summer conditions - s1 case.

B.12 and Figure B.13, for both wide ditch and primary watercourse, respectively.

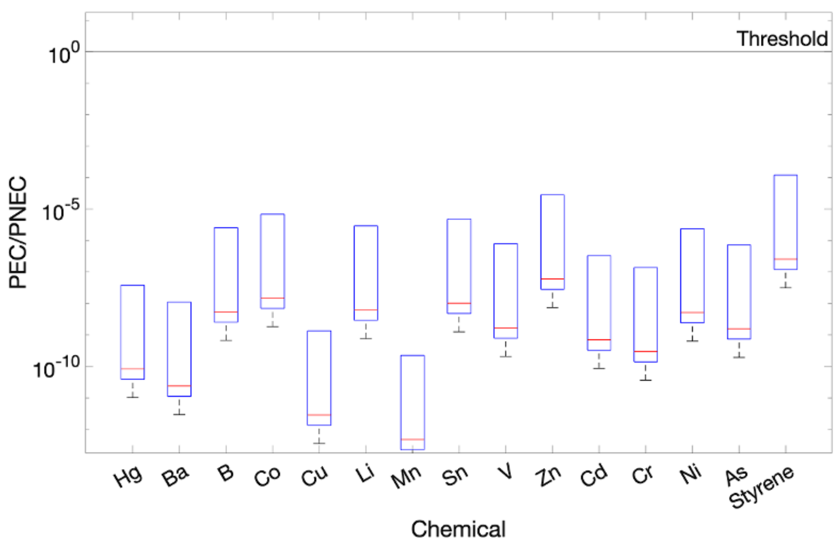

Figure B.10.: Advective flow case conditions, M3 wide ditch under summer conditions - s2 case.

B.3. CUMULATIVE RELEASE RATE

Four samples corresponding to four different days were analysed from the leaching tests: day 1, day 2, day 6 and day 13. To ensure complete information, linear interpolation was used to determine the leaching values for the missing data points. Cumulative concentrations up to day 13 were then calculated. The leaching results, initially expressed in mg/l, were then converted to mg/kg product concentrations using the following equation.

$$C_{[mg/kg]} = \frac{C_L \cdot V_L}{M_L} \tag{B.1}$$

Where:

- $C_{[mg/kg]}$ is the equivalent concentration of the leaching in mg/kg of material released from leaching conditions in 1 day [mg/kg].
- C_L is the leaching concentration in one day [mg/l].
- V_L is the volume of water added in one day of leaching [l].

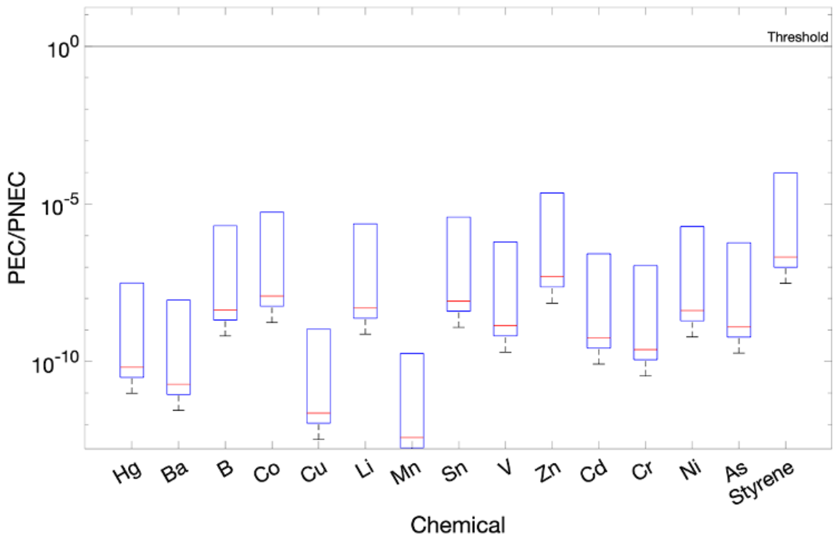

Figure B.11.: Advective flow case conditions, M3 primary watercourse under summer conditions - s2 case.

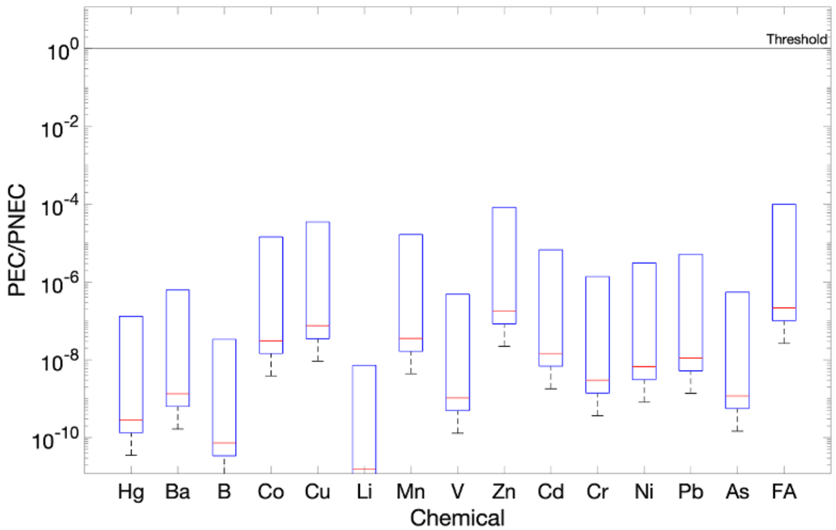

Figure B.12.: Advective flow case conditions, M4 wide ditch under summer conditions - s2 case.

B

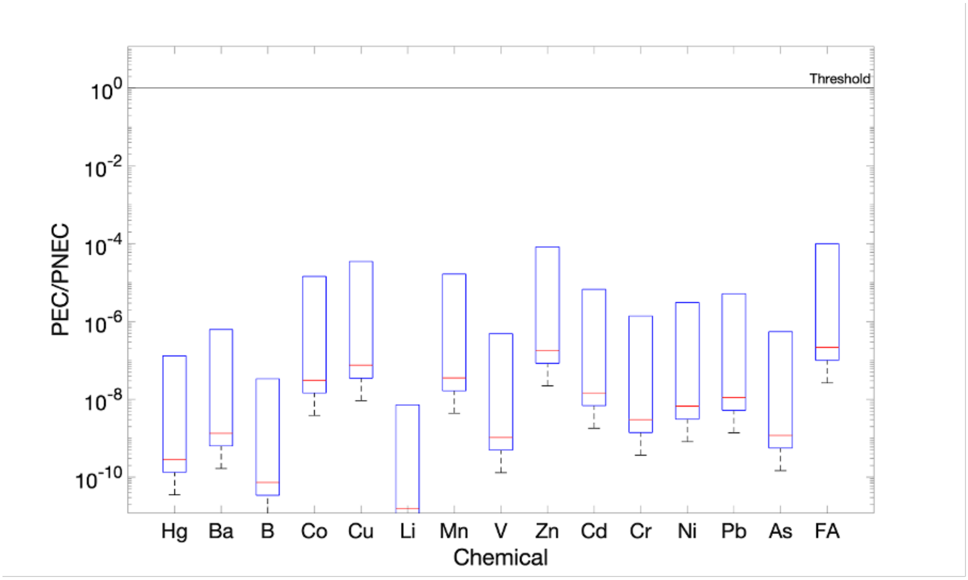

Figure B.13.: Advective flow case conditions, M4 primary watercourse under summer conditions - s2 case.

- M_L is the mass of the material used for leaching test [0.3 kg].

Linear interpolation was used to estimate the intermediate time points between day 1 and day 13. The cumulative curve was constructed by calculating all time points within this interval. At day 13, the results represent the total mass released by 0.3 kg of material under laboratory leaching conditions. The results obtained were then evaluated in terms of potential release in a 1 m compartment of the canal using the following formula for summer and winter conditions.

$$C_{R,s} = \frac{C_{[mg/kg]} \cdot M_{sub,s}}{V_{w,s}} \tag{B.2}$$

$$C_{R,w} = \frac{C_{[mg/kg]} \cdot M_{sub,w}}{V_{w,w}} \tag{B.3}$$

Where:

- $C_{R,s}$ and $C_{R,w}$ are the new concentrations released in one day from the canal bank protection over 1 m of length of bio-composite canal bank protection under summer and winter conditions, respectively [mg/m^3].
- $C_{[mg/kg]}$ is the equivalent concentration in mg/kg released in one day under laboratory leaching test conditions, calculated in Eq. B.1.

- $M_{sub,s}$ and $M_{sub,w}$ are the submerged masses of canal bank protection element over 1 m length, under summer and winter conditions respectively [kg].

- $V_{w,s}$ and $V_{w,w}$ are the volume of water over 1 m of length of bio-composite canal bank protection element under summer and winter conditions respectively [m^3].

The new calculated concentrations represent the Predicted Effects Concentration (PEC) over a 13-day period for a canal bank protection element covering a length of 1 m. These values were then compared with the Predicted No Effects Concentration (PNEC) collected to assess the environmental risk after 13 days. The results indicated that the PEC/PNEC ratio for all four bio-composite alternatives is below the safety threshold. Given this, the results presented refer to the worst case scenario, characterised by stagnant conditions and the wide ditch profile. It was decided not to include the results for the primary watercourse and the advective scenario, as the PEC/PNEC ratios in these cases would be even lower than those presented here, falling consistently below the safety threshold of 1.00.
Figure B.14 show the environmental risk in terms of PEC/PNEC values over thirteen days under both summer and winter season conditions.

B

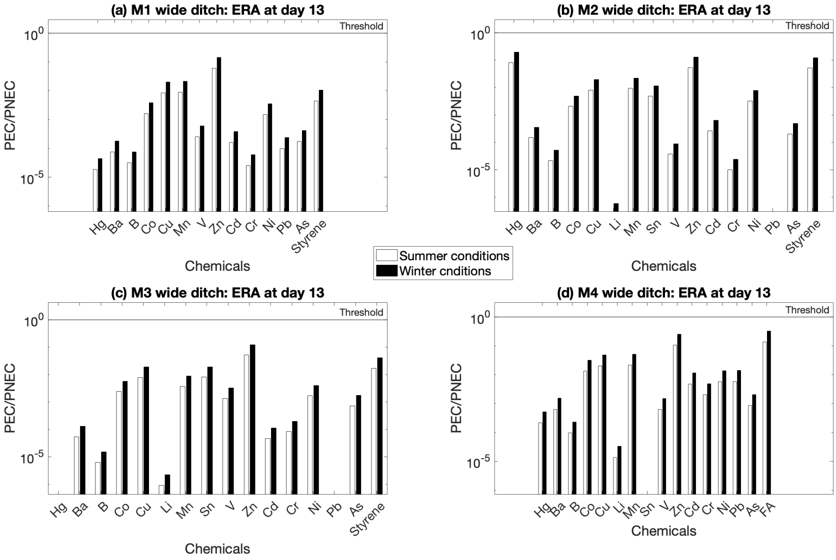

Figure B.14.: Cumulative Environmental risk for all four bio-composites expressed as PEC/PNEC on day 13, stagnant case under summer and winter conditions for wide ditch: (a) M1; (b) M2; (c) M3; (d) M4.

C

APPENDIX C

Risk of Rainfall Caused Leaching from Bio-Composite Material based Building Façades into the Aquatic Environment - Supplementary File

C

C.1. EXPERIMENTAL LEACHING TESTS

C.1.1. SIMULATED RAINWATER

In order to create a stock synthetic rainwater solution, we began with the ion concentrations reported as outputs in the European Commission ERM-CA408 report [1]. The final ions concentrations are listed in Table C.1.

Table C.1.: Simulated rainwater characteristics (Ricci et al., 2010).

Substance [-]	**Certified value [mg/l]**	**Uncertainty [mg/l]**
NH_4^+	0.91	0.028
Cl^-	1.96	0.07
F^-	0.194	0.008
Mg^{2+}	0.145	0.022
NO_3^-	2.01	0.09
PO_4^{3-}	1	0.05
SO_4^{2-}	1.46	0.04
EC [μS/cm]	18.7	1.8
pH	6.3	0.6

The chemicals employed in the synthesis of the synthetic rainwater solutions were selected on the basis of the availability of the TUDelft Waterlab. The selected chemicals are listed in Table C.2.

Table C.2.: Chemicals used to create the stock solution of synthetic rainwater.

Chemical -	**MW [g/mol]**
$MgCl_2$	95.21
K_2SO_4	156.25
NH_4NO_3	80.04
$NaNO_3$	84.99
NH_4Cl	53.49
NaH_2PO_4	119.98

Stoichiometric calculations were conducted to ascertain the quantity of each chemical necessary to prepare a solution with a $10,000$-fold dilution. For each chemical selected, an ultra-pure water solution was prepared based on the mass calculated in the stoichiometric calculations. Subsequently, 100 μL of each solution was combined to create the 1x stock solution of rainwater. The preparation of the stock solutions is detailed in the Table. C.3.

Table C.3.: Composition of initial stock solutions used to make synthetic rainwater.

Compound amount in 1l	$MgCl_2$	K_2SO_4	NH_4NO_3	$NaNO_3$	NH_4Cl	NaH_2PO_4
(mmoles/l) - limiting agent	0.006	0.015	0.007	0.025	0.043	0.011
1X (mg/l)	0.568	2.375	0.567	2.153	2.319	1.263
For 1L, 100X solution (mg/L)	56.798	237.495	56.741	215.277	231.915	126.336
For 100 ml, 100X solution (g)	0.006	0.024	0.006	0.022	0.023	0.013
For 100 ml, 10000X solution (g)	**0.568**	**2.375**	**0.567**	**2.153**	**2.319**	**1.263**
100 μl of each 10,000 X stock solution						

C

BACKGROUND CONCENTRATION

In order to ascertain the effective leaching of the material, it is necessary to evaluate and remove the background concentrations of ions in rainwater from the observed leaching. The background concentrations of the chemicals detected in the leaching effluent (Mg, K, P, and Na) are represented by the numbers in orange. The quantity of HCl was added to adjust the pH of the synthetic rainwater, with the resulting value displayed in red in Table C.4.

Table C.4.: Background concentrations.

Ions	MW (g/mol)	Chemical	MW (g/mol)	Salt added i1 mg	Ions	Total ions i1 mg	Background mg/L
NH_4	$1.8{\cdot}10^{+01}$	$MgCl_2$	$9.5{\cdot}10^{+01}$	$2.2{\cdot}10^{-02}$	NH4	$3.5{\cdot}10^{-02}$	**9.1**$\cdot10^{+02}$
Mg	$2.4{\cdot}10^{+01}$	K_2SO_4	$1.7{\cdot}10^{+02}$	$1.0{\cdot}10^{-01}$	Mg	$5.7{\cdot}10^{-03}$	**1.5**$\cdot10^{+02}$
K	$3.9{\cdot}10^{+01}$	NH_4NO_3	$8.0{\cdot}10^{+01}$	$2.2{\cdot}10^{-02}$	K	$4.6{\cdot}10^{-02}$	**1.2**$\cdot10^{+03}$
Na	$2.3{\cdot}10^{+01}$	$NaNO_3$	$8.5{\cdot}10^{+01}$	$8.4{\cdot}10^{-02}$	Na	$5.7{\cdot}10^{-01}$	**1.5**$\cdot10^{+04}$
Cl	$3.5{\cdot}10^{+01}$	NH_4Cl	$5.3{\cdot}10^{+01}$	$9.0{\cdot}10^{-02}$	Cl	$7.6{\cdot}10^{-02}$	**2.0**$\cdot10^{+03}$
NO_3	$6.2{\cdot}10^{+01}$	NaH_2PO_4	$1.2{\cdot}10^{+02}$	$4.9{\cdot}10^{-02}$	NO_3	$7.8{\cdot}10^{-02}$	**2.0**$\cdot10^{+03}$
PO_4	$9.5{\cdot}10^{+01}$	HCl	$3.6{\cdot}10^{+01}$		PO_4	$3.9{\cdot}10^{-02}$	**1.0**$\cdot10^{+03}$
SO_4	$9.6{\cdot}10^{+01}$	NaOH	$4.0{\cdot}10^{+01}$	$9.4{\cdot}10^{+01}$	SO_4	$5.7{\cdot}10^{-02}$	**1.5**$\cdot10^{+03}$
Ions	**MW (g/mol)**	**Chemical**	**MW (g/mol)**	**Salt added i2 mg**	**Ions**	**Total ions i2 mg**	**Background mg/L**
NH_4	$1.8{\cdot}10^{+01}$	$MgCl_2$	$9.5{\cdot}10^{+01}$	$6.6{\cdot}10^{-02}$	NH_4	$1.1{\cdot}10^{-01}$	**9.1**$\cdot10^{+02}$
Mg	$2.4{\cdot}10^{+01}$	K_2SO_4	$1.7{\cdot}10^{+02}$	$3.1{\cdot}10^{-01}$	Mg	$1.7{\cdot}10^{-02}$	**1.5**$\cdot10^{+02}$
K	$3.9{\cdot}10^{+01}$	NH_3NO_3	$8.0{\cdot}10^{+01}$	$6.6{\cdot}10^{-02}$	K	$1.4{\cdot}10^{-01}$	**1.2**$\cdot10^{+03}$
Na	$2.3{\cdot}10^{+01}$	$NaNO_3$	$8.5{\cdot}10^{+01}$	$2.5{\cdot}10^{-01}$	Na	1.70	**1.5**$\cdot10^{+04}$
Cl	$3.5{\cdot}10^{+01}$	NH_4Cl	$5.3{\cdot}10^{+01}$	$2.7{\cdot}10^{-01}$	Cl	$2.3{\cdot}10^{-01}$	**2.0**$\cdot10^{+03}$
NO_3	$6.2{\cdot}10^{+01}$	NaH_3PO_4	$1.2{\cdot}10^{+02}$	$1.5{\cdot}10^{-01}$	NO_3	$2.3{\cdot}10^{-01}$	**2.0**$\cdot10^{+03}$
PO_4	$9.5{\cdot}10^{+01}$	HCl	$3.6{\cdot}10^{+01}$		PO_4	$1.2{\cdot}10^{-01}$	**1.0**$\cdot10^{+03}$
SO_4	$9.6{\cdot}10^{+01}$	NaOH	$4.0{\cdot}10^{+01}$	2.80	SO_4	$1.7{\cdot}10^{-01}$	**1.5**$\cdot10^{+03}$

To evaluate the effective leaching from the bio-composite materials, the background concentrations were removed from the observed leaching values, indicating the fraction of observed leaching derived exclusively from rainwater. The results are illustrated in Figure C.1. As it can be seen in Figure C.1, for M3, the phosphorus (P) detected in the leaching represents exclusively the background concentration contained in the synthetic rainwater utilized as influent. This can be used as an internal standard, affirming the precise amount incorporated into the rainwater.

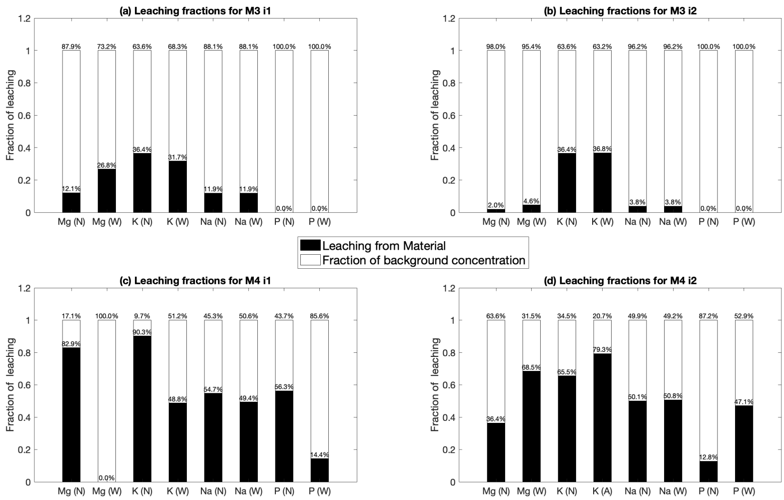

Figure C.1.: Effective leaching from the material (N: new sample; W: weathered sample) and effective leaching due to the synthetic rainwater composition.

C.2. SENSITIVITY ANALYSIS

In this section the Matlab script concerning the sensitivity analysis that was carried out to simulate leaching concentrations and rain intensities is provided for material M4 New sample. The same code has been applied to the other samples (not shown here) in order to carry out the sensitivity analysis.

C.2.1. MATLAB SCRIPT

Sensitivity case s1

```
% Constants
intensity = 0.005; % Rain intensity in m/h
A_real = 54; % Actual surface area in m2
V_pond = 781.250; % Volume of water in the pond
    in m3

% Data: cumulative leaching amounts (ug/L) for
   various metals after 4 rainfall events
% M4
N8040_F1 = [1.69; 29; 6.7; 704; 8.96; 420.841;
   85.8];
```

```
PNEC_8040_F1 = [114.7; 2900; 6.3; 410; 34;
   10.5; 14.4];
metals_M4_f1 = {'Ba', 'B', 'Cu', 'Mg', 'Mn','P'
   , 'Zn'};

% Number of Monte Carlo samples
numSamples = 10000;

% Preallocate arrays for storing results
PEC_PNEC_M4F1_case1 = zeros(numSamples, length(
   N8040_F1));
deterministic_PEC_PNEC = zeros(length(N8040_F1)
   , 1);

% Monte Carlo simulation to generate PEC/PNEC
   ratios
for i = 1:length(N8040_F1)
% Fit an exponential distribution to the
   leaching data
data = [0; N8040_F1(i)];
expParams = mle(data, 'distribution', '
   exponential');

% Simulate leaching concentrations (C_L)
C_L = exprnd(expParams, numSamples, 1);

% Calculate real leaching concentration (
   C_L_real)
C_L_real = (C_L * intensity * A_real) / V_pond;

% Calculate PEC/PNEC ratio
PEC_PNEC = C_L_real / PNEC_8040_F1(i);

% Store PEC/PNEC ratios for this metal
PEC_PNEC_M4F1_case1(:, i) = PEC_PNEC;

% Deterministic approach
deterministic_C_L_real = (N8040_F1(i) *
   intensity * A_real) / V_pond;
deterministic_PEC_PNEC(i) =
   deterministic_C_L_real / PNEC_8040_F1(i);
end

% Plot the PEC/PNEC ratio as histogram and
   deterministic comparison
```

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```
figure;
for i = 1:length(N8040_F1)
subplot(3, 3, i);
histogram(PEC_PNEC_M4F1_case1(:, i), 50, '
   Normalization', 'pdf');
hold on;
m1 = xline(deterministic_PEC_PNEC(i), 'r', '
   LineWidth', 2, 'DisplayName', 'Deterministic
   ');
m2 = xline(mean(PEC_PNEC_M4F1_case1(:, i)), 'b'
   , 'LineWidth', 2, 'DisplayName', 'Monte
   Carlo Mean');
hold off;
title(['PEC/PNEC for ', metals_M4_f1{i}]);
xlabel('PEC/PNEC');
ylabel('PDF');
legend([m1,m2],{'Deterministic', 'Monte Carlo
   mean'});
%legend([deterministic_line, monte_carlo_line],
    'Location', 'best');
end

% Plot the boxplot of PEC/PNEC ratios for
   Sensitivity Case 1
figure;
hold on;

% Create boxplot without colors
boxplot(PEC_PNEC_M4F1_case1, 'Labels',
   metals_M4_f1);

% Plot deterministic results as points with
   colors
colors = lines(length(metals_M4_f1));
for i = 1:length(metals_M4_f1)
scatter(i, deterministic_PEC_PNEC(i), 100, '
   filled', 'MarkerEdgeColor', 'k', '
   MarkerFaceColor', colors(i, :));
end

% Customize plot labels and title
title('PEC/PNEC Ratio Variation for Simulated
   Leaching');
xlabel('Metals');
ylabel('PEC/PNEC Ratio');
```

```
set(gca, 'YScale', 'log');
yline(1, '-', 'Threshold');
hold off;

% Display numerical values for PEC/PNEC ratios
disp('PEC/PNEC Ratio Summary for Sensitivity
   Case 1:');
for i = 1:length(metals_M4_f1)
    disp(['Metal: ', metals_M4_f1{i}]);
    disp(['Mean (Monte Carlo): ', num2str(mean(
       PEC_PNEC_M4F1_case1(:, i)))]);
    disp(['Median (Monte Carlo): ', num2str(
       median(PEC_PNEC_M4F1_case1(:, i)))]);
    disp(['Standard Deviation (Monte Carlo): ',
        num2str(std(PEC_PNEC_M4F1_case1(:, i)))
       ]);
    disp(['95th Percentile (Monte Carlo): ',
       num2str(prctile(PEC_PNEC_M4F1_case1(:, i
       ), 95))]);
    disp(['Exceedance Probability (PEC/PNEC >
       1) (Monte Carlo): ', num2str(mean(
       PEC_PNEC_M4F1_case1(:, i) > 1))]);
    disp(['Deterministic PEC/PNEC Ratio: ',
       num2str(deterministic_PEC_PNEC(i))]);
    disp(' ');
end
```

Sensitivity case s2

```
        % Constants
A_real = 54; % Actual surface area in m2
V_pond = 781.250; % Volume of water in the pond
    in m3

% Data: cumulative leaching amounts (ug/L) for
   various metals after 4 rainfall events
% M4
N8040_F1 = [1.69; 29; 6.7; 704; 8.96; 420.841;
   85.8];
PNEC_8040_F1 = [114.7; 2900; 6.3; 410; 34;
   10.5; 14.4];
metals_M4_f1 = {'Ba', 'B', 'Cu', 'Mg', 'Mn','P'
   , 'Zn'};


% Rain intensity parameters (in m/h)
rain_min = 0.005;
```

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```
rain_max = 0.015;

% Number of Monte Carlo samples
numSamples = 10000;

% Preallocate arrays for storing results
PEC_PNEC_M4F1_case2 = zeros(numSamples, length(
   N8040_F1));
deterministic_PEC_PNEC = zeros(length(N8040_F1)
   , 1);

% Monte Carlo simulation to generate PEC/PNEC
   ratios
for i = 1:length(N8040_F1)
% Fix the leaching concentration (C_L) using
   deterministic data
C_L = N8040_F1(i);
% Simulate rain intensities (H_i) between 0.005
    and 0.015
H_i = rain_min + (rain_max - rain_min) * rand(
   numSamples, 1);
%Calculate real leaching concentration (
   C_L_real)
C_L_real = (C_L .* H_i .* A_real) / V_pond;
% Calculate PEC/PNEC ratio
PEC_PNEC = C_L_real / PNEC_8040_F1(i);

%Store PEC/PNEC ratios for this metal
PEC_PNEC_M4F1_case2(:, i) = PEC_PNEC;

%Deterministic approach for the midpoint rain
   intensity
        deterministic_H_i = (rain_min +
           rain_max) / 2;
deterministic_C_L_real = (C_L *
   deterministic_H_i * A_real) / V_pond;
deterministic_PEC_PNEC(i) =
   deterministic_C_L_real / PNEC_8040_F1(i);
end

% Plot the PEC/PNEC ratio as histogram and
   deterministic comparison
figure;
for i = 1:length(N8040_F1)
    subplot(3, 3, i);
```

```
    histogram(PEC_PNEC_M4F1_case2(:, i), 50, '
       Normalization', 'pdf');
    hold on;
    l1 = xline(deterministic_PEC_PNEC(i), 'r',
       'LineWidth', 2,            'DisplayName',
       'Deterministic');
    l2 = xline(mean(PEC_PNEC_M4F1_case2(:, i)),
        'b', 'LineWidth', 2, 'DisplayName', '
       Monte Carlo Mean');
    hold off;
    title(['PEC/PNEC for ', metals_M4_f1{i}]);
    xlabel('PEC/PNEC');
    ylabel('PDF');
    %legend('PDF','Deterministic', 'Monte Carlo
        mean');
    legend([l1,l2],{'Deterministic', 'Monte
       Carlo mean'});
 end

% Plot the boxplot of PEC/PNEC ratios for
   Sensitivity Case 1
figure;
hold on;

% Create boxplot without colors
boxplot(PEC_PNEC_M4F1_case2, 'Labels',
   metals_M4_f1);

% Plot deterministic results as points with
   colors
colors = lines(length(metals_M4_f1));
for i = 1:length(metals_M4_f1)
    scatter(i, deterministic_PEC_PNEC(i), 100,
       'filled', 'MarkerEdgeColor', 'k', '
       MarkerFaceColor', colors(i, :));
end

% Customize plot labels and title
title('PEC/PNEC Ratio Variation for Simulated
   Rain Intensity');
xlabel('Metals');
ylabel('PEC/PNEC Ratio');
set(gca, 'YScale', 'log');
yline(1, '-', 'Threshold');
hold off;
```

```
% Display numerical values for PEC/PNEC ratios
disp('PEC/PNEC Ratio Summary for Sensitivity
   Case 1:');
for i = 1:length(metals_M4_f1)
    disp(['Metal: ', metals_M4_f1{i}]);
    disp(['Mean (Monte Carlo): ', num2str(mean(
       PEC_PNEC_M4F1_case2(:, i)))]);
    disp(['Median (Monte Carlo): ', num2str(
       median(PEC_PNEC_M4F1_case2(:, i)))]);
    disp(['Standard Deviation (Monte Carlo): ',
        num2str(std(PEC_PNEC_M4F1_case2(:, i)))
       ]);
    disp(['95th Percentile (Monte Carlo): ',
       num2str(prctile(PEC_PNEC_M4F1_case2(:, i
       ), 95))]);
    disp(['Exceedance Probability (PEC/PNEC >
       1) (Monte Carlo): ', num2str(mean(
       PEC_PNEC_M4F1_case2(:, i) > 1))]);
    disp(['Deterministic PEC/PNEC Ratio: ',
       num2str(deterministic_PEC_PNEC(i))]);
    disp(' ');
end
```

Sensitivity case s3

```
% Constants
A_real = 54; % Actual surface area in m2
V_pond = 781.250; % Volume of water in the pond
    in m3

% Data: cumulative leaching amounts (ug/L) for
   various metals after 4 rainfall events
% m4
N8040_F1 = [1.69; 29; 6.7; 704; 8.96; 420.841;
   85.8];
PNEC_8040_F1 = [114.7; 2900; 6.3; 410; 34;
   10.5; 14.4];
metals_M4_f1 = {'Ba', 'B', 'Cu', 'Mg', 'Mn','P'
   , 'Zn'};

% Rain intensity parameters (in m/h)
rain_min = 0.005;
rain_max = 0.015;

% Number of Monte Carlo samples
numSamples = 10000;
```

```
% Preallocate arrays for storing results
PEC_PNEC_combined = zeros(numSamples, length(
   N8040_F1));
deterministic_PEC_PNEC_combined = zeros(length(
   N8040_F1), 1);

% Monte Carlo simulation to generate PEC/PNEC
   ratios
for i = 1:length(N8040_F1)

% Simulate leaching concentrations (C_L) using
   exponential     distribution
    data = [0; N8040_F1(i)];
    expParams = mle(data, 'distribution', '
       exponential');
    lambda = expParams;
    C_L = exprnd(lambda, numSamples, 1);

% Simulate rain intensities (H_i) between 0.005
    and 0.015
    H_i = rain_min + (rain_max - rain_min) *
       rand(numSamples, 1);

% Calculate real leaching concentration (
   C_L_real)
    C_L_real = (C_L .* H_i .* A_real) / V_pond;

% Calculate PEC/PNEC ratio
    PEC_PNEC = C_L_real / PNEC_8040_F1(i);

% Store PEC/PNEC ratios for this metal
    PEC_PNEC_combined(:, i) = PEC_PNEC;

% Deterministic approach using mean leaching
   concentration and mid-point rain intensity
    deterministic_C_L = N8040_F1(i);
    deterministic_H_i = (rain_min + rain_max) /
        2;
    deterministic_C_L_real = (deterministic_C_L
        * deterministic_H_i * A_real) / V_pond;
    deterministic_PEC_PNEC_combined(i) =
       deterministic_C_L_real / PNEC_8040_F1(i)
       ;
end
```

C

```
% Plot results: Histogram and deterministic
   comparison
figure;
for i = 1:length(N8040_F1)
    subplot(3, 3, i);
    histogram(PEC_PNEC_combined(:, i), 50, '
       Normalization', 'pdf');
    hold on;
    n1 = xline(deterministic_PEC_PNEC_combined(
       i), 'r', 'LineWidth', 2, 'DisplayName',
       'Deterministic');
    n2 = xline(mean(PEC_PNEC_combined(:, i)), '
       b', 'LineWidth', 2, 'DisplayName', '
       Monte Carlo Mean');
    hold off;
    title(['PEC/PNEC for ', metals_M4_f1{i}]);
    xlabel('PEC/PNEC');
    ylabel('PDF');
          legend([n1,n2],{'Deterministic', '
             Monte Carlo mean'});
end

% Display summary statistics
disp('PEC/PNEC Ratio Summary for Combined
   Sensitivity Analysis:');
for i = 1:length(metals_M4_f1)
    disp(['Metal: ', metals_M4_f1{i}]);
    disp(['Mean (Monte Carlo): ', num2str(mean(
       PEC_PNEC_combined(:, i)))]);
    disp(['Median (Monte Carlo): ', num2str(
       median(PEC_PNEC_combined(:, i)))]);
    disp(['Standard Deviation (Monte Carlo): ',
        num2str(std(PEC_PNEC_combined(:, i)))])
       ;
    disp(['95th Percentile (Monte Carlo): ',
       num2str(prctile(PEC_PNEC_combined(:, i),
        95))]);
    disp(['Exceedance Probability (PEC/PNEC >
       1) (Monte Carlo): ', num2str(mean(
       PEC_PNEC_combined(:, i) > 1))]);
    disp(['Deterministic PEC/PNEC Ratio: ',
       num2str(deterministic_PEC_PNEC_combined(
       i))]);
    disp(' ');
```

```
end

% Plot the boxplot of PEC/PNEC ratios for the
   combined sensitivity analysis
figure;
hold on;

% Create boxplot without colors
boxplot(PEC_PNEC_combined, 'Labels',
   metals_M4_f1);

% Plot deterministic results as points with
   colors
colors = lines(length(metals_M4_f1));
for i = 1:length(metals_M4_f1)
    scatter(i, deterministic_PEC_PNEC_combined(
       i), 100, 'filled', 'MarkerEdgeColor', 'k
       ', 'MarkerFaceColor', colors(i, :));
end

% Customize plot labels and title
title('PEC/PNEC Ratio Variation for Combined
   Sensitivity Analysis');
xlabel('Metals');
ylabel('PEC/PNEC Ratio');
set(gca, 'YScale', 'log');
yline(1, '-', 'Threshold');
hold off;
```

C.3. PERCENTAGE LEACHING RATE

The percentage leaching release was calculated based on the total chemical content leached from materials M3 and M4 and the chemical composition of the raw ingredients (cellulose, reeds, calcite, etc.) and their fraction in the material recipe. The chemical analysis of the raw ingredients was described in our previous study [2]. The percentage leaching has been calculated for all chemicals detected in the leached effluent using the following equations:

- **Maximum expected leaching**:

$$Max_L = \frac{C_i \cdot m_{sample}}{V_{L,i}} \quad \text{(C.1)}$$

Where:

- Max_L refers to the highest amount of chemical that can be released from the material based on its original chemical contaminants in [μg/L].
- C_i is the initial content [mg/kg] is the mass of the contaminant detected in the raw materials' chemical analysis.
- m_{sample} is the mass of the sample [kg] is the mass of the biocomposite sample used to carry out irrigation leaching tests.
- $V_{L,i}$ [l] is the volume of the leaching based on the intensity of the rain simulated, where i = 1, 2.

- **Percentage leaching release**:

$$\%leaching = \frac{L_{obs}}{Max_L} \tag{C.2}$$

Where:

- % leaching is the percentage of chemical released, based on the original chemical contamination of the material.
- L_{obs} is the observed leaching refers to the amount of leaching [μg/L] detected in the leaching effluent after removing the synthetic rainwater background concentrations.
- Max_L is the maximum expected leaching refers to the highest amount of chemical that can be released from the material based on its original contamination in [μg/L], defined in Eq. C.1.

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[2] A. Nativio, O. Jovanovic, Z. Kapelan, and J. P. van der Hoek. “Human health risk assessment framework for new water resource recovery-based bio-composite materials.” In: *Water Health* 22(4) (2024), pp. 652–672. doi: 10.2166/wh.2024.168.

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ABOUT THE AUTHOR

Arianna Nativio

Arianna Nativio was born on 13 February 1994 in Rome, Italy. She completed her undergraduate and graduate studies at the University of Rome "La Sapienza." During her master's programme, she undertook a period of study at the University of Mons, Mons, Belgium, in the Chemical Engineering department, participating in the "Erasmus +" programme in order to complete her master's thesis. The thesis examined the issue of fire safety in Passive Houses, and validated the FDS software, under the supervision of Roberto Bubbico (University of Rome "La Sapienza") and Sylvain Brohez (University of Mons).
Over the course of her academic career, she developed an interest in the application of risk assessment methodologies in a range of competence fields, including fire safety, human health risk assessment, and environmental risk assessment, with a particular focus on chemical and microbial risks. During her master's programme, she undertook an internship in collaboration with two universities in Rome: the University of Rome "Tor Vergata" and the University of Rome "Roma Tre". During the internship, she gained valuable insights into the safety regulations governing the use of bioplastic materials such as PLA in food packaging. In addition to her academic pursuits, Arianna engaged in professional activities for approximately six months in Rome, where she served as a safety officer. Her responsibilities included the assessment of potential risks associated with construction sites for electrical cabins and underground water pipelines. Subsequently, she moved to the Netherlands to

begin her PhD at Delft University of Technology (TUDelft), in the Water Management Department, under the supervision of Zoran Kapelan and Jan Peter van der Hoek. As part of the European project WIDER UPTAKE (Horizon 2020), her PhD focused on the risk assessment of human health and environmental risks associated with the production and application of a novel type of water resource recovery-based bio-composite materials. The materials in question are intended to be made from a variety of recovered resources from the water sector. These include cellulose fibres recovered from wastewater, as well as reed and grass collected from surface water management, and a bio-filler using calcite pellets collected as a by-product of the softening process of drinking water treatment.

LIST OF PUBLICATIONS

PUBLICATIONS

1. **Nativio A.**, Kapelan Z., van der Hoek J.P., (2022). Risk assessment methods for water resource recovery for the production of bio-composite materials: Literature review and future research directions, Environmental Challenges, **9**, 100645.

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4. **Nativio A.**, Jovanovic O., van der Hoek J.P., Kapelan Z., (*Under Review*). Risk of Rainfall Caused Leaching from Bio-Composite Material based Building Façades into the Aquatic Environment.

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1. **Nativio A.**, Jovanovic O., Kapelan Z., van der Hoek J.P., (2020, 7-8 October, Netherlands). Assessment and management of health and quality risks for (waste)water reuse and resource recovery. The 14^{th} IHE PhD Symposium 2020.

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