VOLUME 26 / March 2024

detritus

Multidisciplinary Journal for Circular Economy and Sustainable Management of Residues

Editor in Chief:
RAFFAELLO COSSU

detritusjournal.com

an official journal of:
iwwg
international waste working group

ISSN 2611-4135 / ISBN 9788862650397
DETRITUS - Multidisciplinary Journal for Circular Economy and Sustainable Management of Residues

Detritus is indexed in:

- Emerging Sources Citation Index (ESCI), Clarivate Analytics, Web of Science
- Scopus, Elsevier
- Google Scholar

The journal contents are available on the official website: www.detritusjournal.com
Legal head office: Cisa Publisher - Eurowaste Srl, Via Beato Pellegrino 23, 35137 Padova - Italy / www.cisapublisher.com

Graphics and layout: Elena Cossu, Anna Artuso - Studio Arcoplan, Padova / studio@arcoplan.it
Printed by Cleup, Padova, Italy
Front page photo credits: Timothy Bouldry, United States - Waste to Photo 2017 / Sardinia Symposium

For subscription to printed version, advertising or other commercial opportunities please contact the Administration Office at administration@eurowaste.it

Papers should be submitted online at https://mc04.manuscriptcentral.com/detritusjournal
Instructions to authors may be found at https://detritusjournal.com/guide-for-authors/
For any enquiries and information please contact the Editorial Office at editorialoffice@detritusjournal.com

Registered at the Court of Padova on March 13, 2018 with No. 2457

www.detritusjournal.com

VOLUME 26 / March 2024

detritus

Multidisciplinary Journal for Circular Economy and Sustainable Management of Residues

Editor in Chief:
RAFFAELLO COSSU

detritusjournal.com

an official journal of:

iwwg
international waste working group

CISA

Detritus - Multidisciplinary Journal for Waste Resources and Residues - is aimed at extending the "waste" concept by opening up the field to other waste-related disciplines (e.g. earth science, applied microbiology, environmental science, architecture, art, law, etc.) welcoming strategic, review and opinion papers. **Detritus is indexed in Emerging Sources Citation Index (ESCI) Web of Science, Scopus, Elsevier and Google Scholar**. Detritus is an official journal of IWWG (International Waste Working Group), a non-profit organisation established in 2002 to serve as a forum for the scientific and professional community and to respond to a need for the international promotion and dissemination of new developments in the waste management industry.

detritus | Multidisciplinary Journal for Circular Economy and Sustainable Management of Residues

CISA

Editorial

WE HAVE TO BE HONEST ABOUT CIRCULAR ECONOMY

Introduction

Debates relating to waste management (WM) are frequently reduced to the topic of Circular Economy (CE). However, the focus of CE does not extend to all fields of waste management. Moreover, waste management should not be considered a self-standing discipline, but rather as a part of a more global form of environmental management. WM therefore should ensure it operates in line with the United Nations Sustainable Development Goals (UN-SDGs) and aim to meet the Planetary Boundaries goals (Richardson et al. 2023, Earth beyond six of nine planetary boundaries. Science Advances, 9, 37).

Although waste is currently acknowledged as a resource, it should be taken into account that during separate collection, pre-treatment, and recycling significant volumes of residues are produced. These residues should be quantified and their compositions determined before being treated and/or safely stored in sinks.

In our view, kitchen and yard wastes (K+Y) are not adequately addressed in the context of a Circular Economy. To be deemed suitable for reuse, the produced compost needs to be of good quality with a low pollutant content: conversely, the composted K+Y waste should be disposed. Accordingly, kitchen and yard waste should be better integrated in the CE concept.

The incineration of residual waste is often included in the context of CE, although our opinion is that it is a contaminant sink and that material and product recycling alone should be comprised under the term CE. Indeed, as is the case in Germany, for example, incineration should invariably envisage total energy use (electrical and /or thermal). Pyrolysis and gasification may be considered differently as new products are created.

A frequently neglected group of pollutants in CE is represented by fine and ultra-fine particles, generated throughout all CE handling and treatment steps. Specific efforts should be aimed at eliminating or reducing the presence of these particles in order to prevent environmental pollution and detrimental effects on public health.

Recyclability of a series of waste types subject to separate collection and waste disposal

Waste components are characterized by varying rates of recycling, with glass, metals and to a significant extent, paper yielding consistently high rates; on the contrary, recovery rates for plastics are insufficient, while used textiles are rarely recycled, although they may be reused as second-hand clothes or cleaning rags.

It should of course be taken into account that materials such as paper, plastics, glass and metals, cannot be recycled infinitely; as an example, paper and plastics can only be subjected to the recycling process 3-8 times, thus implying a need to deal with the remaining residues. As the number of cycles increase, toxic compounds may accumulate during the recycling of mixed paper. Approximately 79% of pretreated waste paper is used in the production of new paper in Germany, or is exported to other countries; the remaining materials are largely disposed of as waste.

The situation regarding mixed waste plastics is rather more complex, with the majority being recycled into to new, low value materials at a rate of up to 30% only. For this reason, large quantities of mixed plastic materials are thermally treated or landfilled, with Germany exporting approx. 25% to developing countries.

Economic Aspects of Circular Economy

The European Union (EU) Waste Framework Directive (WFD) establishes that only waste fractions for which a market demand exists may be used in the manufacture of new products. At first glance, this approach makes sense. But what does the lack of a market mean? Does it imply that recycled products cannot be reused and have to be disposed? What happens with recovered waste paper, for example, when the market is saturated or paper prices are very low but the material properties are suitable for return into the material cycle? Will this material be recovered? In Germany, this situation became a reality for wastepaper and plastics when China changed their import rules. As a result, there was an abundance of these baled waste components available that could not be marketed and thereby caused significant costs and handling issues. The situation deteriorated further for plastics when oil prices fell; as a result, over a certain period, new materials were cheaper than recycled ones. Consequently, new markets were identified for baled wastepaper and waste plastics in Turkey, India, Malaysia and other Asian countries.

The overarching goal of CE is the conservation of natural resources by returning recycled waste materials back into the material cycle; emissions and wastes for disposal have to minimized. Cost reduction is of the utmost importance, but should not, in our opinion, dictate whether a material or product can be recycled and reused or not.

The export of wastepaper and plastics to Asian countries, for example, is carried out under the official condition that in the receiving countries the material will be handled

Editor in chief:
Raffaello Cossu
email: raffaello.cossu@gmail.com

Detritus / Volume 26 - 2024 / pages 1-2
https://doi.org/10.31025/2611-4135/2024.18363

by certified companies in line with standards similar to those adopted as in the exporting country. Unfortunately, this is not always the case, as shown by media reports documenting severe environmental damage with plastic litter ending up in the oceans. The export of used garments and shoes to DCs, particularly Africa and South America, for the specific purpose of helping poorer nations, has largely failed. The same is true for still functional electronic devices that end up - in the same way as textiles - in dumps, rivers or scattered on the land. In the case of electronic devices, the poor process applied in recovering useable materials from computers, phones, etc. is also associated with high health risks. In Europe, both products are officially classified under the heading export of used goods rather than waste.

Effect of Circular Economy on the Environment

It is evident that the powerful effects produced by CE on the environment should be given much deeper consideration. As indicators for the quality of the environment, we propose using the nine Planetary Boundaries (PBs) which humanity should not be allowed to cross.

Leaving aside additional aspects such as transport and pretreatment of waste materials, CE exerts positive effects on the majority of PBs; as an example, paper recycling leads to a reduction in CO_2 emissions and freshwater use, whilst also saving biotopes due to a lower consumption of wood. The avoidance of loss of biodiversity during CE should be further investigated for example by using a modelling approach. In so doing, the impact of the various recycling steps and modes on the loss or gain of biodiversity would become more transparent. This type of model should be much simpler to implement in routine use than an LCA.

The Spillover Index and Extended Producer Responsibility

An additional aspect is represented by the impact of social and environmental issues on CE, including the "Spillover Index" (https://dashboards.sdgindex.org/map/spillovers). Resources from many of the less developed nations are used in the manufacture of a wide range of products; these resources are often obtained under unacceptable labor and environmental conditions. The Spillover Index *measures how much the actions taken by individual countries in supplying resources to industrialized countries - including tropical wood and all kinds of ores - affect, the ability of other countries to achieve the UN SDGs* (https://sdgs.un.org › goals). The Spillover Index attributes all impacts produced by material mining, including carbon emissions, to the importing country. The latter implies that the industrialized country responsible for importing the goods is responsible for the environmental impact caused by the mining of materials in the exporting country. In this case, the importing country should first consider the negative impact of the mining process in their cost and environmental balance (negative Spillover Index). On the other hand, the Spillover Index approach may be used to ensure and consider the avoided environmental impact generated when a product is reused rather than being newly manufactured. The avoided impact on the environment in both the resource-exporting countries (e.g., mining of rare earth metals, cobalt) and the producing country (e.g., water pollution, destroyed habitats) may be positively valued in the industrialized country as complying with the UN-SDGs and/or the Planetary Boundaries (positive Spillover Index). This approach would also incentivize increased product repair, reuse and recycling of materials. Moreover, importing countries are expected to use all necessary political and financial power to improve the social and environmental situation in the mining industry of the exporting country. This Spillover Index is not governed by a law but is intended to act as guidance or an incentive to achieve improved sustainability.

Extended Producer Responsibility (EPR) represents a further tool for use in ensuring better product design and reuse. The OECD defines Extended Producer Responsibility (EPR) as an environmental policy approach in which a producer's responsibility for a product is extended to the post-consumer stage of a product's life cycle. An EPR policy is characterized by the shifting of responsibility (physically and/or economically; fully or partially) upstream toward the producer and away from municipalities; and the provision of incentives to producers to take into account environmental considerations when designing their products.

This may sound like a powerful tool, but in Germany it is only valid with regards to packaging waste, batteries and WEEE. In addition, as mentioned earlier in connection with the management of wastepaper and plastics, actual practices and claims made are at times often characterized by significant discrepancies.

When considering these three approaches with a view to achieving increased sustainability, eventual overlaps should be addressed and reconciled.

Conclusions

Waste prevention is invariably highlighted as a major priority in the waste hierarchy, although it is frequently not sufficiently pursued, thus requiring the use of increasingly concerted efforts. In this context, efforts should be directed specifically at minimizing energy consumption in CE and producing energy at the site of operation to reach energy independence.

Since the export of used goods and separately collected paper and plastics to DCs represents a significant contribution to CE balance in the exporting country (where it is counted as recycled), this aspect needs to be given careful urgent reconsideration. Failing this, these exports need to be stopped.

In conclusion, the authors propose to further develop CE by considering, in addition to other aspects, the measures proposed herein, aimed at increasing the transparency and completeness of CE with an approach which should never be ideologically driven.

Rainer Stegmann
Hamburg University of Technology, Germany
stegmann@tuhh.de

Tingting Liu
Beijing University of Technology, China
tingting.liu@bjut.edu.cn

detritus | Multidisciplinary Journal for Circular Economy and Sustainable Management of Residues

CISA

A RISK-BASED APPROACH FOR WASTE MANAGEMENT IN THE MODERN CIRCULAR ECONOMY: PROPOSITIONS FROM THE EU RECYCLING INDUSTRIES

Pierre Hennebert [1,*], Alejandro Navazas [2] and Emmanuel Katrakis [2]

[1] *Conseil-Developpement-Environnement, France*
[2] *European Recycling Industries' Confederation (EuRIC)*

Article Info:
Received:
2 September 2023
Revised:
18 January 2024
Accepted:
5 February 2024
Available online:
25 February 2024

Keywords:
Waste collection
Extended producer responsibility
Waste classification
End-of-waste status
Prematerial
Risk in the intended use

ABSTRACT

EuRIC, the European Recycling Industries' Confederation, proposes five regulatory actions to enhance material circularity: i) Set stable regulations based on the principle of "one substance - one assessment" along with realistic, evidence-based scientific risk assessments; ii) Prioritise increasing waste collection for a better elimination of substances of concern to reducing the concentration limit in recycled products; iii) Strict enforcement of an Extended Producer Responsibility (EPR) scheme for all restricted or banned substances, where exemptions should be carefully considered by evidence-based science; iv) Align the classification hazard systems used for waste materials with those used for products; v) Grant an end-of-waste status (EoW) at the output of a controlled, certified industrial loop. Those propositions create a level playing field for collection, sorting, and waste preparation within EU and an improved waste shipment. The underlying question is striking the right balance between the precautionary and responsibility principles in the circular economy. Given the presence of hazardous "legacy" substances and the prolonged life of certain products within an evolving regulatory framework, the recycling industry proposes controlled-risk solutions aligned with the intended use or recycled materials for products not yet ecodesigned. The recommendations suggest a shift in the waste definition, considering the fate of matter within the waste hierarchy – emphasizing prevention, management, and policy alignment with the principles of the circular economy. So, materials that can be prepared for reuse or recycling are categorized as pre-materials, while those suitable only for other recovery methods such as energy recovery or landfilling are considered wastes.

1. INTRODUCTION

Is garden biomass matter brought by citizens to civic amenity centers a waste (which can only be transported and managed at waste licensed facilities with strict and costly administrative control) or is it a resource that can be used (after some preparation) as mulch, energy, or soil amendment? The situation may appear straightforward, but this question frequently arises in the day-to-day management of circular economy affairs in a recent case in France (Public debate about Hynovera project in 2023, personal communication), the biomass, possessing a waste status, would be prohibited from undergoing pyrolysis for synthetic fuel production. This limitation arises as the planned facility is not intended to function as a waste management facility.

Waste should be managed by risk in the modern circular economy, like products. Risk is the probability (amount, frequency) of effective harmful exposure to a hazard: risk = hazard x exposure of a target (Figure 1). A no-risk situation is more easily achieved by reducing exposure to the hazard than by reducing or removing a hazard. Risk reduction is easier than hazard reduction. Hazardous substances, while deemed or considered harmful, have or had utility owing to their physical, chemical, or biological properties. For instance, lead compounds function as UV stabilizers in PVC window frames, enhancing their durability, and brominated flame retardants serve as essential safeguards against fire hazards. If these substances face prohibition, achieving zero concentration in recycled material may not always be feasible today due to their legacy presence in the waste.

The debate on hazard versus risk has become prominent in legislative discussions concerning both products and waste, as evident in EuRIC (2023) examples. In this context, "products" refers to articles or preparations (mix-

* Corresponding author:
Pierre Hennebert
email: pierre.hennebert@gmail.com

Detritus / Volume 26 - 2024 / pages 3-14
https://doi.org/10.31025/2611-4135/2024.18353

FIGURE 1: Illustrating the concept of "no exposure" signifies the absence of risk, emphasizing a hazard-free approach. (Madelung, 2023).

tures) classified under the Classification, Labelling, and Packaging of Substances and Mixtures (CLP) regulation (EC, 2008). The central question revolves around how to reasonably (finding a balance between advantages and disadvantages) control the risks associated with the presence of hazardous substances (toxic/ecotoxic) in products, whether sourced from virgin materials or recycled materials, and waste (which serves as the raw material for products).

Increasingly, there is a trend toward reducing concentration limits for numerous substances in products, independent of their intended use. Some substances are outright prohibited due to their classification as persistent organic pollutants (POPs). In practice, a considerable number of substances will need to have concentrations reduced to zero or below the detection limits of chemical analyses, which themselves are continuously decreasing.

This approach is essentially a "no hazard" strategy rather than a risk-oriented one, aligning with a societal inclination toward the welfare state and a political tendency to safeguard public opinion by increasingly protecting citizens against any potential hazard.

The adoption of "absolute risk," "no risk," or "worst-case" approaches essentially translates to a "hazard-only equals no hazard" strategy. For the circular economy, this poses considerable challenges, reaching the point of making it impractical to sort waste fractions with very low concentrations. Consequently, there are material losses in the recycling loop and increased costs for recycling processes, including downcycling, incineration, or landfilling of now non-recyclable fractions.

While the European Commission's Eco-design for Sustainable Products Regulation (ESPR) and the Chemical Strategy for Sustainability (CSS) aim for a "toxic-free" approach, addressing most hazardous substances in products, there are complexities introduced by legacy substances and the extended lifespan of certain products. Given the evolving regulatory landscape, the recycling industry suggests promoting controlled risk solutions for both the intended use and recycled materials in the interim.

This paper is a contribution to the discussion identified by the European Commission (EC) in 2018 (EC, 2018a): "*reflection on the appropriate balance between the overall long-term benefits from circular use of these materials and the overall long-term health and environmental concerns relating to substances present in that material*." and in 2020 (EC, 2020a): "*As a principle, the same limit value for hazardous substances should apply for virgin and recycled material. However, there may be exceptional circumstances where a derogation to this principle may be necessary. This would be under the condition that the use of the recycled material is limited to clearly defined applications where there is no negative impact on consumer health and the environment, and where the use of recycled material compared to virgin material is justified on the basis of a case-by-case analysis*." EuRIC supports that approach and pledges for its complete and evidence-based scientific implementation.

The paper is structured around five propositions (sections 1 to 6), offering solutions to enhance material circularity from the perspective of recycling organizations. These propositions also yield additional benefits for waste shipment and contribute to a level playing field within the EU (section 7). As a natural outcome, there is a suggestion to reevaluate the definition of waste in alignment with the waste hierarchy (section 8). The conclusion underscores the necessity for a comprehensive societal debate (section 9).

The reader will find in EuRIC (2023) detailed citations, examples, numerical data and discussions that are presented only shortly here.

2. PROPOSITION 1: STABLE REGULATIONS BASED ON "ONE SUBSTANCE – ONE ASSESSMENT" AND REALISTIC SCIENCE-BASED RISK ASSESSMENTS

The foundation of the waste management proposal, whether hazardous or not, based on risk in the intended use, is outlined in the Introduction section. This section delves into critical aspects, including (i) transitioning multiple substance regulations, (ii) reassessing substances, (iii) realistically evaluating risk in intended use rather than hazard, and (iv) emphasizing the necessity for a responsible, science-based policy rather than a political, conservative, precautionary-based approach, all from the standpoint of the recycling industry. The utilization of the SCIP (Substances of Concern In Products) database and the potential to mitigate certain hazard properties of materials are subsequently explored.

2.1 Recyclers have to face multiple and moving regulations of substances and materials

Waste legislations, including specific Directives or Regulations, persistent organic pollutant (POP) legislation, and product legislations, undergo revisions every five years. Typically, these revisions involve the introduction of new substances and a reduction in concentration limits or a ban on hazardous substances in products and recycled materials.

To address the challenge of substances regulated across multiple pieces of legislation (while not necessarily addressing the continuously decreasing concentration limits), the European Commission has introduced the "one substance – one assessment" method (EC, 2019; EC, 2020a), which is discussed further below.

2.2 Many substances are currently not accurately assessed by their producers, and a significant number undergo re-assessment by the European Chemicals Agency – ECHA

An example is found in the brominated substitutes for regulated brominated flame retardants (BFRs) in plastics used in electrical and electronic equipment (Hennebert, 2021). The comprehensive status of the 34 substances in producers' catalogs and in the ECHA and industry list of plastics additives is as follows: 12 substances lack a dossier, 10 substances lack hazard statement(s) (6 are under reassessment by ECHA as "persistent, bioaccumulative, and toxic" - PBT, future persistent organic pollutants (POPs), and as "endocrine disruptor" - ED), and 12 substances have complete dossiers (2 are under reassessment as PBT or ED). Among the 7 substitutes on the ECHA-industry list of plastic additives (non-POPs, non-regulated BFRs), all but one have no declared hazard statement(s), and all are currently being re-evaluated by ECHA (3 as PBT, 2 as ED, and 2 as PBT + ED).

As the premise for reassessment is based on potential hazard (due to chemical similarity), these 7 substances could likely be assessed in the future as PBT (POP) and/or ED, potentially leading to restrictions. Plastics produced today with these additives will likely face challenges in recyclability, resulting in "regrettable substitution" and the creation of new "legacy" substances. Proposition 3 could address this issue.

Chemicals are initially assessed as pure substances, first for hazard, and then hazardous chemicals are either banned or evaluated for risk in their intended use (with a given concentration in "mixtures or preparations") for authorization, potentially with limiting concentrations.

In addressing concerns related to the inaccurate assessment of chemical substances, the European Chemicals Agency (ECHA) has implemented a "generic approach to risk management" (EC, 2020a). This approach initiates predefined risk management measures, such as packaging requirements, restrictions, and bans, based on the hazardous properties of the chemical and general considerations of their exposure. Initially focused on carcinogenic substances, it has seen limited exemptions defined by law. The intention is to expand its application to include other harmful chemicals, such as those impacting the immune, neurological, or respiratory systems, as well as chemicals toxic to specific organs (EC, 2020a).

However, experts like Bridges et al. (2023) express concern that this approach may overemphasize hazard assessment without sufficiently considering exposure estimates and risks to both humans and the environment. They argue that a sustainable chemical assessment should encompass both hazard and exposure estimate and express reservations about relying solely on qualitative hazard assessments. They emphasize the importance of evaluating potency, a critical aspect of hazard assessment. Furthermore, they underscore the significance of adopting a weight-of-evidence approach and suggest the necessity for a more comprehensive and practical strategy for chemical risk assessment.

The data utilized for risk assessments must reflect realism, considering factors such as ingestion rate and transfer rate. A discussion on a practical assessment of carcinogenic polycyclic aromatic hydrocarbons (PAHs) in tyre granules is presented in (EuRIC, 2023). The substantial benefits of reducing social costs and environmental burdens through a realistic risk assessment are noteworthy (EuRIC, 2023).

The position of the recycling industry is that the "One substance – one assessment" principle should not be oversimplified and reduced to merely assessing "hazard to humans." Instead, it should remain a scientifically realistic risk approach tailored to the intended use(s). The Chemical Strategy for Sustainability (EC, 2020a) should not alter this perspective, and recovered material should adhere to this method.

2.3 The circular economy must be a science-based policy

A risk-based approach is grounded in science and should rely solely on scientific data. The emerging social science question is... "*How to reconcile scientific evidence with other forms of evidence, and with the various political, societal and other non-scientific factors that inform the process of governance?... In order to strengthen the role of science in European governance, the creation of a pro-science climate at all levels of the institutions, business circles and civil society is urgently needed… A conservative, precaution-based approach to assessment has taken hold, hindering access to innovative products and techniques… Science is becoming increasingly subjective and politicised, a trend that risks eroding public trust in the EU, undermining its legitimacy as well as its capacity to address the challenges…*" (Guégen and Marissen, 2022). The authors discuss "*how evidence-based and science-based decision-making can be further integrated into the EU decision-making process*", in particular that scientific assessment conducted at EU level (frequently by the Joint Research Centre) should be validated by policy-makers and published before decision. To promote science in the management of substances, the same authors propose a dialogue between the professional circles and the NGOs. The dialogue is nevertheless open: in the European Green Deal (EC, 2019), section 2.1.8 "*A zero pollution ambition for a toxic-free environment: The Commission will review how to use better*

the EU's agencies and scientific bodies to move towards a process of 'one substance – one assessment' and to provide greater transparency when prioritising action to deal with chemicals.". In the communication "Chemicals Strategy for Sustainability Towards a Toxic-Free Environment" (EC, 2020a), it is stated that a different limit value could apply for recycled material in clearly defined applications where there is no negative impact on consumer health and the environment (full citation in the Introduction).

EuRIC, or recyclers at large, shall not conduct risk assessments. The responsibility for assessing the risk of substances in articles or materials that eventually become waste or pre-material lies with the producers. EuRIC relies on the risk assessments conducted by producers for their specific uses. In cases where waste or pre-material comprises a mixture of different origins, recyclers shall provide data on the total concentration of substances and their distribution in the material streams for a given use. Some distributions of contaminants are presented in Section 3.1.

The EU Waste Framework Directive mandates producers to document the presence of substances of very high concern (SVHCs) in articles or complex objects (products) in a new database called SCIP, launched online in January 2021. Articles containing SVHCs from the Candidate List at concentrations above 0.1% w/w, placed on the EU market, must be recorded. Unfortunately, for the recycling industry, this database is of limited use (Friege et al., 2021). Composition data in SCIP is available by item parts, making it challenging to convert to the composition of an unsorted or sorted waste stream. To be valuable for the recycling industry, an extraction tool based on product categories and materials (typically polymers) should be developed.

2.4 Proposition #1

Regulating substances in products and waste through a risk-based approach involves establishing concentration limits for the use of substances in products and recycled materials. This is achieved through a realistic scientific assessment of the risks associated with the intended use, considering not only the hazard of toxicity to humans but also considering the climate and energy balance in the circularity of materials.

Recycled materials containing (legacy) substances of concern should be authorized for use with concentrations that may be higher than those permitted for virgin products, particularly in controlled loops. This approach aligns with a balanced risk-based and circularity perspective, encompassing the savings of virgin materials and reduction of CO2 emissions.

3. PROPOSITION 2: A MORE EFFECTIVE ELIMINATION OF SUBSTANCES OF CONCERN (SOC) CAN BE ACHIEVED BY INCREASING THE COLLECTION RATE OF MATERIALS RATHER THAN BY LOWERING THE SOC CONCENTRATION IN RECYCLED MATERIALS

This section demonstrates that increasing the collection rate sorts out more banned or controlled substances than reducing the concentration limits in recycled products, due to the distribution of contaminants skewed by some large "nugget" values. Such distributions are first illustrated. The effect of reducing the concentration limit and of increasing the collection rate depends on this distribution and are then presented.

3.1 To eliminate substances in material loops: Is it more effective to increase the collection of materials (i.e., waste) or lower the concentration in recycled material?

Twenty histograms depict the distribution of characteristics in (potentially contaminated) natural media such as soil and sediments, as well as (unprocessed and processed) waste (EuRIC, 2023, with references to additional published examples). These distributions are often skewed by some high values that prove critical for the mean concentration or value. Non-normal distributions are observed in natural media, but human activities contribute to the creation of highly concentrated portions (hot spots), significantly increasing the spatial, temporal, or batch variability of many characteristics. This situation is further exacerbated in waste, where many parts frequently have low or zero concentration, and a few parts exhibit high concentrations (Figure 2).

An important initiative within the recycling industry involves developing and implementing methods to identify and separate components with undesired substances that exceed concentration limits. It is evident from the data that, because of these skewed or asymmetric distributions, removing the last percentiles from a population significantly reduces the average concentration. Determining the relative impact of increasing material collection versus decreasing the concentration limit in recycled material on the removal of substances of concern from the material loop is not straightforward. The response depends on the distribution of concentrations of legacy contaminants in different particles of waste. A theoretical calculation illustrating the relative effects of lowering the concentration allowed in recycled products or increasing the collection rate is presented. Assuming a realistic distribution where 90% weight/weight have 0 mg/kg and 10% w/w have a 10% concentration of a substance of concern (SoC), equivalent to 100,000 mg/kg, the mean concentration of the batch is 1% or 10,000 mg/kg. The initial collection rate is 50%, and the initial concentration allowed in recycled material (concentration limit – CL) is 1,000 mg/kg. The effects of reducing the SoC concentration allowed in recycled material by 50% and increasing the collection rate of the waste by 50% are detailed in the Supplementary Information and presented in Figure 3.

The persistence of Substances of Concern (SoC) comprises the SoC in the recycled fraction (green) and the SoC in the "other fate" fraction (grey). Reducing the SoC concentration limit by 50% results in a 0.5% decrease in the mass of recycled waste (from 455 kg to 452.5 kg/tonne of waste) and a 4.5% reduction in SoC persistence (from (0.5+5) to (0.25+5) kg SoC/ton of waste). Increasing the collection rate by 50% leads to a 50% increase in the mass

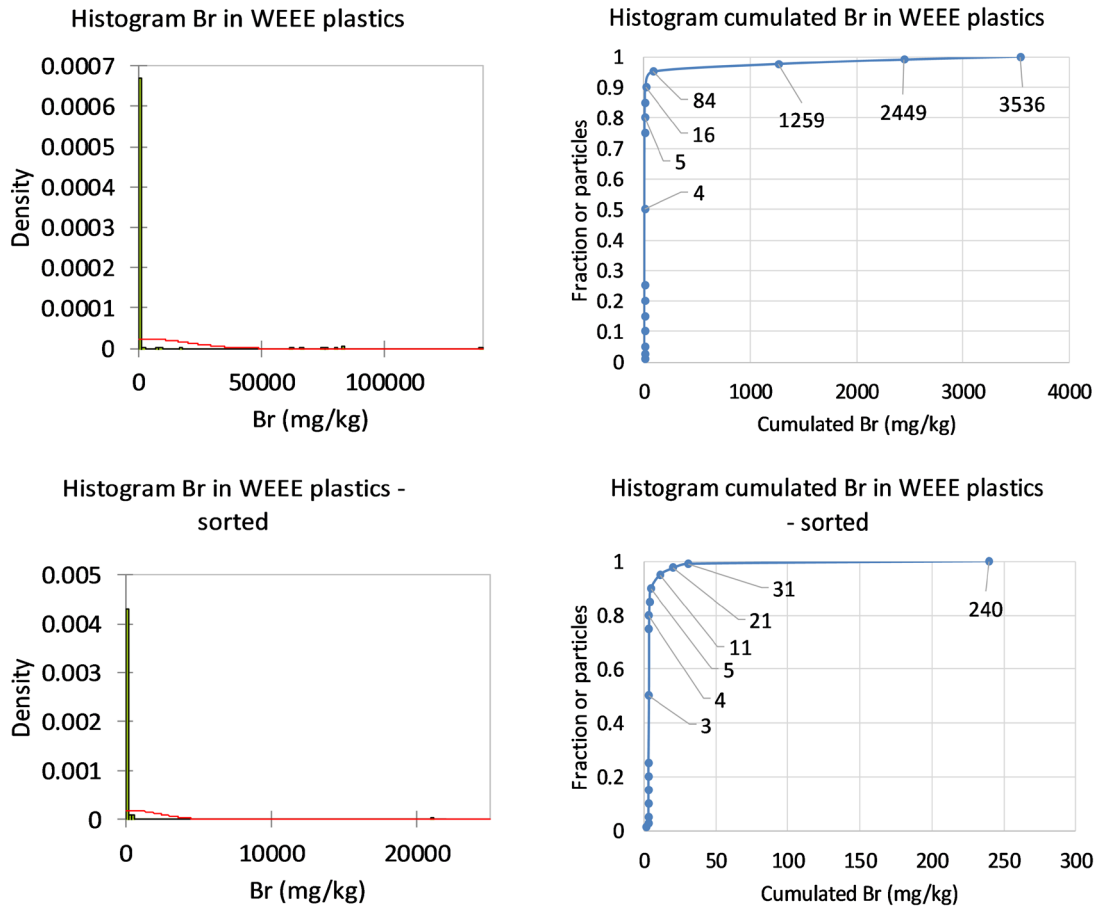


FIGURE 2: Particle concentration of bromine in waste of electrical and electronic equipment (WEEE) plastic scraps (left), mean concentration of bromine in the cumulated fraction of particles (right) with the mean cumulated concentrations of the 50th, 75th, 90th, 95th, 97.5th, 99th and 100th percentiles of the particles. The normal distribution with same mean and s is indicated (red line), clearly not fitting. Upper figures: plastics after shredder. Lower figures: plastic after density (1.08 kg/liter) sorting (Hennebert and Beggio, 2021).

of recycled waste (from 455 kg to 682.5 kg/tonne of waste) and a 40.9% reduction in SoC persistence (from (0.5+5) to (0.75+2.5) kg SoC/ton of waste). The non-linear effects of reducing the concentration limit and increasing the collection rate are attributed to the asymmetric distribution of additives or contaminants in the waste streams, distorted by some high values, with a majority of low or zero-value parts. The conclusion is that increasing the collection rate significantly reduces the persistence of SoC in material loops compared to reducing the concentration limit, emphasizing the need to prioritize efforts on increasing the collection rate. Producers and importers, who have profited from these goods, should assume greater responsibility for handling substances of concern, and the initial step is to enhance the collection rate.

Meanwhile, the everyday solution employed by the recycling industry to address the presence of hazardous substances in materials involves removing the fraction containing the hazard, especially when the contaminant is not uniformly distributed among the particles of the shredded waste. Examples of this approach include the selective dismantling of Waste Electrical and Electronic Equipment (WEEE) and End-of-Life Vehicles (ELV), as well as the sorting of plastics from WEEE by density to eliminate banned flame retardants. Other solutions for some cases are to remove some hazard properties - HPs (Hennebert, 2022):

- HP 4 'Irritant' and HP 8 'Corrosive' by acidity or alkalinity: acid/base neutralisation including passive or active carbonatation
- Reducing or oxidizing waste: redox neutralisation
- HP 9 'Infectious': sterilisation
- HP 14: if the waste does not have a near-neutral pH (pH 5.5-8.5), the share of ecotoxicity due to acidity or alkalinity and the associated soluble metals can be reduced up to non-active concentration by neutralisation and precipitation of metals of the waste. This must be done on the waste stream or batch and not (only) on the laboratory sample.
- HP 15 'Waste capable of exhibiting a hazardous property not directly displayed by the original waste': recommendations for safer backfilling of some waste can be found in Hennebert (2022).

These methods, however, have limitations, and it's not always possible to eliminate all hazardous substances. In the case of sorting, with current technologies, achieving a zero concentration cannot always be guaranteed.

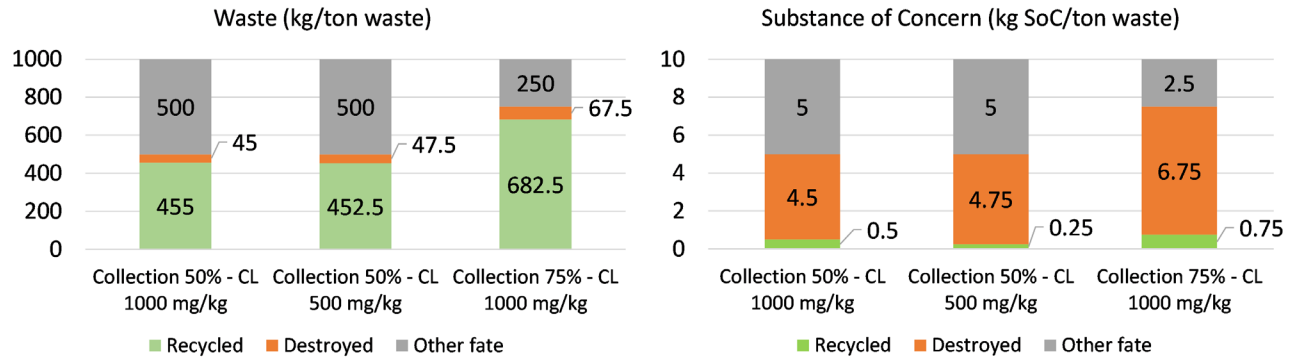


FIGURE 3: Theoretical calculation illustrating the impact of decreasing the concentration limit of a substance or increasing the collection rate of waste on the quantity of recycled material (left) and the amount of sorted-out and destroyed (CL) substance (right).

3.2 Proposition #2

Effective elimination of prohibited or regulated substances is achieved more efficiently by increasing the waste collection rate. In heterogeneous mixed waste, where the concentration distribution of certain parts is skewed, enhancing the collection rate proves to be more efficient than reducing the concentration limit in recycled material.

4. PROPOSITION 3: EXTENDED PRODUCER RESPONSIBILITY FOR THE HAZARDOUS, RESTRICTED, BANNED, REASSESSED SUBSTANCES AND EXEMPTIONS

To ensure effective control of regulated substances in material loops, it is imperative for the producers or importers of products containing controlled substances to take responsibility for those substances. Producers and marketers must be aware of the composition of their products. When a substance is restricted or banned, the establishment of an Extended Producer Responsibility (EPR) organization should be mandated. This organization would be responsible for funding the efficient tagging, identification, separate collection, sorting, and management of the portions of any waste stream containing these substances. Products and waste containing these substances can then be identified, and their management can be financially supported. The recycling industry can play a crucial role in assisting the EPR body. An additional and related aspect pertains to the property of recycled material. The scope of the Extended Producer Responsibility (EPR) system can be financial or both financial and organizational, as explicitly outlined in the Waste Framework Directive (WFD). However, the WFD does not explicitly include the case of an EPR system with financial, organizational, and operational actions. Furthermore, the ownership of recycled material is not defined in the WFD. EuRIC's experience indicates that EPR systems that tend to be operational often appropriate the recycled material. This situation eliminates real competition when an EPR has received a public mandate, sometimes acquiring a financial and organizational monopoly. This may lead to the selective and unequal appropriation of only valuable materials, which can be resold exclusively to members of the EPR system, affecting all producers and products without discrimination to prevent "cherry-picking" within a product family:

- either a company or companies organize their own take-back system, without a public mandate,
- either an EPR system receives financial and/or organisational power from the public authorities, according to contractual specifications with the authorities. This private law entity acts on the basis of an approval, that is to say a public mandate.

"No entity mandated by a public authority to manage a waste stream and being a total or partial monopoly by law can have an operational role on the market it manages and oversees. This a blatant breach of equality resulting from the abuse of a dominant position with private recycling companies, which must compete through tender procedures to obtain a share of the market falling under the scope of the EPR Schemes." (EuRIC, 2022).

No EPR organisation acting under a public mandate should carry out recycling operations and capture (valuable) recycled material itself.

EPR systems, when granted a public mandate, are often licensed as a hybrid entity, operating as both a non-profit organization and a for-profit company in EU Member States. This dual role raises questions about their potential involvement in operational activities, such as owning or co-owning recycling plants or participating in material capture.

Some manufacturers or marketers wish to regain via EPR ownership of the recycled material, even though they relinquished this ownership (against payment) when selling the articles, and this payment in fact includes now the net cost of recycling that the recyclers have negotiated for long, with or without an Extended Producer Responsibility eco-organization. Note that this claim has variable geometry: for instance, it does not address plastics that are not recyclable today, including plastics containing brominated flame retardants that were formerly authorized but are now POP and not recyclable. As everyone knows, certain parts have market value once processed by recyclers, and others have no recovery or are hazardous waste that must be destroyed or stored by specialized companies, and are therefore costs. Picking the best cherries is pleasant at first glance but economically disastrous for the recycler. The

seller has sold: he cannot claim new ownership. Eco-organizations receive a public mandate. Collecting the cost of recycling from the consumer on a public mandate and paying it back to the recycler does not make the eco-organization(s) the owner(s) of the recyclate(s). This principle of reality must be installed as a principle of collaboration and law for all circular economy loops.

EuRIC asserts the need for representation of the recycling industry within the governing body of EPR Schemes. Any EPR organization must adhere to Articles 8 and 8a of the WFD, which mandate the organization of collaboration among all stakeholders, including waste players at each stage. Numerous passages in the WFD emphasize the involvement and collaboration of all actors, including the recycling industry.

Building a robust circular economy necessitates a fair sharing of value between EPR organizations and collectors/recyclers. EPR organizations should not relegate the recycling industry to mere subcontractors but engage in a partnership characterized by an industrial project with long-term objectives. This relationship should not reflect the unbalanced dynamics observed between supermarket purchasing centers and the agri-food industry/farmers.

4.1 Proposition #3

Extended Producer Responsibility (EPR) should be established for all substances subject to restrictions, bans, or reassessments, with exemptions carefully evaluated based on evidence-based science. EPR organizations operating under a public mandate should not engage in recycling operations or directly capture valuable recycled materials.

5. PROPOSITION 4: HARMONISATION OF WASTE HAZARD CLASSIFICATION WITH PRODUCT CLASSIFICATION

Substances may have hazard statement code attributed by the notifier to ECHA, or by ECHA. Mixtures and preparations (called here "products") have hazard classification and labelling if the individual or summed concentrations of substances with hazard statement codes exceed concentration limits. Classification of waste as hazardous or not for 15 hazard properties HP 1 to HP 15 is first defined in the European list of waste (hazardous, non-hazardous, or "mirror entry", meaning hazardous or not depending on the concentration of hazardous substances in the waste or on tests results, that must be assessed on a representative sample). A guidance document is available (EC, 2018b) and practical solutions for classification are presented in Hennebert (2019). Note that the summation rules of concentrations and the concentration limits are not always the same between products and waste. Two problems of classification should be improved.

5.1 Waste classification by « worst case » substances

Laboratory analyses provide total element concentrations and not concentrations of element-containing substances, except for some limited cases with specific analytical methods (such as lime CaO or chromium VI). Since hazard statement codes are assigned to substances and not to elements, it is necessary to speciate the elements into mineral or organo-mineral substances, often relying on hypotheses.

Some classifiers, by precautionary principle and lack of knowledge of the waste science (processes, mineralogy, composition, physico-chemical domain of stability of substances) use the most hazardous mineral or organo-mineral substances to speciate an element. That method does not correspond to the reality of the waste (excepted some industrial waste that are intermediate in the chemical industry and do not join the common waste flows) and incorrectly classifies the waste as hazardous. More scientific methods are available, using physicochemical information, process information and avoiding hazardous intermediate substances from chemical industries that are not found in waste, to have a more realistic assessment (Hennebert, 2019).

5.2 Classification of HP 14 'Ecotoxic'

5.2.1 The use of multiplying factors for the concentration of the ecotoxic substances

To avoid discrepancy between waste and products, the multiplying factors of the concentration of the most ecotoxic substances (so-called M-factors, acute and chronic) should be used for the calculation of the sum of weighted concentrations of ecotoxic substances for HP 14. Many M-factors are available in the harmonised classification of substances (published by ECHA as an Excel file) and other M-factors have been published (Hennebert et al., 2014, 2016).

5.2.2 Assessment of HP 14 'Ecotoxic' by tests

The establishment of a validated European battery of ecotoxicological tests has been a longstanding topic. Currently, there are approximately 25 proposed tests and concentration limits (not an exhaustive list, as detailed in Hennebert, 2018). Building on a European interlaboratory trial conducted in 2006 and published in 2009 (Moser and Römbke, 2009), along with the associated test battery (Moser et al., 2010), a standardized battery applicable across all European countries is proposed. This battery includes six normalized tests, excludes variants and options, and features validated concentration limits determined by a group of 23 waste samples, both non-hazardous and hazardous, serving as a reference method based on both list and chemical composition. It is recommended to utilize only this battery, without modifying the sample (such as neutralizing the leachate), without incorporating options that may introduce high inter-laboratory variability rendering the results unusable (Hennebert et al., 2022).

5.2.3 Human and environmental bioavailability of substances

The assessment of waste should consider the bioavailability of the substances (EU 2017, 2018). According to ECHA guideline: "*In general, there are no specific environmental test methods developed to measure biological availability of substances or mixtures.*" (ECHA, 2017). Bi-

oavailability of elements and substances of waste is not measurable "in general". The bioavailable fraction is not limited to the (de-ionised water) leachable fraction: ingestion, inhalation, dermal contact are significant routes of exposure. It seems today that the best method to assess bioavailability for classification for ecotoxicity (HP 14) is to use a battery of biotests with validated concentration limits by matching with a reference method, as explained above (Hennebert 2019). The assessment of ecotoxicity of waste by a 1000 times diluted leachate of the waste (10 000 l/kg rather than 10 l/kg) is not relevant: the dissolution of 100 mg of element/l (corresponding to 10 000 l/kg) is a method to attribute hazard statement code to substances with element as ecotoxic acute or chronic level 1 to 4 (ECHA, 2017), and not to classify a mixture. Published data indicates that method classifies only one waste from 81, while the classical method classifies 50 wastes as hazardous, from the same set of 81 data (recalculated from, Hennebert 2018).

5.3 Proposition #4

Hazard classification of mixtures of substances in products and wastes: Progressively align the waste classification with the product classification, especially for HP 14 "Ecotoxic" hazard property, considering varying degrees of ecotoxicity (by M-factors), and advocate for the adoption of an EU laboratory test battery with validated concentration limits.

EuRIC suggests that DG ENV initiate a working group on harmonized classification through ecotoxicological tests applicable in EU countries, incorporating validated concentration limits.

6. PROPOSITION 5: TACIT END-OF-WASTE STATUS AT THE OUTPUT OF A CONTROLLED CERTIFIED INDUSTRIAL LOOP

6.1 The implementation of the end-of-waste has slowed down

According to many authors (as in EC, 2020b): "*However, now 10 years after its legal formulation [2008], it is clear that the implementation of end-of-waste has failed in most countries, for many reasons. First of all, at the EU level, end-of-waste criteria have only been defined for three different waste types: iron scrap, copper scrap and glass cullet. This despite the fact that the EU Joint Research Centre has developed criteria for several other waste types, such as paper, plastic, compost and aggregates. Many end-of-waste proposals have been halted since it has proven difficult for member states to reach an agreement.*" (Johansson and Forsgren, 2020). Member States have further implemented the process, but it has halted or at least slow down since 2016 (France, UK). The reasons are: excessive slowness, excessive precautionary principle, a part of arbitrary commission "expert" judgment who's some can be opposed to, delegation to local authorities that have not always the expertise, single waste by single waste approach with individual (small business) demanders that have not always the resources for best quality dossiers… Some propositions to improve this situation are presented in EC, 2020a.

6.2 Proposition to circumvent/solve the halting of EoW: "non-waste", "waste use potential", "certified material", "non-waste product", "secondary raw material"

The revised Waste Framework Directive (EU, 2018) states in recital 17 and article 6(1) that secondary raw material should have the end-of-waste status: "*In order to provide operators in markets for secondary raw materials with more certainty as to the waste or non-waste status of substances or objects and to promote a level playing field, it is important that Member States take appropriate measures to ensure that waste that has undergone a recovery operation is considered to have ceased to be waste if it complies with all the conditions laid down in Article 6(1) of Directive 2008/98/EC as amended by this Directive.*". The criteria for achieving end-of-waste status include a defined purpose, a corresponding demand, adherence to technical requirements, and the absence of adverse effects in the intended use. Given that secondary raw materials (or preferably called, raw materials from recycling) are inherently produced for a specific purpose, meet demand, and satisfy technical specifications while ensuring compliance with regulations safeguarding human health and the environment, these materials should, in principle, be eligible for end-of-waste status at the national and, ideally, EU levels. Member States or the EU should confer this status when waste has undergone a recovery operation.

Twenty-six years ago, the need for inclusion of resource in the definition of waste was already stressed (Bontoux and Leone, 1997; Pongrácz and Pohjola, 1997). The experts of EU Joint Research Centre JRC proposed in 1997 a report to the European Parliament "The Legal Definition of Waste and its Impact on Waste Management in Europe" with a section "*5. Towards a distinction between waste and non-waste… All the issues presented above show how crucial the distinction between waste and non-waste can be for all the actors. On the one hand, a legitimate concern from the legislator exists to ensure the proper handling of wastes, avoiding negative impacts on the environment and on public health (i.e. reducing risk). On the other hand, the legislation must promote the recovery of resources, preserve the Single Market and obey international obligations (World Trade Organization and Basel Convention)*". National approaches are detailed and a list of criteria for non-waste was proposed (Bontoux and Leone, 1997). One of the recommendations of the authors is "*To apply a risk assessment approach to the broad issue of shipment and handling of waste. However, this is closely linked to the processes used, and as such related to the technical state-of-the-art. Certification of facilities, processes and operators could be a way to promote and ensure the development of "best waste management practices.*". The authors, in fact, proposed the establishment of an end-of-waste status for the recovery of resources in certified industrial recycling industries 26 years ago, as outlined in this section of the paper.

Pongrácz (2002) states that "*"waste" means any substance or object which has been used in a step, which cannot, in its current state and under current technical and economic conditions, be reused for the same functions or as*

material (except backfill) in another step of a circular flow, and which the holder discards or intends or is required to discard … The main aim of waste management besides waste evasion is turning wastes to non-wastes".

Since then, other options were investigated. Waste use potential, a dossier that explains all the possibilities and the qualities of a waste, should promote waste as resources, not changing the actual waste definition (van Ewijk and Stegemann, 2020). Another option to escape to the dichotomy waste/product is to produce material with (quality) technical certificate co-defined by the producers and the users (Johansson and Forsgren, 2020; Johannson, 2022). The approach of compliance with quality standards has been largely used in UK with the name "Quality Protocol" using the new category of "non-waste product" (UK 2023a).

The terms "non-waste," "certified material," "non-waste product," "secondary raw material," or "pre-material" should be considered as having a product status. The potential hazardous nature of a waste alters safety requirements and the level or intensity of preparation operations but does not change the nature of these operations. The straightforward approach is that, once it exits the modern collection and recycling facilities, the material should be treated like any other raw material and enjoy the end-of-waste status (Hennebert, 2023).

In a report for the European Commission (EC, 2020b), it is proposed that the economic operators take the responsibility of the end-of-waste status, without prior approval by the authorities, and with ex-post control if necessary: "*Simplifying certain aspects of the decision-making process by referring to the 'ex-post' assessment of the EoW decisions taken by the economic operators.*" (p 131).

In France, the tacit (implicit) end-of-waste status by production installations exists since 2016 (MEDDE 2016). There is in 2023 a project of law "for the green industry" to allow waste managers to self-declare the end-of-waste of their material (with the same conditions as in the Waste Framework Directive) without prior approval by the administration, that can ex-post control their actions, including on requirement of NGOs or industries. That proposition is in line with the Article 6(1) of the WFD (EU 2018) which states: "*Member States shall take appropriate measures to ensure that waste which has undergone a recycling or other recovery operation is considered to have ceased to be waste if it complies with the following conditions…*" and with line with the Article 6(4) which states: "*Where criteria have not been set at either Union or national level under paragraph 2 or 3, respectively, a Member State may decide on a case-by-case basis, or take appropriate measures to verify, that certain waste has ceased to be waste on the basis of the conditions laid down in paragraph 1…*": "verify that certain waste has ceased to be waste" means that the regional producers or a single producer can claim the end-of-waste status and the authority checks whether the conditions are met. Ex-post decision making would fall under the category of appropriate measures of articles 6(1) and 6(4).

6.3 Proposition #5

EU-wide tacit end-of-waste status for the material supplied by certified industrial recycling facilities.

7. FURTHER ADVANTAGES OF THESE 5 PROPOSITIONS

7.1 Simplified EU waste shipment

Trans-boundary waste shipments are essential because not all countries possess the necessary waste treatment technologies. If a waste shipment is not prohibited, it must comply with either:

- 'green list' waste controls (also known as Article 18 controls), which are simplified controls for most non-hazardous materials, or
- notification controls (sometimes known as 'amber list' controls, typically hazardous waste), which require consent from all the competent authorities involved before it can be shipped.

In this latter case there are 12 administrative steps to receive a decision of notification (UK 2023b). Additionally, the classification of waste (as hazardous or not) differs from one EU country to another, and even between regions of a country like Germany. With the 5 propositions of this paper, the waste shipment between certified industrial recycling facilities will be eased. The implicit/tacit end-of-waste status for materials potentially upon entering but certainly at the output of an industrial recycling facility will reduce administrative burden and divergent national/regional interpretation for transport of the material to be recycled. As a first step, waste transport should be improved by the so-called "fast-track" system.

7.2 EU Level playing field of waste management

The implementation of waste regulations varies across Europe, leading to unequal business conditions. The annual assessment of environmental regulation implementation in the 27 countries highlights the need for progress in waste management in many Member States. The five propositions in this paper aim to establish a level playing field in collection, sorting, and preparation, promoting fair competition and enhancing waste collection and management in less advanced countries.

8. THE DEFINITION OF WASTE SHOULD ALIGNE WITH THE HIERARCHY OF WASTE PREVENTION, MANAGEMENT AND POLICY

'Waste' means any substance or object which the holder discards or intends or is required to discard (EU Waste Framework Directive 2008-2018).

The EU waste regulation is designed to avoid human and environmental exposure to contaminants when discarded. That exposure occurs typically in linear economy by littering and secondarily by incorrect landfilling. Waste has a legal status which aims to avoid the risks for the environment and public health if it is abandoned. The definition is based on the act of discarding, rather than the value of the material. Already in 2002, "*The main aim of waste management besides waste leaks should be today turning wastes to non-wastes*" (Pongrácz, 2002). In the circular economy, waste is collected in modern systems and treated in controlled industrial loops, so that there is virtually

no human and environmental exposure (the probability of exposure to the hazard, i.e., the risk, is very low).

In the linear and low-tech circular economy, waste can be abandoned or stored and this is probably the reason why its regulation is dominated by the hazard approach and the precautionary principle. In the high-tech industrial circular economy (Figure 4), waste is a resource that must be managed by risk, and not be defined solely by the abandonment by its holder.

There are different propositions to define materials in the circular economy: "non-waste" (proposed in 1997 by Bontoux and Leone of the Joint Research Centre of the EU, and deepened by Pongrácz and Pohjola, 1997 and Pongrácz, 2002), "certified material" (Johansson and Forsgren 2020), "non-waste product" (UK 2023a), "secondary raw material" (EURIC 2019, 2020) and the related product status.

8.1 Propositions of "pre-material" and new definition of waste

In compliance with occupational safety and health regulations and industrial standards during processing, and adhering to product regulations during its second life, the material transitioning into a secondary raw material, or pre-material, should be handled similarly to other hazardous or non-hazardous raw materials (virgin). It should obtain the end-of-waste status upon entering the loop (as detailed in Section 6).

It is proposed to create separate definitions of pre-materials (that are resources) and wastes (to be incinerated or eliminated) (Figure 5):

- Pre-materials are materials that can be prepared for reuse or recycled as material with end-of-waste status.
- Wastes are matter that can only be used as a resource by other recovery, e.g. energy recovery, or that can only be disposed of. Waste is not defined by the action or intention of its owner to dispose of it.

9. CALL FOR A DEBATE ON WASTE MANAGEMENT BY RISK

9.1 EU underlying principles of the discussion on hazard and risk: precaution versus responsibility

The underlying challenge is how to effectively manage contaminants while enhancing material circularity. An administrative approach, often tied to the precautionary principle and hazard-based methods, tends to favor incineration and landfilling. On the other hand, a more liberal approach, rooted in responsibility, self-regulation, and a risk-based strategy, encourages reuse and recycling. Striking the right balance between a centralized precautionary stance ("The administration rejects due to potential hazards to people and the environment...") and a decentralized approach that promotes industry-led, risk-conscious solutions for reuse or specific applications in secondary materials is a pressing question, as discussed in a report for the European Commission (EC 2020b): "*The balance between the precautionary principle and the liberal market is kept differently in the different MS.*" (p 20). "*Risk control versus hazard control: The industry states that the check on hazardous properties of the substances contained by End of Waste and/or By-Products should be assessed in term of bioavailability and bio accessibility. In other words, does the substance represents a real risk for human health and environment during all the life cycle stages? A major focus could be laid on risk control/reduction rather than hazard reduction/control. Waste classification, however, is solely hazard-based. As a result, the EoW [end-of-waste] or BP [by-product] assessment by authorities tends to be a hazard-based approach. Often these authorities use the hazard control approach out of respect for the precautionary principle, which is justifiable although it could hinder circular economy.*" (p 130). "*Simplifying certain aspects of the decision-making process by referring to the 'ex-post' assessment of the EoW decisions taken by the economic operators.*" (p 131).

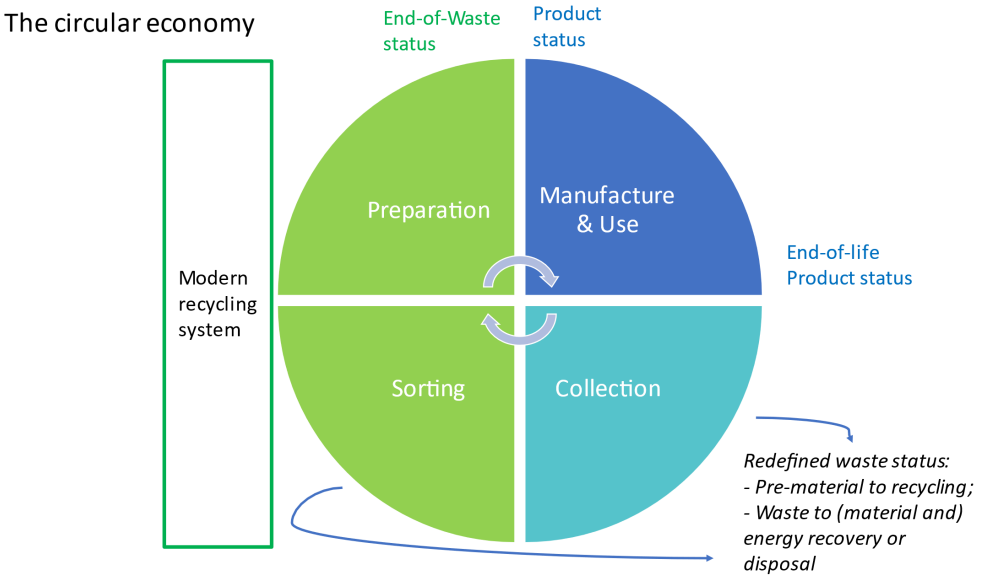


FIGURE 4: The circular economy and the corresponding status that materials/waste should have throughout the loop.

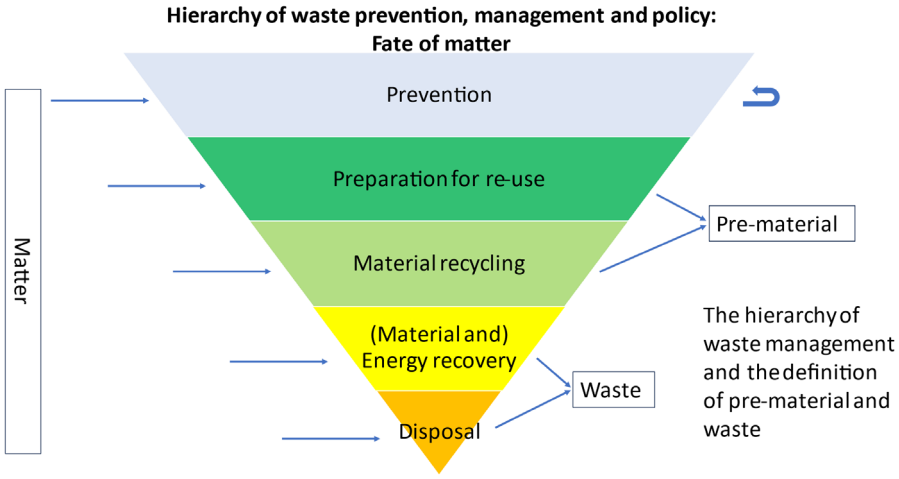


FIGURE 5: The definition of "pre-material" and "waste" based on the fate of materials within the waste hierarchy.

The ongoing discussion surrounding various products, materials, and waste could potentially find comprehensive solutions, particularly through the eco-design and "toxic-free" approach advocated by the European Commission. However, given the persistence of legacy substances and the prolonged lifespan of certain products, the recycling industry (namely EuRIC, the European Recycling Industries' Confederation), suggests that solutions emphasizing controlled risk in the intended use should be endorsed.

9.2 Call for a European Cooperation in Science and Technology (COST) action to debate

A large debate among the industry, the policy makers, the representatives, the NGOs, the consumers, the academic people involved in waste, products, substances, social aspects and law is necessary to promote the principle of responsible risk and to control the unlimited principle of precaution. A COST (European Cooperation in Science and Technology) Action is an interdisciplinary research network that brings researchers and innovators together to investigate a topic of their choice for 4 years. COST Actions are typically made up of researchers from academia, SMEs, public institutions and other relevant organisations or interested parties. Are funded: meetings, workshops, conferences, technical visits, research visits, communications, web sites. The objective is to share the ideas of this paper, and hopefully bring them to live. EuRIC participates in an initiative of the International Waste Working Group (IWWG), a scientific society, in the ongoing project "PREMAT FORUM", a forum to discuss waste management by risk and pre-material within the meaning of this paper.

10. CONCLUSIONS

In the circular economy, the management of recycled materials based on risk in the intended use plays a crucial role. The recycling industry suggests five proposals to endorse this approach, thereby fostering increased material recycling and facilitating waste shipment between certified industrial companies. These propositions could potentially warrant an EU-wide end-of-waste status for the material, potentially at the collection stage but certainly at the output of the certified recycling facility. To align with its status as a valuable resource, the legal classification of discarded materials should be determined by its place in the waste management hierarchy:

- Pre-materials: materials prepared for reuse or recycling.
- Wastes: materials only suitable for resource recovery (e.g., energy recovery) or disposal.

A COST (European Cooperation in Science and Technology) action is underway, led by the International Waste Working Group (IWWG, a scientific society) team, aimed at emphasizing the risk-based approach for waste management in the circular economy. The objective is to build consensus among stakeholders and enhance recycling practices.

ACKNOWLEDGEMENTS

This work has been funded by EuRIC. This work has been done without AI support.

REFERENCES

Bontoux L, Leone F. The legal definition of waste and its impact on waste management in Europe. A report prepared by IPTS for the Committee for Environment, Public Health and Consumer Protection of the European Parliament. European Commission, Joint Research Centre (JRC), Institute for Prospective Technological Studies (IPTC), Isla de la Cartuja, Sevilla, Spain, 1997. https://op.europa.eu/en/publication-detail/-/publication/30e68ead-92a2-443c-bec7-84beee24023a/language-en

Bridges J W., Greim H, van Leeuwen K, Stegmann R, Vermeire Th, den Haan K. 2023. Is the EU chemicals strategy for sustainability a green deal? Regulatory Toxicology and Pharmacology 139 (2023) 105356. https://doi.org/10.1016/j.yrtph.2023.105356

EC 2008 (CLP). Regulation EC No 1272/2008 of the European Parliament and of the Council of 16 December 2008 on classification, labelling and packaging of substances and mixtures, amending and repealing Directives 67/548/EEC and 1999/45/EC, and amending Regulation (EC) No 1907/2006. 31.12.2008 Official Journal of the European Union L 353/1. http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32008R1272&rid=1 .

EC 2018a. Options to address the interface between chemical, product and waste legislation. Communication from the Commission to the European parliament, the Council, the European Economic and Social Committee and the Committee of the Regions on the implementation of the circular economy package. COM(2018) 32 final.

EC 2018b. European Commission. Commission notice on technical guidance on the classification of waste (2018/C 124/01). OJEU 9.4.2018. 134 p.https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:52018XC0409(01)&qid=1530609217830&from=EN

EC 2019. The European Green Deal. Communication from the Commission to the European Parliament, the European Council, the Council, the European Economic and Social Committee and the Committee of the Committee of the Regions. COM(2019) 640 final. 11.12.2019. 24 p.

EC 2020a. Chemicals Strategy for Sustainability Towards a Toxic-Free Environment. Communication from the Commission to the European parliament, the Council, the European Economic and Social Committee and the Committee of the Regions. COM(2020) 667 final. 14/10/2020. 25 p.

EC 2020b. Study to asses Member States (MS) practices on by-product (BP) and end-of-waste (EoW). Reference: N° 070201/2018/793241/ENV.B.3. Final Report. Authors: Umweltbundesamt GmbH (EAA) and ARCADIS Belgium NV.

ECHA 2017. Guidance on the Application of the CLP Criteria Guidance to Regulation (EC) No 1272/2008 on classification, labelling and packaging (CLP) of substances and mixtures Version 5.0 July 2017. 647 p. https://echa.europa.eu/guidance-documents/guidance-on-clp

EU 2017. Council Regulation (EU) 2017/997 of 8 June 2017 amending Annex III to Directive 2008/98/EC of the European Parliament and of the Council as regards the hazardous property HP 14 'Ecotoxic'. Official Journal of the European Union. 14.6.2017. L 150/1. https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX-:32017R0997&rid=1

EU 2018. Directive 2018/851 Waste Framework Directive amending Directive 2008/98/EC of the European Parliament and on the Council of 19 November 2008 on waste and repealing certain Directives. OJ L 312, 22.11.2008, p. 3-59). (consolidated version) https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX-%3A02008L0098-20180705

EuRIC 2019. Top 5 Priorities of the Recycling Industry for the Period 2019-2024. Brochure. 8 p. https://euric-aisbl.eu/index.php?option=com_content&view=article&id=163:top-5-priorities-of-the-recycling-industry-for-the-period-2019-2024&catid=16:position-papers&Itemid=116

EuRIC 2020. Sound Management of Waste & Chemicals requirements by the recycling industry. Prepared by Christer Forsgren. Brochure 8 p. https://euric-aisbl.eu/resource-hub/reports-studies/sound-management-of-waste-chemicals-requirements-by-the-recycling-industry

EuRIC 2022. EPR Schemes, EuRIC Position, Circular Economy – Fair competition – State-of-the art recycling, 8 November 2022. 5 p. https://euric.org/images/Position-papers/euric_position_paper_epr_schemes.pdf

EuRIC 2023. Risk-based approaches for waste management in the modern circular economy. Pierre Hennebert. Available upon request to EuRIC. 100 p. https://euric.org/images/Files%20to%20be%20linked/Risk-based%20approaches%20for%20waste%20management%20Report%202024-01-31%20002.pdf

Friege H, Zeschmar-Lahl B, Kummer B, Wagner J. 2021. The new European database for chemicals of concern: How useful is SCIP for waste management? Sustainable Chemistry and Pharmacy 21 (2021) 100430. https://doi.org/10.1016/j.scp.2021.100430

Guéguen D, Marissen V. 2022. Policy-making in the European Union: coexisting or conflicting concepts? College of Europe. Bruges Political Research Papers 88 / 2022. https://www.coleurope.eu/sites/default/files/research-paper/wp88%20Marisen_Guegen.pdf

Hennebert P, Beggio G. 2021. Sampling and sub-sampling of granular waste: size of a representative sample in terms of number of particles. Detritus 17 – 2021, 1-12. https://doi.org/10.31025/2611-4135/2021.15139

Hennebert P, Humez N, Conche I, Bishop I, Rebischung F. 2016. Assessment of four calculation methods proposed by the EC for waste hazard property HP 14 'Ecotoxic'. Waste Management 48 (2016) 24–33. DOI: 10.1016/j.wasman.2015.11.044

Hennebert P, Stoffel A-F, Hubner M, Fortmann D, Merdy P, Beggio G. 2022. The inherent variability of some environmental analytical methods hampers the circular economy of materials. Detritus. 17 p. DOI 10.31025/2611-4135/2022.16225. https://digital.detritus-journal.com/articles/the-inherent-variability-of-some-environmental-analytical-methods-hampers-the-circular-economy-of-materials/2497 + Supp info

Hennebert P, van der Sloot H, Rebischung F, Weltens R, Geert L, Hjelmar O. 2014. Classification of waste for hazard properties according to the recent propositions of the EC using different methods. Waste Management 34 (2014) 1739–1751. PII: S0956-053X(14)00247-5, DOI: 10.1016/j.wasman.2014.05.021

Hennebert P. 2018. Proposal of concentration limits for determining the hazard property HP 14 for waste using ecotoxicological tests. Waste Management 74, April 2018, 74-5. https://doi.org/10.1016/j.wasman.2017.11.048

Hennebert P. 2019. Hazard classification of waste: review of available practical methods and tools. Detritus. 07, 13-28. https://doi.org/10.31025/2611-4135/2019.13846

Hennebert P. 2021. The substitution of regulated brominated flame retardants in plastic products and waste and the declared properties of the substitutes in REACh. Detritus 16 – 2021, 16-25. https://doi.org/10.31025/2611-4135/2021.15122

Hennebert P. 2022. Risk management of hazardous solid waste according by hazardous property including mercury contaminated wastes. Detritus, 20 – 2022, 78-89. https://doi.org/10.31025/2611-4135/2022.15212

Hennebert P. 2023. Hazardous properties of mineral and organo-mineral additives and management of hazardous plastics. Detritus 2023, 23 – 2023, 83-93. https://doi.org/10.31025/2611-4135/2023.17275

Johannson O. 2022. Did end of waste bring the end of waste? Editorial. Detritus, 20 – 2022, 1-2. https://doi.org/10.31025/2611-4135/2022.15220

Johansson N, C. Forsgren. 2020. Is this the end of end-of-waste? Uncovering the space between waste and Products. Resources, Conservation & Recycling 155 (2020) 104656. https://doi.org/10.1016/j.resconrec.2019.104656

Madelung S. 2023. Tire circularity and sustainability, in Tire recycling – making the wheel go round … from an environmental and policy perspective. EuRIC MTR conference, Brussels, 18/04/2023. p 84 of 250 p.

MEDDE 2016. Ministère de l'Ecologie, du Développement Durable et de l'Energie (France). Notice to operators of waste treatment facilities and operators of production facilities using waste as a substitute for raw materials (in French). Official Journal of January 13, 2016. https://www.legifrance.gouv.fr/jorf/id/JORFTEXT000031825201 .

Moser, H., and Römbke, J. (Eds), 2009. Ecotoxicological characterization of waste - Results and experiences of a European ring test. Springer Ltd.,NewYork, USA. 308 pp. All results and raw data at http://ecotoxwasteringtest.uba.de/h14/index.jsp

Moser, H., Römbke, J., Donnevert, G., Becker, R., 2010. Evaluation of biological methods for a future methodological implementation of the Hazard criterion H14 'ecotoxic' in the European waste list (2000/532/EC). Waste Manage. Res. 29 (2), 180–187.

Pongrácz E, Pohjola VJ. 1997. The conceptual model of waste management. Proceedings of the ENTREE'97, 12–14 November 1997, Sophia Antipolis, France, p. 65–77.

Pongrácz E. 2002. PhD Thesis. Re-defining the concepts of waste and waste management: Evolving the Theory of Waste Management. Doctoral dissertation. Department of Process and Environmental Engineering, University of Oulu, Finland, 2002. Available in electronic format at: http://www.herkules.oulu.fi/isbn9514268210/.

UK 2023a. Quality protocols. https://www.gov.uk/government/collections/quality-protocols-end-of-waste-frameworks-for-waste-derived-products

UK 2023b. Guidance - Waste: export and import. https://www.gov.uk/guidance/importing-and-exporting-waste

van Ewijk S, Stegemann J A. 2020. Recognising waste use potential to achieve a circular economy. Waste Management 105 (2020) 1–7. https://doi.org/10.1016/j.wasman.2020.01.019

detritus | Multidisciplinary Journal for Circular Economy and Sustainable Management of Residues

CISA

BEHAVIOR OF LANDFILLED STABILIZED FLY ASH TREATED BY DIFFERENT TREATMENT METHODS FOR THE PAST 27 YEARS

Jamie Mae Chee Tan [1,*], Amirhomayoun Saffarzadeh [2] and Takayuki Shimaoka [2]

[1] *Department of Urban and Environmental Engineering, Graduate School of Engineering, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan*
[2] *Department of Urban and Environmental Engineering, Faculty of Engineering, Kyushu University, 916, West 3, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan*

Article Info:
Received:
15 September 2023
Revised:
5 February 2024
Accepted:
28 February 2024
Available online:
20 March 2024

Keywords:
Municipal solid waste incineration
Fly ash
Long-term stability
Landfill
Chelate/acid-treatment
Compost treatment

ABSTRACT

Municipal solid waste incineration (MSWI) fly ash (FA) contains toxic substances and hence, direct landfilling of MSWI FA is prohibited in Japan Complying with Japan's stringent Waste Disposal and Public Cleansing Law, which demands adherence to landfill disposal and effluent standards, is crucial for ensuring environmental safety. To address the issue, various treatment methods including treatment by chemical, phosphoric acid, and melting and solidification can be used to stabilize the MSWI FA through the immobilization of heavy metals. However, the long-term stability of these treatment methods has not been thoroughly investigated. Therefore, the purpose of this study is to evaluate the long-term effectiveness of these three treatment methods for MSWI FA respectively, both independently and in conjunction with compost. This study involves the monitoring of changes in the concentration of heavy metals, including lead (Pb), cadmium (Cd), total-chromium (T-Cr), copper (Cu), and zinc (Zn), that have been leached over a period of 27 years. This study aims to conduct a detailed analysis of the impact of various treatment methods on the concentration levels of these individual heavy metals. Notably, the results suggest that independently, phosphoric acid treatment outperforms chelate treatment in the long run, but when combined with compost, both treatments exhibit enhanced efficacy, suggesting a promising approach for immobilizing heavy metals.

1. INTRODUCTION

Municipal solid waste incineration (MSWI) fly ash contains potentially hazardous substances which are known to have harmful effects on ecosystems and human health, and their accumulation in the environment can pose long-term risks (Mojtaba Ajorloo et al., 2022) (Yun Pan et al., 2013). These hazardous substances originate from the municipal solid waste (MSW) that is incinerated, or formed during the combustion process (David Laner et al., 2012). In 2002, the world generated approximately 0.68 billion tons of municipal solid waste (MSW) in a year (Hoornweg Daniel, 2012). In less than two decades, it increased more than threefold by 2020 at an estimated 2.24 billion tons, and the annual MSW generation is expected to increase by 73% to 3.88 billion tons in 2050 (BRIEF, 2022). As for Japan, the amount of municipal solid waste (MSW) generated has been gradually decreasing in 30 years according to data from the Ministry of the Environment of Japan. In 1991, Japan generated approximately 50.77 million tons of MSW (Ministry of the Environment, Government of Japan, 1995), whereas in 2020, the amount reduced to approximately 41.67 million tons (Ministry of the Environment, Government of Japan, 2022).

Although the statistics show a significant decrease of approximately 18% reduction in overall waste generated in the past three decades, Japan's high population density and mountainous terrains poses the issue of the scarcity of available landfill space to dispose the cumulated MSW (Kosuke Kawai, 2016). Hence, the Government of Japan enforced stricter regulations through the revision of the Waste Disposal and Public Cleansing Law in 1991 as an effort to achieve waste volume reduction (History and Current State of Waste Management in Japan, 2014). Incineration not only reduces MSW volume by approximately 85% to 90% and decreases the mass of original MSW by 60% to 90%, it also has the advantage of energy recovery (Yuying Zhang et al., 2021) (Xiang-Guo Li et al., 2012). As a result, incineration became the most common method used to manage MSW in Japan up until today (Hiratsuka-Sasaki A., 2020). In fact, with advance technology and environmentally friendly incineration equipment, Japan is one of the

* Corresponding author:
Jamie Mae Chee Tan
email: jmctan15@gmail.com

https://doi.org/10.31025/2611-4135/2024.18357

leading countries for waste incineration (Md Manik Mian et al., 2017).

However, MSWI essentially produces two-types of solid by-products, that is fly ash (FA) and bottom ash (BA) (Feng-He Wang et al., 2015) (Margarida J. Quina et al., 2010). In general, MSWI FA is more dangerous than MSWI BA because it contains relatively higher proportion of hazardous substances that can have negative environmental impacts on air, water, and soil quality if not properly managed before landfill disposal (Evangelina Atanes et al., 2019) (Yun Pan et al., 2013) (David Laner et al., 2012). Some of these toxic elements released includes organic pollutants, and high levels of leachable toxic heavy metals (THMs) such as lead (Pb), cadmium (Cd), and chromium (Cr) (Rahman Zeeshanur, 2019) (Wan Chen et al., 2017). These THMs from the MSWI FA pollutes natural resources through leachate accumulation from water-soluble chemicals mixing with the moisture present in the landfill, and hence, direct landfilling of MSWI FA is prohibited in Japan without effective immobilization of THMs (Hiroki Kitamura et al., 2016). The concentration of the THMs has to meet Japan's landfill disposal criteria and effluent standards before landfilling (Ministry of the Environment, Government of Japan, 2015) (Shimaoka Takayuki, 1996). Various treatment methods are used to stabilize the MSWI FA by immobilizing the THMs to largely reduce the substantial amount of hazardous compound in the MSWI FA. To address this issue, treatment methods including (1) cement solidification, (2) treatment by chemical, (3) acid and other solvent, and (4) melting and solidification can be used to stabilize the MSWI FA through immobilization of heavy metals (Zhikun Zhang et al., 2022) (Mojtaba Ajorloo et al., 2022) (Cao Yi-nan et al., 2021) (Zeyuan Liu et al., 2019) (Shimaoka Takayuki, 1996).

Cement solidification is the most common method for stabilizing MSWI FA in Japan due to its effectiveness in immobilizing hazardous contaminants and encapsulating them in the cement matrix (Pengfei Ren et al., 2022 'a'). However, the effectiveness of heavy metals immobilization is heavily influenced by the conditions of the treatment process as well (Charles H. K. Lam et al., 2010). In the long-run, the pH value in the cement matrix will be affected by carbonation during natural aging, and the high concentration of toxic heavy metals in FA may result in physical deterioration of the cement matrix, which increases the treatment cost, and also raises concerns on the long-term stability and durability of the cement-solidified MSWI FA (Bing Du et al., 2019).

Simultaneously, the long-term stability of alternative treatment methods (2), (3), and (4) have not been thoroughly studied. Therefore, this study was conducted for the past 27 years to comprehensively investigate the long-term stability of the three treatment methods respectively. The aim is to assess whether the treated and landfilled MSWI FA will persistently produce harmful levels of leachate over an extensive duration. This analysis creates the opportunity to evaluate the potential for discontinuing ongoing landfill monitoring after a specified period. The MSWI FA samples in this study are from the same source treated with different methods. After treatment, the samples are stored in large columns simulating the external environment that landfilled ashes are exposed to. The changes in concentration of heavy metals leached, particularly lead (Pb), cadmium (Cd), total-chromium (T-Cr), copper (Cu), and zinc (Zn), were monitored for the past 27 years.

2. MATERIALS AND METHODS

2.1 Ash samples and pre-treatment methods

The MSWI FA used in this study is from the same source, and treated with different methods, namely chelate treatment, phosphoric acid treatment, compost, combination of compost and chelate treatment, combination of compost and phosphoric acid treatment, and melting and solidification (Table 1). After treatment, the samples are stored in columns simulating a semi-aerobic landfill structure which is widely used in Japan (Figure 1) (K. Miyawaki et al., 2000). The top end of the column is exposed to natural rainfall, which seeps through the ashes, forming leachate and the leachate is collected at the bottom of the column. The BAFACG group has a 60:20:15:5 ratio corresponding to BA: FA: Garbage: Compost. BAFA(U) and SMS has a 3:1 ratio for BA:FA whereas PMS has a 4:1 of BA to FA ratio. The rest of the samples are purely FA and BA respectively.

TABLE 1: Fly ash with different treatment methods and its abbreviation.

Column No.	Sample Name	Abbreviation
1	Bottom Ash + Untreated Fly Ash + Crushed Garbage + Compost	BAFACG(U)
2	Bottom Ash + Chelate-treated Fly Ash + Crushed Garbage + Compost	BAFACG(C)
3	Bottom Ash + Phosphoric-acid-treated Fly Ash + Crushed Garbage + Compost	BAFACG(P)
4	Untreated Bottom Ash	BA(U)
5	Untreated Fly Ash	FA(U)
6	Untreated Bottom Ash + Fly Ash	BAFA(U)
7	Surface melting slag Fly Ash + Bottom Ash	SMS
8	Plasma melting slag Fly Ash + Bottom Ash	PMS
9	Chelate-treated Fly Ash	FA(C)
10	Phosphoric-acid-treated Fly Ash	FA(P)

Where (U) = untreated, (C) = chelate-treated, (P) = phosphoric-acid-treated

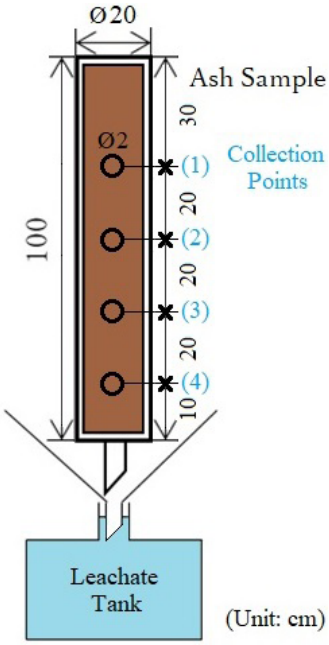


FIGURE 1: Column sketch.

2.2 Sample Collection Method

The leachate (hereinafter effluent) was collected from the leachate tank annually since 1995 for column experiment. As for ash collection, 2cm hole was drilled on 4 collection points, at the depth of 90cm, 70cm, 50cm, and 30cm as shown in Figure 1. 120g of ashes were collected from every point.

2.2.1 Sample Prepration

30g of ash samples were oven dried at 105°C for 24h to remove moisture for X-ray fluroscence (XRF) test, while another 30g were oven dried at 50°C for 24h for X-ray diffraction (XRD) test. 10g of the 105°C oven-dried ash samples were further heated at 600°C for 2h to calculate the Loss on Ignition (LOI). The 50°C dried ash samples were manually grounded using the mortar and pestle until powder form was achieved for XRD test. Thin section for polarization microscopy and scanning electron microscopy with energy dispersive X-ray (SEM-EDX) spectroscopy were made with selected ash sample pieces of approximately 3mm to 5mm in length, height, and width. The points to investigate were selected using polarized light microscopy.

To prepare for JLT-13 following Notification 13 of the Environment Agency, 500mL of super pure water were mixed with 50g ash sample to achieve a liquid to solid (L/S) ratio of 10, and shaken horizontally for 6h at 200 oscillations per minute. The samples were then filtered through a glass-fiber filter, followed by separating 50mL of the filtered sample for analyzing. For column experiment, 500mL of leachate samples were collected from all ten columns. Similarly, the leachate was filtered through a glass-fiber filter and 50mL were separated for analyzing.

For both the column experiment and leaching test, 5mL of 61% nitric acid (HNO_3) was added to the 50mL of filtered sample prepared in a conical flask, which was left to evaporate until 10mL of solution remains using the HPR-4030 hot plate that was preheated to 150°C. Another 5mL of 61% HNO_3 was subsequently added to the 10mL solution. Glass lids were placed onto every conical flask before evaporating the solution again until 5mL remains. The 5mL solution was diluted with 1% HNO_3 in a 50mL volumetric flask.

2.2.2 Analytical Methods

The chemical composition of MSWI FA were determined by using XRF spectrometer (Rigaku RIX3100). 4g of oven-dried ash samples were formed into pressed pellets by pulverization with a 4:1 ash sample to binder ratio. X-ray diffraction (XRD, MultiFlex, Rigaku) was applied for bulk mineral detection using Cu-K radiation within the 2-theta range of 2e75 and scanning step of 0.02 at the voltage of 44 kV and the beam current of 30 mA. Phase identification was carried out using Jade (v. 6.1) and PDXL (v. 2.1.2.0) software packages. Subsequently, the mineral compositions on the thin section were identified using SEM-EDX spectroscopy (Hitachi SU3500).

The concentration of heavy metals and light metals leached were determined by using Inductively Coupled Plasma Optical Emission Spectroscopy (720 ICP-OES). The prepared samples were tested against standard solutions of 0.005mg/L, 0.01mg/L, 0.02mg/L, 0.050mg/L, 0.100mg/L, 0.500mg/L, and 1.000mg/L.

3. RESULTS AND DISCUSSIONS

In this section, the targeted samples for discussion are the BAFACG group: BAFACG(U), BAFACG(C), BAFACG(P), and FA group: FA(U), FA(C), FA(P). Firstly, the bulk chemical and mineral composition analysis is provided, followed by detail analysis on the factors that resulted in the immobilization of heavy metals, with respect to the treatment method, according to the timeline of 27 years in total.

3.1 Bulk chemical composition analysis

XRF test was conducted to determine the constituents present in the ash samples. XRF is an elemental analysis technique that provides quantitative chemical information (Seifollah Nasrazadani, 2016). According to Table 2, the MSWI ash samples comprises mainly of silicon dioxide (SiO_2), aluminum oxide (Al_2O_3), iron (III) oxide (Fe_2O_3), and calcium oxide (CaO).

Interestingly, the FA group: FA(U), FA(C), and FA(P) have higher CaO weight percentage (wt%) than that of SiO_2. Inversely, samples consisting BA have higher SiO_2 content. These three trace constituents, which are also amphoteric heavy metals: Pb, Cu, and Zn displayed significant concentrations. Cd and Cr have a smaller concentration in comparison, but Cd and Cr are considered harmful heavy metals, hence, these five trace constituents are selected for discussion in this study.

3.2 Phase identification of minerals and weathering phenomenon of the MSWI fly ash

While the bulk chemistry data offer a reliable projection of the total elemental composition of the non-homogenous

TABLE 2: Bulk composition analysis of the ten samples (XRF).

Sample Name		BAFAC-G(U)	BAFAC-G(C)	BAFAC-G(P)	BA(U)	FA(U)	BAFA(U)	SMS	PMS	FA(C)	FA(P)
Major Constituent (mass%)	SiO_2 [%]	25.5	33.9	34.5	29.3	18.7	25.9	33.8	40.2	20.6	11.7
	Al_2O_3	16.2	16.4	16.3	18.6	8.8	17.4	17.7	19.4	10.1	6.5
	Fe_2O_3	7.6	7.7	7.8	17.4	2.1	15.1	11.4	3.6	2.3	1.7
	CaO	23.3	20.9	20.9	19.5	38.0	24.7	26.5	30.3	40.0	33.6
	Sub Total	72.5	78.9	79.6	84.8	67.7	83.1	89.4	93.6	73.0	53.5
Minor Constituent (mass%)	TiO_2 [%]	1.26	1.26	1.24	1.47	0.79	1.18	1.24	1.34	0.88	0.61
	MnO	0.11	0.10	0.12	0.21	0.07	0.17	0.17	0.17	0.07	0.06
	P_2O_5	2.59	2.86	3.74	1.97	0.72	1.49	2.66	0.16	0.80	25.1
	MgO	2.86	2.79	2.79	2.50	2.17	2.47	2.69	2.56	2.47	1.08
	Na2O	1.30	1.43	1.60	1.09	0.67	0.90	1.85	0.67	0.70	4.54
	K2O	0.52	0.56	0.58	0.37	0.02	0.27	0.48	0.11	0.05	0.23
	Cl	0.13	0.14	0.11	0.08	0.13	0.10	0.24	0.44	0.12	0.70
	S	0.05	0.05	0.05	0.10	1.49	0.14	0.04	0.39	1.13	0.47
	F	0.03	0.03	0.03	0.01	0.19	0.09	0.00	0.03	0.24	0.21
	Sub Total	8.84	9.22	10.26	7.80	6.25	6.81	9.37	5.87	6.45	32.95
Trace Constituent (ppm)	Zn [ppm]	5865	5034	5497	4511	16188	7444	4650	496	16776	5907
	Cu	2388	2536	1847	3507	822	2342	1341	207	831	650
	Pb	3865	4871	4364	1729	2414	2826	715	49	4130	1941
	Cr	243	228	231	782	304	601	1182	715	294	215
	Ni	103	106	97	311	83	188	162	26	81	77
	Ba	851	791	756	1235	339	1014	1100	1460	468	362
	Sb	0	0	0	106	0	0	0	0	0	1
	Sn	139	157	162	305	289	235	101	49	317	227
	Sr	359	316	324	292	59	251	392	502	93	134
	As	26	33	29	12	16	19	5	0	28	13
	V	3	3	3	4	2	3	4	3	2	2
	Cd	107	102	102	98	174	120	95	79	199	105
	Co	7	6	6	3	1	3	7	13	2	3
	Sub Total [%]	1.40	1.42	1.34	1.29	2.07	1.50	0.98	0.36	2.32	0.96
	LOI [%]	9.8	10.4	8.9	6.1	24.0	8.5	0.3	0.2	18.3	12.6
	Total [%]	82.75	89.58	91.15	93.93	75.97	91.47	99.75	99.85	81.73	87.45

MSWI ash samples, it does not provide information about the speciation and source of the elements (Saffarzadeh Amirhomayoun et al., 2011). Therefore, the collective utilization of rapid analytical technique (XRD), and microanalytical technique (optical microscopy and SEM-EDX spectroscopy), are essential for the recognition of crystalline phases and the characterization of the phase transformation phenomenon in the MSWI ash (Estevanus Kristian Huliselana et al., 2010).

Usually, fresh MSWI fly ash consist mainly of Ca-containing phases such as portlandite ($Ca(OH)_2$), calcium chloride hydroxide (CaClOH), and anhydrite ($CaSO_4$) (Pengfei Ren et al., 2022 'b'), along with chloride salts (halite (NaCl) and sylvite (KCl)) (Kaixing Zhao et al., 2020). Whereas minerals like lime (CaO) and $Ca(OH)_2$ can be found in the fresh bottom ash (Yunmei Wei et al., Mineralogical characterization of municipal solid waste incineration bottom ash with an emphasis on heavy metal-bearing phases, 2011 'b'). However, in the BAFACG group, quartz (SiO_2) and calcite ($CaCO_3$) are the major crystalline phases being recognized instead as shown in Figure 2a. The secondary minerals detected are $CaCO_3$ and hematite (Fe_2O_3), which is rather different in comparison to the minerals that are commonly found in fresh MSWI FA and BA. Secondary minerals are formed as a byproduct of weathering, and the formation occurs near the site where primary minerals are being attacked (William H. Schlesinger, 2020). As for the FA group in Figure 2b, ettringite and calcite are the major crystalline phases, while the detection of the principal secondary mineral gypsum ($CaSO_4{\cdot}H_2O$) suggests that changes occurred in the primary anhydrite ($CaSO_4$) as a result weathering, and the access of water molecule from the landfill column is responsible for the crystallization of secondary gypsum.

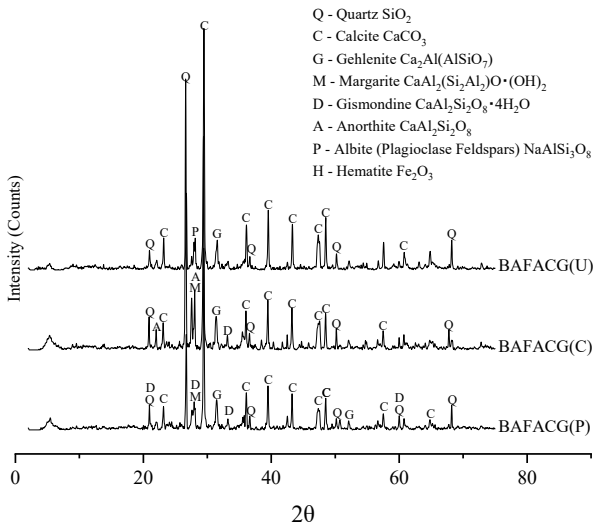


FIGURE 2: X-ray diffractogram of (a) BAFACG group ash sample, and (b) FA group ash sample.

3.2.1 Influence of weathering on heavy metals

The presence of CaO in MSWI FA results in a significantly high alkaline content, posing challenges to its potential for reuse. Nevertheless, the presence of carbon dioxide (CO_2) within the MSWI ash offers a solution by facilitating the transformation of Ca-containing phases such as CaO and $Ca(OH)_2$ from fresh MSWI FA into thermodynamically stable $CaCO_3$ (H. Mehdizadeh et al., 2021), thereby reducing the alkalinity of the ash. Carbonation is expressed by the following equations (Giampiero P. Sorrentino et al., 2023):

$$2CaClOH + CO_2 \rightarrow CaCO_3 + CaCl_2 + H_2O \quad (1)$$

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \quad (2)$$

Even though the results from XRD and SEM-EDX tests only shows the mineral phases and its chemical composition of the weathered MSWI FA in the current year (Year 27), the abundant formation of calcite ($CaCO_3$) minerals (Figure 3a and Table 3) and the absence of the aforementioned Ca-containing phases as shown in Figure 2 suggests that carbonation reaction occurred throughout the years of the MSWI ash weathering in the landfill column, thereby reducing the alkalinity of the MSWI ash.

The principal secondary mineral hematite (Fe_2O_3) is considered as a crystalline ferric mineral. This mineral was present in the SEM-EDX analysis for all samples in the BAFACG and FA group. Due to the large amount of data, the discussion will be represented by the results of BAFACG(U) sample. Table 3 shows the chemical composition of BAFACG(U) in the SEM-EDX analysis in Figure 3. Fe_2O_3 is particularly in abundance at Point B, C, and D in Figure 3b. At Point B, a small amount of Zn, a bivalent metal, was detected. The substitution of Fe with bivalent metals (hereinafter metallic inclusions) such as Pb, Cu, and Zn, which are bounded to crystalline ferric minerals, takes place in the course of glass alteration. When glass alteration occurs, dissolution of metallic inclusions results in the leaching of Pb, Cu, and Zn metal (Yunmei Wei et al., 2011 'a'). This phenomenon influences the leaching concentration of heavy metal.

3.3 Leaching characteristics of MSWI fly ash

Leaching test was conducted in three separate years to study the leaching characteristics of the five selected heavy metals. For BAFACG group, the results are from Year 0 (Y0), Year 5 (Y5), and Year 27 (Y27), while the timeline of FA group begins from Year 1 (Y1), followed by Y5 and Y27. With only results from 3 different years, it is difficult to determine an accurate change in behavior of the heavy metals. However, it is still important to ensure that the THMs (Pb, Cd, T-Cr) satisfies Japan's landfill disposal standards to prevent contamination in the environmental systems (Rahman Zeeshanur, 2019). Hence, this section assesses the heavy metals released and its compliance with landfill disposal standards.

From the results in Table 4 and Table 5, the high concentration of chloride salt in five years (Y5) in the study indicates high soluble chloride (Cl) content in FA, which is detrimental to the reuse of FA due to the potential risks

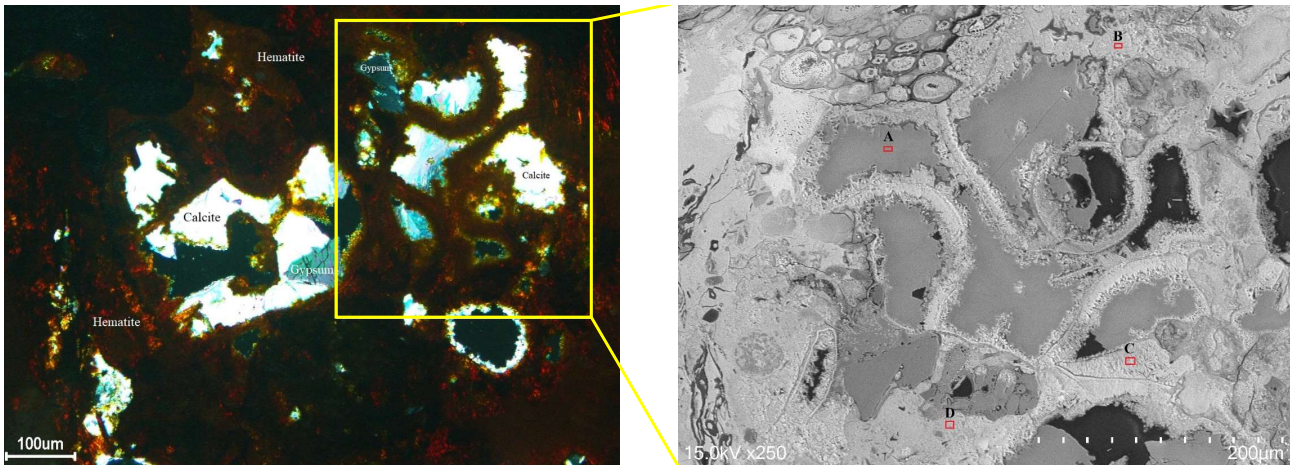


FIGURE 3: Photomicrograph of (a) presence of iron-rich constituent, calcite, and gypsum in BAFACG(U) under crossed-polarized light (xPL), and (b) a 90° anticlockwise BSE image of fig. 3a with four label points.

TABLE 3: Chemical composition of corresponding to the points in Figure 3b.

Point	A	B	C	D
Element	Wt%			
CK	10.77	5.44	8.12	4.74
OK	37.76	27.27	26.85	27.23
MgK	0.67	0.22	-	0.26
AlK	0.50	2.30	1.14	2.85
SiK	0.63	4.22	1.77	5.81
PK	-	0.29	0.13	0.37
SK	1.48	0.06	-	0.10
ClK	-	0.16	-	-
KK	0.17	0.13	-	0.24
CaK	41.84	2.62	1.89	3.83
FeK	6.18	57.00	60.09	54.56
ZnK	-	0.29	-	-

posed to the environment (Kaixing Zhao et al., 2020) (Xiongfei Chen et al., 2016) (Wei-Sheng Chen et al., 2012). This high chloride content also assists in the leaching of Pb, Cd, and Zn metals during dissolution, increasing the content of these harmful heavy metals at the landfill and in the environmental systems if not carefully treated and disposed (Mojtaba Ajorloo et al., 2022).

In Y1 and Y5, the Pb leached from FA(U) was above the landfill disposal standard, while the leached Pb, Cd, and T-Cr of the remaining samples already satisfied the landfill disposal standard since the beginning of the study. By Y27, the THMs (Pb, Cd, and T-Cr) leached from both BAFACG and FA group is well below Japan's landfill disposal criteria of 0.3 mg/L for Pb and Cd, and 1.5 mg/L for Cr^{6+} (Shimaoka Takayuki, 1996). While the data does satisfy the landfill disposal standard, it is important to note that solely relying on these criteria does not provide complete assurance that the treated FA is safe for landfill disposal.

3.4 Behavior of heavy metals in the effluent

A major concern related to the operations of landfills is the inevitable consequences of heavy metals releasing with leachate (C. Righi et al., 2022). Landfill leachate containing high levels of THMs affects the environmental system through water contamination if the MSWI ash is not given proper treatment to meet the Japanese effluent standards (Yunmei Wei et al., 2022 'c') (Hiratsuka-Sasaki A., 2020) (Ministry of the Environment, Government of Japan, 2015). However, even if the concentration of individual THMs is not very high, it does not mean that the total amount of heavy metals in the leachate is negligible (Athanasius P. Bayuseno, 2011).

The behavior of heavy metals in the effluent of thermal-treated FA has been very consistent throughout the

TABLE 4: Leached concentration of heavy and light metals in BAFACG group corresponding to timeline of the study.

Sample Name		BAFACG(U)			BAFACG(C)			BAFACG(P)		
Year		0	5	27	0	5	27	0	5	27
	pH	11.3	7.9	8.9	10.5	7.8	8.8	10.5	8.1	9.0
Leached Concentration (mg/L)	Pb	0.06	0.07	0.04	0.05	0.49	0.04	0.05	0.37	0.02
	Cd	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.01
	Cr	0.02	0.02	0.01	0.02	0.02	0.01	0.02	0.02	0.01
	Zn	0.10	0.28	0.05	0.10	0.25	0.05	0.10	0.34	0.05
	Cu	0.53	0.64	0.03	0.10	0.18	0.02	0.40	0.17	0.02
	Ca	381	60.1	21.0	339	69.6	22.6	430	64.3	19.1
	Na	647	98.2	2.13	805	214	2.15	680	121	1.83
	Cl	35.5	2075	1.05	19.9	2320	0.62	17.3	2320	0.64

TABLE 5: Leached concentration of heavy and light metals in FA group corresponding to timeline of the study.

Sample Name		FA(U)			FA(C)			FA(P)		
Year		0	5	27	0	5	27	0	5	27
	pH	12.2	12.6	11.7	12.2	12.6	10.1	7.2	7.3	8.5
Leached Concentration (mg/L)	Pb	95.0	23.5	0.02	0.09	0.16	0.01	0.05	0.05	0.01
	Cd	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
	Cr	0.03	0.02	0.02	0.02	0.02	0.01	0.02	0.02	0.01
	Zn	9.80	1.11	0.04	0.02	0.58	0.05	0.02	6.03	0.03
	Cu	0.26	0.02	0.01	0.02	0.02	0.03	0.02	0.02	0.01
	Ca	9100	7300	12.6	8600	6250	7.02	6400	3205	20.8
	Na	-	-	0.39	-	-	1.07	-	-	3.56
	Cl	17000	14000	3.60	17000	11750	1.86	13000	6575	4.83

study. This treatment successfully encapsulates the heavy metals long-term through high temperature heating. Thus, the discussion for this treatment method is omitted for this paper. As for other treatment methods, significant changes can be observed from the concentration of heavy metals leached from the beginning of the study (Year 0) up until today (Year 27).

3.4.1 Immobilization mechanisms of chelate/acid treatment

pH value of the effluent plays a huge influence in the immobilization of heavy metals in MSWI FA. The ash in the FA group is soft and fine apart from FA(C), which coagulated from the treatment but crushes relatively easily. Figure 4 shows the effluent pH changes of FA group for the past 27 years.

In Figure 5, from Y1-Y5, the leaching of Pb decreased for all FA group. Chelate treatment proved effective on immobilizing Pb in FA as the Pb leached were significantly lower in comparison to FA(U) and FA(P). Phosphoric-acid treatment not only reduces the effect of the high dissoluble chloride content, but also reduces the high alkalinity of MSWI fly ash (Guo Xian Ma, 2013). The pH value of FA(P) falling into the acidic spectrum promotes the leachability of amphoteric metal Pb, reflected by the steep fall in the Pb concentration in Figure 5.

From Y6-Y15, leached Pb from the FA group fell below the Japanese effluent standard of 0.1 mg/L, with the exception of an outlier, FA(P) in Y14. The soluble Cl leached (Figure 6) from FA(P) effluent decreases in similar pattern as leached Pb, and the slight increase in soluble Cl leached in Y12-Y15 and Y22-Y25 resulted in the leached Pb fluctuation (Mojtaba Ajorloo et al., 2022). From Y16-Y27, both chelate and acid treatment displays effectiveness in immobilizing Pb by meeting the effluent criteria.

The pH value of the effluent also plays an important role in the immobilization of Cd (Mojtaba Ajorloo et al., 2022). The leached Cd from Y1-Y5 in Figure 7 corresponds to the effluent pH in Figure 4. Chelate treatment is the most effective in stabilizing Cd, in the span of two years. From Y6-Y27,

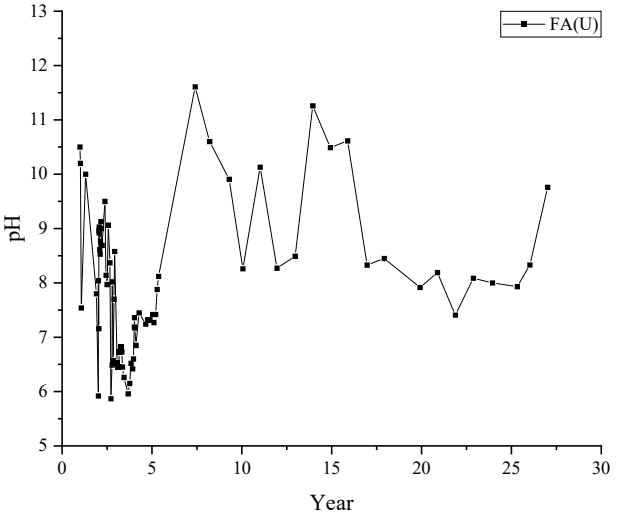


FIGURE 4: pH value of the effluent in the FA group: (a) FA(U), (b) FA(C), and (c) FA(P).

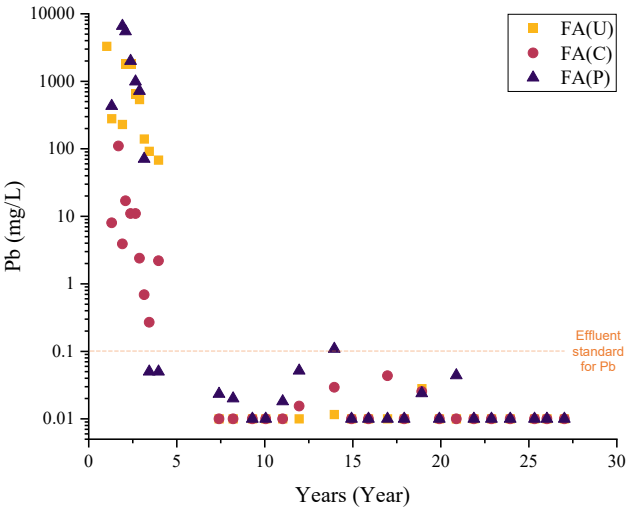


FIGURE 5: Leached Pb concentration (FA group).

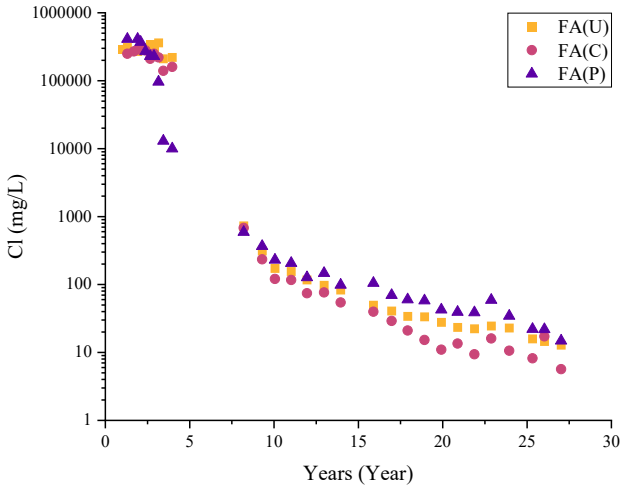


FIGURE 6: Leached concentration of chloride salt Cl (FA group).

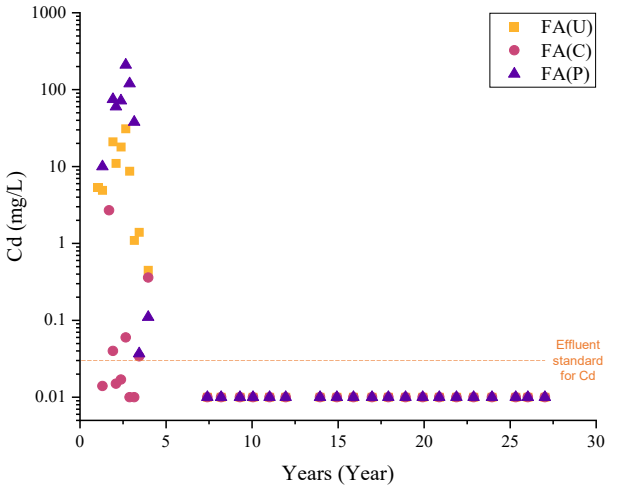


FIGURE 7: Leached Cd concentration (FA group).

leached Cd meets the effluent standard of 0.03 mg/L and is at the machine's detection limit. This pattern is expected to continue in the long-term.

In Figure 8, the immobilization of Zn from Y1-Y5 is of similar pattern as that of Pb and Cd. However, Zn is more sensitive to the changes in pH as compared to Pb and Cd. The slight fall in pH from Y18-Y25 (Figure 4) resulted in the fluctuation of leached Zn in Figure 8. Despite the leached Zn of FA group meeting the effluent standard of 2.0 mg/L since Y6, the possibility of it remaining below the criteria is uncertain in the long-run regardless of the treatment method in this case, especially if the fluctuation of effluent pH occurs between 7.0 and 8.0.

Chelate and acid treatment proved to be effective on the stabilization of T-Cr as the leached T-Cr meets the Japanese effluent standard of Cr^{6+} of 0.5 mg/L from the beginning of the study (Figure 9). From Y1-Y5, FA treated with phosphoric acid took immediate effect in the immobilization of T-Cr than chelate treatment. In Y14, there is a small spike in leached T-Cr that is similar to that in Pb. In this case, this increase is not of concern as the effluent standard is set for Cr^{6+}. Thus, it is safe to conclude that the immobilization of T-Cr with both chelate and acid is safe and effective in the long-run.

In contrast, these treatment methods are not as effective on Cu as shown in Figure 10. From Y1-Y5, the treatment methods promoted the leaching of Cu instead of immobilizing them. Acid treatment seems to be more effective in stabilizing Cu in the long-run in comparison to chelate treatment. From Y6-Y10, leached Cu of FA(C) did not satisfy the effluent criteria of 3.0 mg/L. Chelate treatment resulted in the coagulation of the ash, forming larger particles that easily crumbles upon small forces acting on it. The other two samples are very fine in comparison to FA(C). The particle size led to the fluctuation of leached Cu in FA(C) as Cu are mostly concentrated in larger particles (Davide Bernasconi et al., 2022).

Between chelate treatment and phosphoric acid treatment, chelate treatment is more stable and less fluactuative in the short-term. On the other hand, phosphoric acid treated FA promotes the leaching of amphoteric metals in the short-run, but shows effective immobilization of heavy metals within 3 years and is more promising in the long-run, especially Cd, T-Cr, Zn, and Cu. Overall, the leaching of heavy metals is heavy influenced by the effluent pH, followed by Cl content and ash particle size.

3.4.2 Immobilization mechanisms of chelate/acid treatment with compost

With the addition of compost alongside chelate or acid treatment, a rich CO_2 environment is created. Crushed garbage consisting of glass shards were also added which enhances the porosity of the ash. Due to these changes, the results varied drastically from using only one treatment method. The particle size and hardness of the BAFACG group ash mix is also much coarser in comparison to the soft and fine ash from FA group. Figure 11 shows the effluent pH changes of BAFACG group for the past 27 years.

From Y0-Y5, the Pb leached fluctuated above and below the Pb effluent standard of 0.1 mg/L (Figure 12).

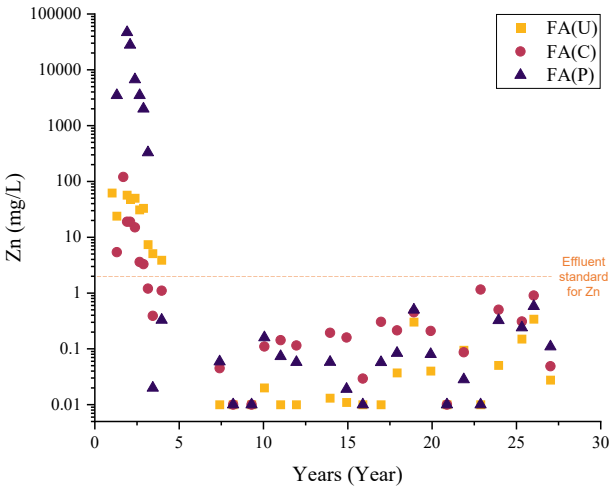


FIGURE 8: Leached Zn concentration (FA group).

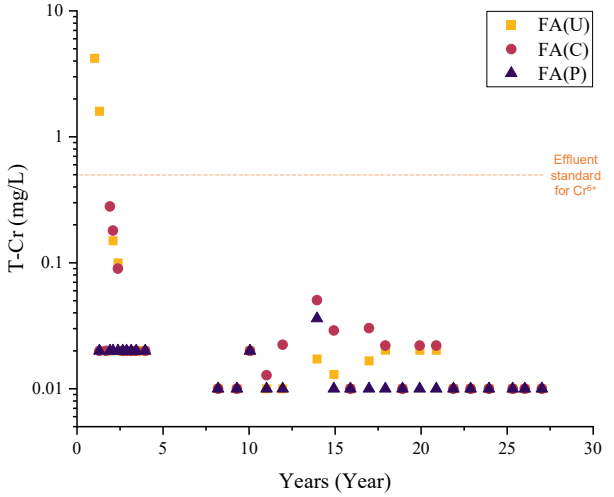


FIGURE 9: Leached T-Cr concentration (FA group).

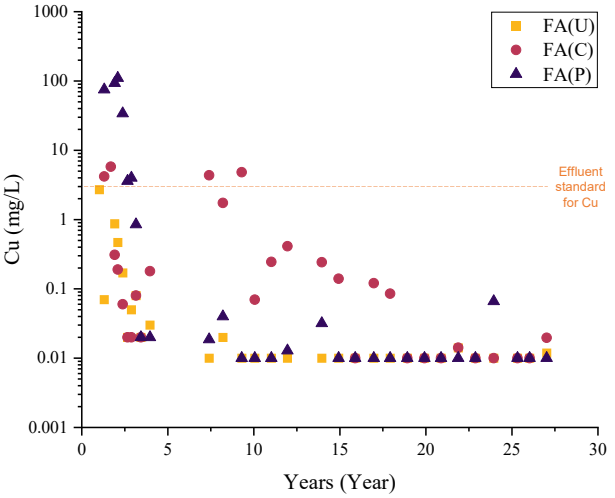


FIGURE 10: Leached Cu concentration (FA group).

treatment methods is equally as effective as using only chelate/acid treatment in the immobilization of Cd.

The drastic changes in Pb leached in the first 5 years is attributed to the heterogeneous ash composition and accelerated carbonation. From Y6-Y15, the leached Pb of BAFACG group satisfies the effluent criteria. The soluble Cl in this ash group is also significantly lower compared to the FA group (Figure 13), hence the lower concentration of leached Pb. The immobilization of heavy metals for FA treated with the combination of compost is highly affected by the accelerated carbonation from the breaking down of compost. From Y16-Y27, the organic matter in the compost eventually broke down, releasing some heavy metals, hence the small increment in leached Pb from BAFACG(U) in Figure 12.

Leached Cd, on the other hand, is generally concentrated above the effluent standard 0.03 mg/L from Y0-Y5 (Figure 14). Apart from accelerated carbonation, the effluent pH of BAFACG group falling below the neutral value of 7 from Y0-Y5 (Figure 11) also promoted the leaching of Cd to a certain extent. From Y4 onwards, the combination of two

In Figure 15, accelerated carbonation largely contributed to the low concentration leaching of Zn from Y0-Y5 in comparison with the leached Zn from the FA group. Although accelerated carbonation is the main factor in immobilizing the amphoteric metal Zn, the effluent pH also plays an important role in maintaining the leached Zn concentration below the effluent standard of 2.0 mg/L. From Y10-Y27, the leaching pattern of Zn mirrors the pH of the effluent, indicating an inverse correlation between Zn and pH.

Leached T-Cr was below the Cr^{6+} effluent criteria of 0.5 mg/L (Figure 16) within a year (Y0-Y1) from the commencement of this study. From Y8-Y27, both treatment methods proved effective in immobilizing T-Cr in the long-run, as shown in Figure 16.

In Figure 17, FA treated with combinations of two treatment methods satisfies the effluent standard of Cu almost immediately. The addition of a CO_2-rich environment fur-

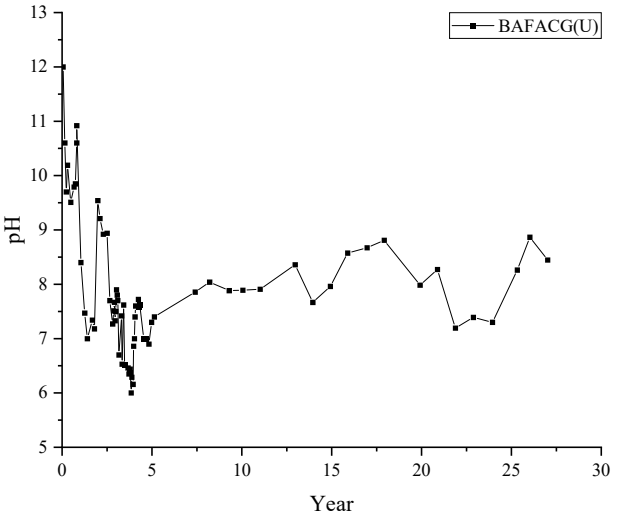


FIGURE 11: pH value of effluent in BAFACG group: (a) BAFACG(U), (b) BAFACG(C), and (c) BAFACG(P).

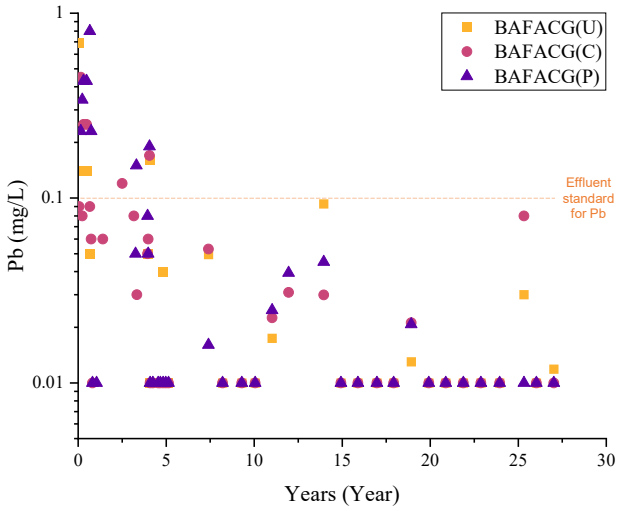


FIGURE 12: Leached Pb concentration (BAFACG group).

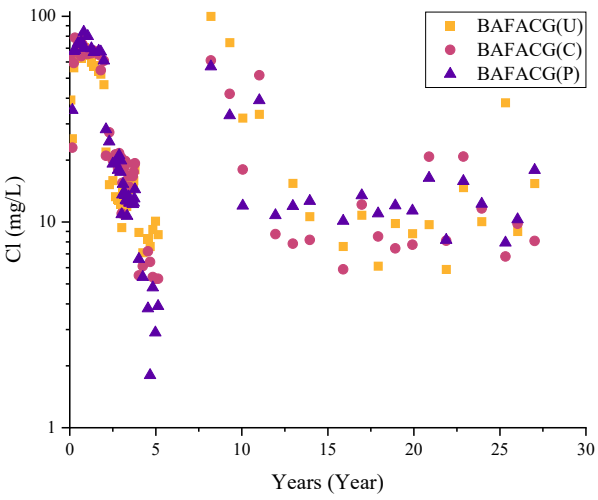


FIGURE 13: Leached concentration of chloride salt Cl (BAFACG group).

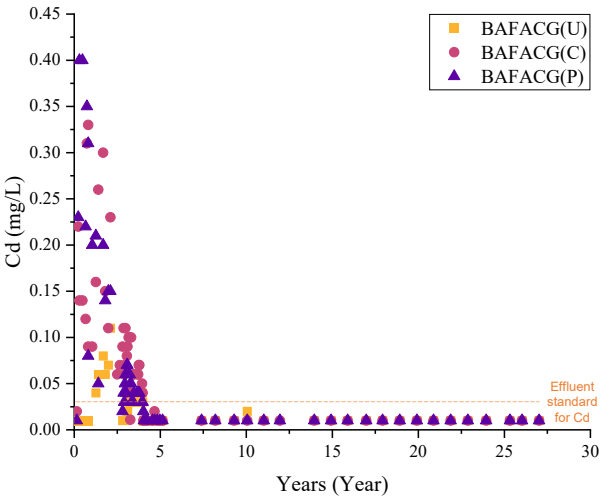


FIGURE 14: Leached Cd concentration (BAFACG group).

ther enhanced the immobilization of Cu. However, relying solely on compost on the stabilization of Cu does not seem as effective as combining the treatment methods in the beginning (Y0-Y3). From Y4-Y15, further reduction in Cu leached as the pH value of BAFACG group shifts towards the alkaline spectrum. As for the remaining 12 years, the leaching of Cu is independent of the pH of the effluent, and the compost has fully broken down by then. However, precipitation reactions with other elements present in the environment may occur, leading to the formation of insoluble compounds such as the copper hydroxides, carbonates, sulfides, or phosphates, which can limit its leaching. Furthermore, the weathering process over a long period of time results in formation of Al- and Fe-hydrates due to mineral alteration that can permanently bind elements such as Cu to provide definitive stability (Saffarzadeh Amirhomayoun et al., 2011).

The porosity and CO_2-rich environment (Figure 18b) contributed by the compost accelerated the carbonation process, which is effective in removing Cl and simultaneously leading to low concentrations of heavy metals in the effluent (Lei Wang et al., 2012). However, it is considered a short-term solution because the organic matter in the compost can eventually break down, releasing the heavy metals back into the environment. Therefore, combining compost with a long-term stabilization method such as chelate or acid treatment is recommended for effective and sustainable treatment of MSWI FA.

4. CONCLUSIONS

The current study was designed to understand the long-term behavior of heavy metals in MSWI FA and the factors influencing their immobilization over a period of 27 years. Comparing treatment methods, we observed that chelate treatment is more effective in the short run in immobilizing heavy metals, while phosphoric acid treatment yields superior long-term results. However, when combined with compost, both chelate and acid treatments exhibit enhanced

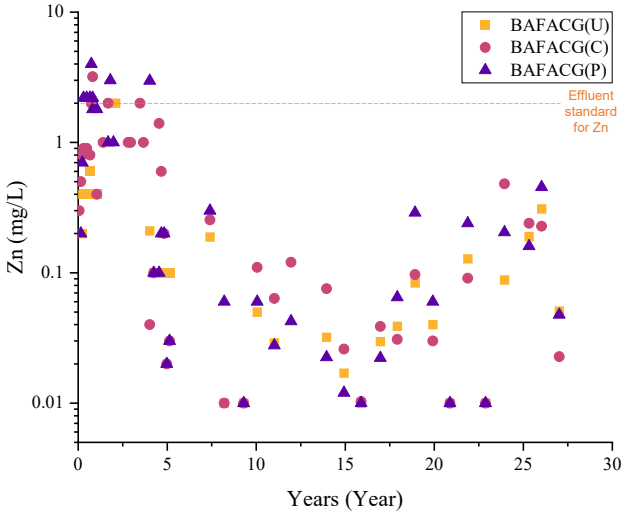


FIGURE 15: Leached Zn concentration (BAFACG group).

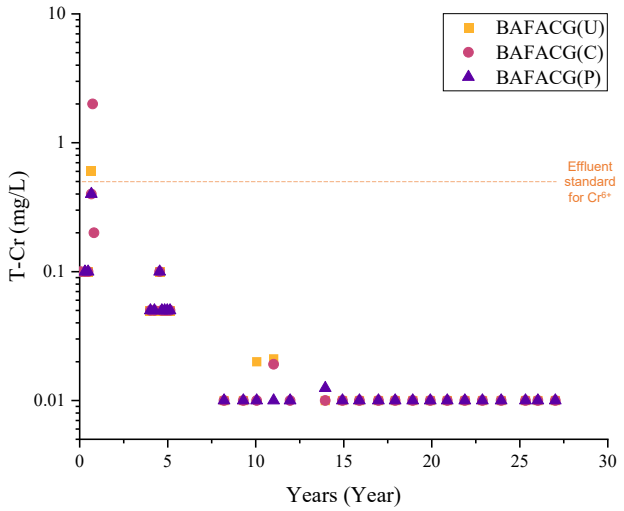


FIGURE 16: Leached T-Cr concentration (BAFACG group).

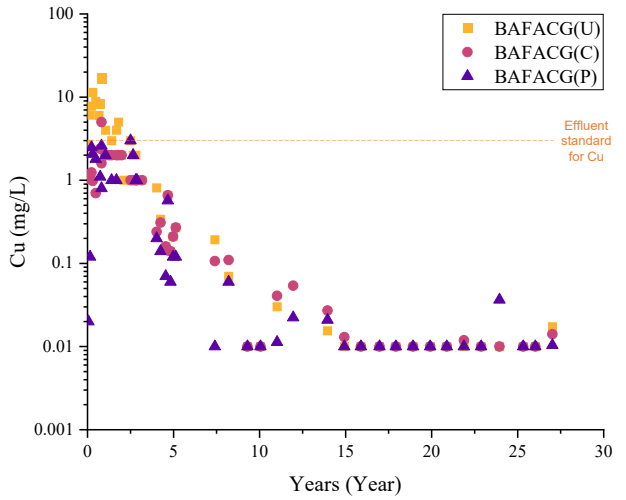


FIGURE 17: Leached Cu concentration (BAFACG group).

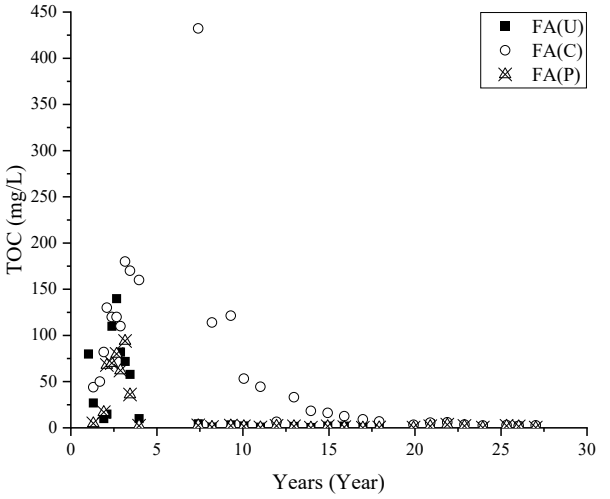


FIGURE 18: TOC concentration of (a) FA group, and (b) BAFACG group.

efficacy, suggesting a promising approach for immobilizing heavy metals. It is worth noting that compost treatment alone is not a feasible method for heavy metal immobilization. Furthermore, all heavy metals analyzed in this study comply with Japan's landfill disposal criteria and effluent standards of Japan, demonstrating the potential for the developed immobilization processes to meet regulatory requirements and reduce environmental impacts.

Several essential factors contributing to the immobilization of heavy metals were identified. These factors, namely carbonation, soluble Cl content, pH value, dissolution, weathering, and particle size have emerged as significant contributors in the immobilization process, in descending order of importance. An inverse relationship between pH and Zn was also observed, especially between the range 7.0 and 8.0, highlighting the role of pH variations in the leaching behavior of Zn. As pH levels fluctuate, it can alter the solubility and mobility of heavy metals, affecting their immobilization and subsequent leaching behavior.

In conclusion, our study provides valuable insights into the long-term behavior and immobilization of heavy metals in MSWI FA. Factors such as carbonation, Cl content, pH value, dissolution, weathering, and particle size have been identified as significant in the immobilization process. These findings contribute to our understanding of waste management strategies and offer a foundation for further research and the development of sustainable practices in handling heavy metal-containing waste materials. Further research is encouraged to deepen our understanding and develop innovative approaches for mitigating the environmental impact of heavy metals in waste materials.

ACKNOWLEDGEMENTS

I would like to express my sincere appreciation to Professor Takayuki Shimaoka, my supervisor, for his unwavering support and guidance. His financial support in the research has played a crucial role in enabling the successful execution of this project. Furthermore, I extend my gratitude to Associate Professor Dr. Amirhomayoun Saffarzadeh, my immediate supervisor, whose extensive expertise in mineralogy has been generously shared with patience.

REFERENCES

Athanasius P. Bayuseno, W. W. (2011). Characterization of MSWI fly ash through mineralogy and water extraction. Resources, Conservation and Recycling, 524-534. doi:10.1016/j.resconrec.2011.01.002

Bing Du et al. (2019). Comparison of long-term stability under natural ageing between cement solidified and chelator-stabilised MSWI fly ash. Environmental Pollution, 68-78. doi:10.1016/j.envpol.2019.03.124

BRIEF. (2022, Feb 11). Solid Waste Management. Tratto da The World Bank, Urban Development: https://www.worldbank.org/en/topic/urbandevelopment/brief/solid-waste-management

C. Righi et al. (2022). Benefits of pre-treating MSWI fly ash before alkali-activation. Sustainable Chemistry and Pharmacy, Article 100671. doi:10.1016/j.scp.2022.100671

Cao Yi-nan et al. (2021). Characteristics of MSWI fly ash with acid leaching treatment. Journal of Fuel Chemistry and Technology Volume 49, 1208-1218. doi:10.1016/S1872-5813(21)60119-6

Charles H. K. Lam et al. (2010). Use of Incineration MSW Ash: A Review. Sustainability, 1943-1968. doi:10.3390/su2071943

David Laner et al. (2012). A review of approaches for the long-term management of municipal solid waste landfills. Waste Management 32, 498-512. doi:10.1016/j.wasman.2011.11.010

Davide Bernasconi et al. (2022). Influence of speciation distribution and particle size on heavy metal leaching from MSWI fly ash. Waste Management, 318-327. doi:10.1016/j.wasman.2021.12.008

Evangelina Atanes et al. (2019). A mixed separation-immobilization method for soluble salts removal and stabilization of heavy metals in municipal solid waste incineration fly ash. Journal of Environmental Management, 359-367. doi:10.1016/j.jenvman.2019.03.122

Feng-He Wang et al. (2015). A comparative study on the heavy metal solidification/stabilization performance of four chemical solidifying agents in municipal solid waste incineration fly ash. Journal of Hazardous Materials, 451-458. doi:10.1016/j.jhazmat.2015.07.037

Giampiero P. Sorrentino et al. (2023). Accelerated and natural carbonation of a municipal solid waste incineration (MSWI) fly ash mixture: Basic strategies for higher carbon dioxide sequestration and reliable mass quantification. Environmental Research, Article 114805. doi:10.1016/j.envres.2022.114805

Guo Xian Ma, H. Y. (2013). Washing of the Ash from One Shanghai Plant Using Phosphoric Acid. Advanced Materials Research, 228-231. doi:10.4028/www.scientific.net/AMR.664.232

H. Mehdizadeh et al. (2021). CO2 treatment of hydrated cement powder: characterization and application consideration. Journal of Materials in Civil Engineering, Article 04021041. doi:10.1061/(ASCE)MT.1943-5533.0003652

Hiratsuka-Sasaki A., M. K. (2020). Inter-Municipal Cooperation on Solid Waste Management in Japan: Its Challenges and Implications for ASEAN Countries. Jakarta: Regional Waste Management – Intermunicipal Cooperation and Public and Private Partnership. ERIA Research Project Report FY2020 no. 12.

Hiroki Kitamura et al. (2016). Geochemically structural characteristics of municipal solid waste incineration fly ash particles and mineralogical surface conversions by chelate treatment. Environmental Science and Pollution Research, 734-743. doi:10.1007/s11356-015-5229-5

History and Current State of Waste Management in Japan. (2014, February). Tratto il giorno November 17, 2022 da https://www.env.go.jp/content/900453392.pdf

Hoornweg Daniel, B.-T. P. (2012). What a Waste : A Global Review of Solid Waste Management. Washington DC: World Bank Group. Tratto da http://hdl.handle.net/10986/17388

K. Miyawaki et al. (2000). The mechanism of lead (Pb) leaching from incinerator fly ash in monodisposal landfill. Waste Materials in Construction Wascon 2000, 588-594. doi:10.1016/S0713-2743(00)80069-0

Kaixing Zhao et al. (2020). Chlorine removal from MSWI fly ash by thermal treatment: Effects of iron/aluminum additives. Journal of Environmental Sciences, 112-121. doi:10.1016/j.jes.2019.08.006

Kosuke Kawai, T. T. (2016). Revisiting estimates of municipal solid waste generation per capita and their reliability. Journal of Material Cycle and Waste Management 18(1), 1-13. doi:10.1007/s10163-015-0355-1

Lei Wang et al. (2012). Accelerated Carbonation of Municipal Solid Waste Incineration Fly Ash Using CO2 as an Acidic Agent for Clinker Production. ENVIRONMENTAL ENGINEERING SCIENCE, 677-684. doi:10.1089/ees.2011.0272

Margarida J. Quina et al. (2010). Chemical stabilization of air pollution control residues from municipal solid waste incineration. Journal of Hazardous Materials, 382-392. doi:10.1016/j.jhazmat.2010.03.016

Md Manik Mian et al. (2017). Municipal solid waste management in China: a comparative analysis. Journal of Material Cycle and Waste Management 19(3), 1127-1135. doi:10.1007/s10163-016-0509-9

Ministry of the Environment, Government of Japan. (1995). Quality of the Environment in Japan 1995. Tratto il giorno November 17, 2022 da https://www.env.go.jp/en/wpaper/1995/eae240000000035.html#2_5_4_1

Ministry of the Environment, Government of Japan. (2015, 10 21). Water / Soil / Ground Environment. Tratto da Ministry of the Environment Government of Japan: https://www.env.go.jp/en/water/wq/nes.html

Ministry of the Environment, Government of Japan. (2022, March). Municipal Solid Waste Generation and Disposal in FY2020. Tratto da https://www.env.go.jp/en/headline/2595.html

Mojtaba Ajorloo et al. (2022). Heavy metals removal/stabilization from municipal solid waste incineration fly ash: a review and recent trends. Journal of Material Cycles and Waste Management, 1693–1717. doi:10.1007/s10163-022-01459-w

Pengfei Ren et al. (2022 'a'). Chapter 10 - Stabilization/solidification of municipal solid waste incineration fly ash. In L. W. Daniel C.W. Tsang, Low Carbon Stabilization and Solidification of Hazardous Waste (p. 141-156). Elsevier. doi:10.1016/B978-0-12-824004-5.00030-X

Pengfei Ren et al. (2022 'b'). CO2 pretreatment of municipal solid waste incineration fly ash and its feasible use as supplementary cementitious material. Journal of Hazardous Materials, Article 127457. doi:10.1016/j.jhazmat.2021.127457

Rahman Zeeshanur, S. V. (2019). The relative impact of toxic heavy metals (THMs) (arsenic (As), cadmium (Cd), chromium (Cr)(VI), mercury (Hg), and lead (Pb)) on the total environment: an overview. Springer Nature Switzerland AG 2019, 21. doi:10.1007/s10661-019-7528-7

Saffarzadeh Amirhomayoun et al. (2011). Impacts of natural weathering on the transformation/neoformation processes in landfilled MSWI bottom ash: A geoenvironmental perspective. Waste Management, 2440-2454. doi:10.1016/j.wasman.2011.07.017

Seifollah Nasrazadani, S. H. (2016). Modern analytical techniques in failure analysis of aerospace, chemical, and oil and gas industries. In Handbook of Material Failure Analysis with Case Studies from the Oil and Gas Industry (p. 39-54). Texas, USA: Butterworth Heinemann. doi:10.1016/B978-0-08-100117-2.00010-8

Shimaoka Takayuki, H. M. (1996). Behaviour of Stabilized Fly Ashes in Solid Waste Landfills. In Waste Management (p. 545-554). Great Britain: Elsevier Science Ltd. doi:10.1016/S0956-053X(96)00096-7

Wan Chen et al. (2017). Comparison of different MSWI fly ash treatment processes on the thermal behavior of As, Cr, Pb and Zn in the ash. Waste Management, 240-251. doi:10.1016/j.wasman.2017.07.011

Wei-Sheng Chen et al. (2012). Removal of chloride from MSWI fly ash. Journal of Hazardous Materials, 116-120. doi:10.1016/j.jhazmat.2012.08.010

William H. Schlesinger, E. S. (2020). The Lithosphere. In E. S. William H. Schlesinger, Biogeochemistry: An Analysis of Global Change (Fourth Edition) (p. 99-139). North California: Academic Press. doi:10.1016/B978-0-12-385874-0.00004-2

Xiang-Guo Li et al. (2012). Utilization of municipal solid waste incineration bottom ash in blended cement. Journal of Cleaner Production, 96-100. doi:10.1016/j.jclepro.2012.03.038

Xiongfei Chen et al. (2016). Chlorides Removal and Control through Water-washing Process on MSWI Fly Ash. Procedia Environmental Sciences, 560-566. doi:10.1016/j.proenv.2016.02.086

Yun Pan et al. (2013). Chemical characteristics and risk assessment of typical municipal solid waste incineration (MSWI) fly ash in China. Journal of Hazardous Materials 261, 269-276. doi:10.1016/j.jhazmat.2013.07.038

Yunmei Wei et al. (2011 'a'). Alteration of municipal solid waste incineration bottom ash focusing on the evolution of iron-rich constituents. Waste Management, 1992-2000. doi:10.1016/j.wasman.2011.04.021

Yunmei Wei et al. (2011 'b'). Mineralogical characterization of municipal solid waste incineration bottom ash with an emphasis on heavy metal-bearing phases. Journal of Hazardous Materials 187, 534-543. doi:10.1016/j.jhazmat.2011.01.070

Yunmei Wei et al. (2022 'c'). Removal of harmful components from MSWI fly ash as a pretreatment approach to enhance waste recycling. Waste Management, 110-121. doi:10.1016/j.wasman.2022.06.041

Yuying Zhang et al. (2021). Treatment of municipal solid waste incineration fly ash: State-of-the-art technologies and future perspectives. Journal of Hazardous Materials, 125-132. doi:10.1016/j.jhazmat.2021.125132

Zeyuan Liu et al. (2019). Comprehension of heavy metal stability in municipal solid waste incineration fly ash with its compositional variety: A quick prediction case of leaching potential. Waste Management, 329-339. doi:10.1016/j.wasman.2018.11.049

Zhikun Zhang et al. (2022). Stabilization of heavy metals in municipal solid waste incineration fly ash via hydrothermal treatment with coal fly ash. Waste Management, 285-293. doi:10.1016/j.wasman.2022.03.022

detritus | Multidisciplinary Journal for Circular Economy and Sustainable Management of Residues

CISA

HEAVY METAL ACCUMULATION ON MICROPLASTICS IN COMPOST - THE ROLE OF BIOFILM

Dilraj S. [1], Ebin Johnson [1], Anantha Singh T.S. [1,*], George K. Varghese [1] and Christian Zafiu [2]

[1] *Department of Civil Engineering, National Institute of Technology Calicut, Kozhikode, Kerala, India*
[2] *Department of Water, Atmosphere and Environment, University of Natural Resources and Life Sciences, Vienna*

Article Info:
Received:
7 September 2023
Revised:
21 February 2024
Accepted:
22 March 2024
Available online:
31 March 2024

Keywords:
Microplastics
Heavy metals
Compost
Bio-film

ABSTRACT

Microplastics, small plastic pieces (<5mm), are emerging contaminants in water, terrestrial, and air environments. This study investigated the possibility that microplastics act as carriers of heavy metals (Cu, Zn, Pb, Mn, Cd) in the municipal solid waste (MSW) compost samples, which were obtained from municipal composting yards at Kozhikode and Kochi, in Kerala, India. The heavy metal accumulation was expected in the biofilm that formed on microplastics during composting. Therefore, five samples were analysed: (i) compost after microplastic separation, (ii) untreated microplastics, (iii) microplastics washed with distilled water, (iv) chemically separated microplastics, and (v) new macro-plastics for comparison. Total Organic Carbon (TOC) and SEM analyses were used to assess the biofilm formation over microplastics. The study showed high microplastic abundance in the compost of both locations, with Kochi having nearly double the count as that of Kozhikode (1600 vs. 840/kg dry compost). Microplastics collected from Kochi exhibited higher biofilm formation, leading to greater heavy metal accumulation and higher concentrations compared to the compost. Heavy metal concentrations generally varied in the following order at both locations: handpicked microplastics > microplastics washed with distilled water > compost free from microplastics > chemically separated microplastic > new macro-plastic, with some exceptions. Heavy metal concentrations were significantly higher in samples from Kochi, due to a larger bio-film formation on the plastics as determined by TOC and SEM analyses. The findings of the study highlight the importance of source segregation and prevention of mixing of organic waste with plastic waste in MSW, to avoid heavy metal transport in terrestrial environment through microplastics.

1. INTRODUCTION

Plastic pollution serves as a prominent reminder of the unsustainable nature of the plastic-dominated era in human civilization. It is estimated that by the year 2030, as much as 53,000,000 metric tons of plastic will be released into the environment (Borrelle et al., 2020; Geyer et al., 2017). These plastics could degrade to microplastics due to physical, chemical and biological factors. Microplastics are generally defined by National Oceanic and Atmospheric Administration (NOAA) as small plastic particles that are having sizes of 5 mm to 1 nm (Masura et al., 2015). They can be formed from primary and secondary sources (Auta et al., 2017). Microplastics are found widely in terrestrial and aquatic environments (Rillig & Lehmann, 2020). In terrestrial environment, compost is considered as a major route for the entry of microplastics to the environment (Vithanage et al., 2021). The presence of microplastics in Municipal Solid Waste (MSW) compost and its role as a carrier of heavy metals were topics of many researches. These studies have reported Lead (Pb), Copper (Cu), Zinc (Zn), Manganese (Mn), and Cadmium (Cd) as the heavy metals of major concern in MSW compost with concentrations varying with the place of study (Bożym, 2017; Fan et al., 2021; Vithanage et al., 2021).

The adsorptions of heavy metals on microplastics can be related to the biofilms which are present on its surfaces (Wang et al., 2020). Biofilms are comprised of a combination of microorganisms, including algae, fungi, and bacteria, along with extracellular polymeric substances (EPS). These EPS play a crucial role in the structure and function of the biofilm (Carson et al., 2013; Shabbir et al., 2020). The biofilms present in microplastics are known to carry toxic metals to different environments and cause adverse impacts (Guan et al., 2020). In this research, microplastics, separated from the compost samples, were collected from the municipal composting yards of Kochi and Kozhikode,

* Corresponding author:
Anantha Singh T.S.
email: singh87@nitc.ac.in

Detritus / Volume 26 - 2024 / pages 27-35
https://doi.org/10.31025/2611-4135/2024.18362

Kerala (India), and analysed for the presence of heavy metals. The objective of the study was to examine how biofilms contribute to the accumulation of heavy metals on microplastics in the MSW compost. The concentration of heavy metals like Pb, Cu, Zn, Mn, and Cd was analysed in different samples: compost free of microplastics, microplastics handpicked from the compost, handpicked microplastics washed with distilled water, chemically separated microplastics, and new macro-plastic samples.

2. MATERIALS AND METHOD

The overall methodology followed in this work is shown in Figure 1.

Compost samples were collected from the composting yards following a standard procedure (Figure 1). Microplastics (1-5mm) were separated from the compost manually by handpicking after sieving. The separated microplastics were divided in three portions and prepared differently for analyses. Analyses were performed to quantify the heavy metals accumulation in the microplastics. Total Organic Carbon (TOC) analysis and Scanning Electron Microscopy (SEM) were employed to understand the biofilm accumulation on the microplastic samples. Finally, the heavy metal concentrations were correlated with the extent of biofilm formation to evaluate the role of biofilm in heavy metal accumulation by microplastics.

2.1 Sampling

The study was carried out on the compost samples collected from the Kozhikode Municipal Corporation's compost plant situated at Njeliyamparamb (11.203257° N, 75.816797° E) and Kochi Corporation's compost plant situated at Brahmapuram (9.99517° N, 76.37163° E). The compost plant owned by the corporations handles the biodegradable waste collected from city's markets and other public places. The map showing the sampling locations is given in Figure 2.

The sampling was made according to the Australian Standard AS4454-2012 for composts, mulches, and soil conditioners. The sample was collected using a shovel, a stainless steel mesh and polyethylene covers. The compost heap was thoroughly mixed with the shovel and 1 kg of compost samples were taken from the top, bottom and middle part of the heave. The samples were stored in the polyethylene covers (Vithanage et al., 2021). The samples

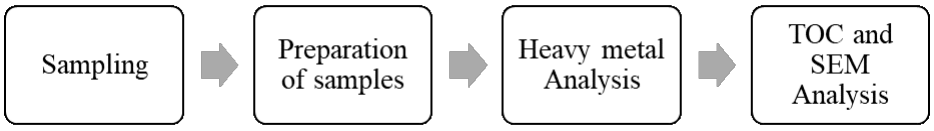


FIGURE 1: Methodology.

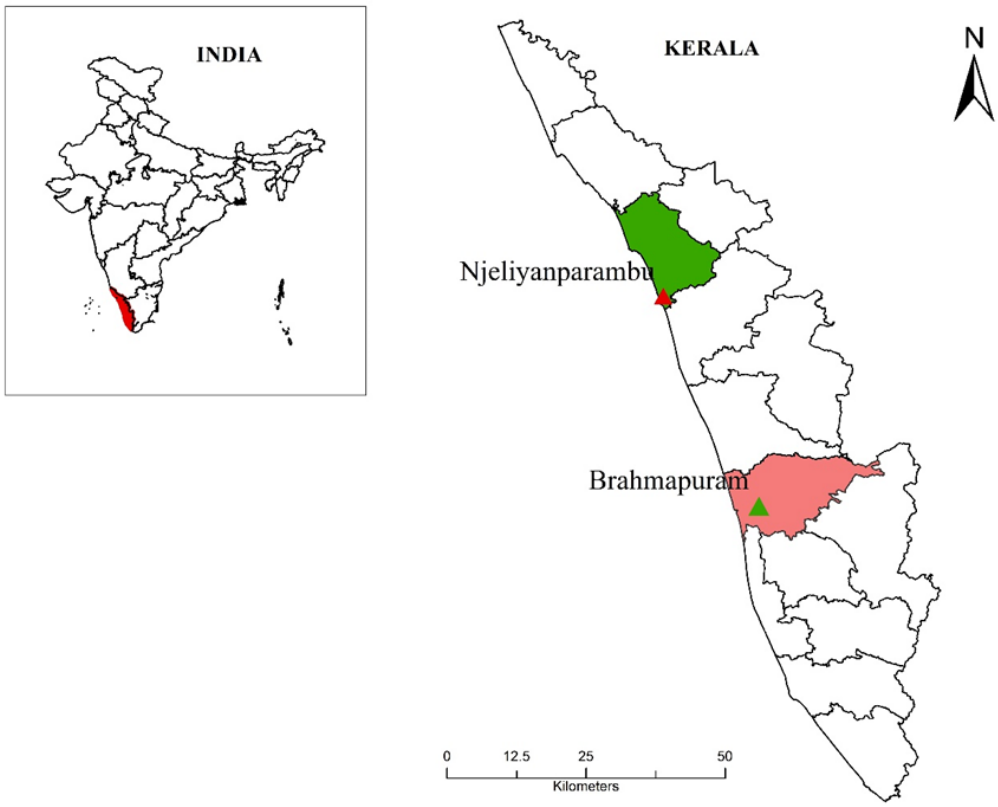


FIGURE 2: Sampling locations.

were brought to the lab and were air dried at 70°C and preserved for further analysis.

2.2 Preparation of Samples

Samples were prepared for the analyses from the composts collected from the two locations. For the analysis of the heavy metal content in biofilms, microplastics subsamples were chosen from the whole sample that matched the morphology (fibre, film or fragment) and polymer types (as determined by FTIR spectroscopy) in both locations. By this procedure it was possible to compare the differences in the heavy metal content in the biofilms on plastics between both locations.

The sample preparation was as follows. The air-dried samples were sieved through 5 mm sieve followed by 1 mm sieve. The portion of compost retained on 1mm sieve was used for the study. The compost, after removing the microplastics (1-5 mm) manually was preserved for analysis (Sample 1). The removed microplastics were quantified. The microplastics hand-picked from both locations with matching morphology and resin type were divided into three portions. The first portion of the handpicked microplastics was preserved for further analysis as hand-picked samples (Sample 2). The second portion of the hand-picked samples was washed with distilled water and was preserved for analysis (Sample 3). The remaining portion of the hand-picked microplastics was subjected to the chemical separation procedure. Chemical separation procedure included the oxidation of the organic matter using Fenton's reagent as the first step. For every 0.1 g of solid Matrix (dry mass), 0.1 ml of a 0.002 mol $FeSO_4$ (Fe (II)) and 1 ml of a 30% H_2O_2 solution were added to provide the necessary iron ions and hydrogen peroxide (Tagg et al., 2016). The samples were digested, filtered, and washed with distilled water. These samples were dried and preserved for analysis as chemically separated microplastics (Sample 4). Also, macro-plastics that were potentially matching the microplastics found in the compost were collected (in both locations) and categorized by morphology and polymer matching criterion, which included morphology (fibre, film, or fragment), colour and polymer type. The best fitting macroplastics according to the morphology, colour and polymer matching criterion were then cut into manageable pieces and were preserved for analysis (Sample 5).

2.3 Heavy Metal Analysis

Heavy metal analysis was conducted to determine the concentrations of Lead, Copper, Zinc, Cadmium and Manganese in the five samples. The samples were digested using Aqua Regia (HCl: HNO_3 = 3:1) at a rate of 15 mL/g of the sample (Bożym, 2017). The standard solutions of heavy metals were prepared by diluting the stock solutions and analysed in flame AAS (PerkinElmer piNacle900F). The limit of detection for the analysed metals were, Cu-10 µg/L, Zn- 20 µg/L, Pb- 10 µg/L, Mn- 20 µg/L and Cd- 10 µg/L. The digested sample solutions were filtered using Whatman filter paper (42) and were diluted again. Both samples and standards were stored in the refrigerator for 24 hours. All chemicals used in the analyses were research-grade.

2.4 TOC and SEM analysis

The biofilm present on the microplastic surface was characterized quantitatively based on the Total Organic Carbon (TOC) (%) and qualitatively using SEM imaging. These analyses were made for the three microplastic samples, that is., hand-picked, distilled water washed and chemically separated ones.

The hand-picked samples and the samples washed with distilled water were subjected to Fenton's reagent and Potassium Hydroxide (KOH) treatment. Subsequently, they were heated at 50°C to extract the biofilms. The samples that were previously separated using Fenton's reagent underwent further heating at 50°C in the presence of HNO_3 and KOH (Prata et al., 2019). The resulting mixture was then filtered using Whatman (42) filter paper and subsequently diluted for TOC analysis. The TOC analysis was carried out using the Shimadzu TOC-L analyzer, following the methodology outlined in method 5310 C (APHA 23rd Edition, 2017 ; P. Li et al., 2022; Zheng et al., 2023).

To corroborate the findings related to the concentration of heavy metals in the microplastic samples and the TOC results, SEM analysis was also performed on the microplastic samples. This analysis encompassed the examination of the hand-picked samples, chemically separated microplastics, and microplastic samples that were washed with distilled water. By employing SEM, the surfaces of these plastic samples were thoroughly investigated, allowing for a comprehensive evaluation of the removal of the biofilms from the samples. Therefore, the SEM analyses served as an additional information to complement the results that were obtained from the heavy metals analyses, providing valuable visual evidence and insights into the microplastic samples under scrutiny.

3. RESULTS AND DISCUSSIONS

The quantification done by manual counting revealed that the number of microplastics (1mm-5mm) per kg of dry weight of compost is 840 items in Kozhikode and 1600 items in Kochi. These values were much higher than what was reported from Germany for microplastics of same size range, which was 39 to 102 items per kilogram of dry weight on a study conducted by Schwinghammer et al. (2020) and between 40 and 60 to 100 and 120 items per kilogram of dry weight on a study conducted by Weithman et al. (2018). This may be due to the higher waste recycling rate of 46% in Germany (Conversio, 2018) that prevents the entry of plastic wastes to MSW, as against the 30% recycling rate in India. Another study conducted on Austrian compost samples shows a count of between 0 - 49 particles per kg of dry waste (size range 2-6.3 mm) (C. Zafiu et al.,2023). The higher recycling rates in Europe reflect also a higher degree of separate collection of plastics and therefore a lower fraction of plastics in MSW. In addition, the composting of MSW is not practiced in many European Countries anymore. Therefore, the lower recycling results in higher presence of plastic in MSW compost in India (Loizia et al., 2021; Pal & Bhatia, 2022; Shah et al., 2023). However, a study from another European country, Netherland, has reported the pres-

ence of PLA microplastic fibers in green waste compost as high as 82,800 items/kg. However, PLA is a different case, as it is a biodegradable polymer, which is (in certain cases) allowed to be disposed of with biowaste. However, when present in compost they are not effectively recycled (Gross & Kalra, 2002; Huerta-Lwanga et al., 2021; Karamanlioglu et al., 2017). In this study, the microplastics encountered were mainly non-biodegradable single use plastics.

3.1 Heavy metal concentrations

The heavy metal concentration of dry compost was analysed, and the results are given in Table 1.

The results in Table 1 show that the concentrations of heavy metals in and on microplastics in both locations followed an order: Hand-picked microplastics > Microplastics washed with distilled water > Microplastics separated using chemicals > matching macro plastic samples. The concentration of heavy metals in compost exceeded that of the chemically separated microplastic samples for all investigated heavy metals in the case of Kozhikode. However, in the samples from Kochi, for Manganese, Zinc, and Copper, chemically separated microplastics had higher concentrations than the compost. In all cases, the concentrations of heavy metals in macro-plastic samples analysed as control was much lower than microplastic samples, indicating accumulation of heavy metals from compost to microplastic. The highest concentration noticed for any heavy metal in the compost and microplastic samples was for Zinc in the samples of Kochi. Zn in MSW generally comes from paper, cardboards wood, plastics, concrete wastes, leather, paints, leaching of batteries, and tire rubber particles (Jones et al., 2014; Rotter et al., 2004). There were instances of much higher occurrence of Zn in composts than our study in other cities of India, for example 10616 mg/kg in the compost of Mumbai and 6693 mg/kg in Delhi (Khare et al., 2023). Zn is a micronutrient for plants and as such, its presence in compost is desirable. At the same time, its excess, like its deficiency in soil, can cause stunted plant growth and decreased photosynthetic activity, inducing chlorosis and necrosis of the leaf (Andresen et al., 2018; Dobrikova et al., 2021). Due to the impacts, US EPA has set 7500 mg/kg as the ceiling concentration of Zn in biosolids, including composts, intended for land application. The concentration limit for exceptional quality biosolids, that can be applied without any restrictions, is 2800 mg/kg (USEPA, 1994). The compost from Kochi had Zn concentrations close to this limit.

After Zn, the next abundant heavy-metals in the compost were Cd and Cu. Kitchen waste, plastics, cinder and lamps are the main sources of copper in MSW (Aendo et al., 2022; Long et al., 2011). Plastics, pigments, soil and food containers may be the possible sources of Cd in MSW (Aendo et al., 2022; Tang et al., 2019; Valadez-Vega et al., 2011). Cd is not essential to plant growth. In the contrary, even low concentrations of Cd in soil can adversely affect plant growth and metabolism (Qadir et al., 2014). US EPA has set 85 mg/kg as the ceiling concentration of Cd in biosolids for land application (USEPA, 1994). Thus, the composts of both Kochi and Kozhikode, with Cd concentrations of more than ten times the threshold concentration, are unsuitable for land application. The current practice of sale of compost in bags at these places should, therefore be discontinued, or measures for reducing the source of Cd should be taken.

Pb and Mn were the two heavy metals that had higher concentration in the compost of Kozhikode than in Kochi. Glass wastes, textiles, and plastics are the sources of Pb in MSW. Manganese sources are predominantly attributed to the improper disposal of bottle caps, blades, and pharmaceuticals, pigments, insecticides and cosmetics (Kanmani & Gandhimathi, 2013; Tang et al., 2019). Irrespective of the higher concentrations of some heavy metals in the compost of Kozhikode, the concentrations of heavy metals in the handpicked microplastics in all cases were higher for the samples from Kochi. The higher organic matter found attached to the microplastics handpicked from the compost of Kochi explains this observation.

In order to compare the adsorption of heavy metals on microplastics with concentration in composts, the ratios of heavy metal concentrations of both sample types were calculated and are shown in Table 2. The ratio of heavy metal concentration in microplastic to that in matching unpolluted macro-plastics was calculated to understand the addi-

TABLE 1: Heavy metal concentrations in Kozhikode (in mg/kg of dry compost).

Sample	Heavy metal concentration (mg/kg of dry weight)									
	Lead (Pb)		Manganese (Mn)		Copper (Cu)		Zinc (Zn)		Cadmium (Cd)	
	Kochi	Kozhikode	Kochi	Kozhikode	Kochi	Kozhikode	Kochi	Kozhikode	Kochi	Kozhikode
Microplastics separated using chemicals	417	315	878	469	873	442	2987	1796	709	445
Microplastics washed with distilled water	878	765	1078	596	914	504	5147	3017	793	697
Handpicked microplastics	912	809	1312	741	1036	798	6980	3960	927	866
Compost free of microplastics	401	594	400	582	856	541	2715	1955	863	851
Matching macro-plastic samples	117		259		209		374		91	

TABLE 2: Ratio of heavy metal concentrations in microplastic samples, compost and matching macro-plastics.

Ratio	Lead		Manganese		Copper		Zinc		Cadmium	
	Kozhikode	Kochi	Kozhikode	Kochi	Kozhikode	Kochi	Kozhikode	Kochi	Kozhikode	Kochi
Handpicked microplastics/compost	1.37	2.27	1.28	3.28	1.47	1.21	2.02	2.57	1.02	1.07
Distilled water washed microplastics/ compost	1.29	2.18	1.02	2.70	0.93	1.07	1.54	1.90	0.82	0.92
Chemically separated microplastics/ Compost	0.53	1.04	0.80	2.12	0.82	1.02	0.92	1.10	0.52	0.82
Handpicked microplastics/ macro-plastic	6.91	7.80	2.86	5.06	3.81	4.95	10.58	18.66	9.51	10.18
Distilled water washed microplastics/ macro-plastic	6.53	7.50	2.30	4.16	2.41	4.50	8.06	13.76	7.65	8.71
Chemically separated microplastics/macro-plastic	2.70	3.56	1.81	3.39	2.11	4.17	4.82	7.99	4.89	7.80

tion of heavy metals to microplastic from compost. These ratios are also shown in Table 2.

The ratios in Table 2 reveal an accumulation of all heavy metals in the handpicked microplastics from Kochi and Kozhikode, indicated by a concentration ratio (concentration in microplastic/concentration in compost) higher than 1.0. Samples from Kochi exhibited a greater adsorption for all metals than the samples from Kozhikode, except for Copper. The highest proportional adsorption on microplastic was found for Mn, with a concentration ratio (microplastic to compost) of 3.28 in the handpicked samples from Kochi. The second highest was found for Zn with a ratio 2.57, closely followed by Pb. Pani et al. (2017) found that Zn and Mn are two heavy metals that are highly adsorbed by biofilms on microplastics. Pani et al., reported that even chemical washing could not remove these metals entirely from microplastics. Cu was also reported to be a heavy metal that has strong affinity towards biofilms (Wang et al., 2021). Cd, on the other hand, was shown to exhibit a lesser affinity towards adsorption by biofilms when compared to Copper, Lead and Zinc (Dong et al., 2003), which was also found in this study. Cd had the lowest concentration ratio (microplastic to compost) of 1.07 for the bio-film-rich handpicked samples compared to other heavy metals.

The ratio of heavy metals in microplastic samples to that in matching unpolluted macro-plastic samples analysed as control, showed that there was strong adsorption of heavy metals to microplastics from compost. There was more than 1800% increase in Zn concentration in the handpicked microplastic collected from Kochi and 1058% in Kozhikode compared to unpolluted plastic. The next highest increase (1018%) in concentration was noticed for Cd in the samples from Kochi in spite of the metal's lower affinity to adsorb to biofilms. The lower concentration of Cd in unpolluted plastics resulted in such a high increase. The ratio (chemically separate microplastic/macro-plastic) for all metals being larger than 1.0 indicates that, even after digestion with Fenton's reagent for the removal of the biofilm, heavy metals were still adsorbed to microplastics. The TOC analysis (described in a subsequent section) showed that there was a remaining biofilm, even after digestion with Fenton's reagent. This indicated that the heavy metals remaining on the plastics after the chemical treatment could originate from the biofilm residues, or that adsorbed directly to the microplastics, or a combination of both.

3.2 TOC results

The TOC of the collected microplastic samples were determined and the results are given in Table 3.

Table 3 shows the results from the TOC analyses that indicate that samples from Kochi exhibited much larger attached biofilms than samples from Kozhikode. There could be multiple reasons for this observation. The waste generation in Kochi is higher than in Kozhikode and consequently there is a higher chance of organic matter to adhere to plastics within the wastes of Kochi. Further, the MSW dumped in the Kochi corporation's yards are processed with larger delay than in Kozhikode due to the smaller capacity of the plant, which allows the formation of larger biofilms. The richer biofilm can explain the higher heavy metal concentrations observed in the microplastic samples from Kochi. Many studies have shown that biofilms formed over microplastics represent adsorption sites for various contaminants including heavy metals (J. Wang et al., 2021; Q. Wang et al., 2023), organic pollutants (Huang et al., 2021) and microorganisms (Hernández-Sánchez et al., 2023).

TABLE 3: TOC results.

Samples	Hand- Picked Samples		Distilled Water Washed Samples		Chemically Separated Samples	
	Kozhikode	Kochi	Kozhikode	Kochi	Kozhikode	Kochi
%TOC	1.97	2.82	0.83	1.54	0.07	0.37

The decrease in TOC percentage across the three samples implies the removal of biofilms adhered to the microplastics by distilled water and chemical treatments. This reduction in biofilm indicates a decrease in adsorption sites and functional groups on the microplastics. The reduction in heavy metal concentrations and the reduction in TOC suggests that the biofilms on the microplastics play a significant role in the adsorption of heavy metals, and their removal leads to a reduction in heavy metal concentrations (Guan et al., 2020). This highlights the importance of separating plastic wastes at source itself, before these get mixed with organic waste. In addition, the microplastic impurities act only as a scavenger for the heavy metal pollution in the MSW, which should be reduced in any way. Good waste management practices can prevent the entry of microplastics and heavy metals to the compost. The quantification results of microplastic in German composts implies that a better segregation and recycling of municipal solid waste is an efficient way of tackling the entry of microplastics to compost (Schwinghammer et al., 2020; Shah et al., 2023). By implementing better waste management strategies, the microplastics presence can be prevented, which in turn controls the transfer of heavy metals through the biofilms attached in them, to different environments.

In order to quantitatively understand the influence of biofilm on the adsorption of heavy metals, graphs were plotted between TOC (%) and heavy metal concentrations (mg/kg) in microplastics. Graphs were plotted separately for Kochi and Kozhikode, as the concentrations of the heavy metals in the compost matrix were different for the two places.

The variation in heavy metal concentrations for the hand-picked samples, distilled water washed samples and chemically separated samples at different TOC (%) are given in Figure 3 (Kochi) and Figure 4 (Kozhikode).

The graphs show that the heavy metal adsorption on the samples is directly proportional to the amount of biofilms adhered to the microplastic surface. The linear relationships between the heavy metal concentrations and TOC are generally strong, except for lead (R^2 = 0.7196 for Kozhikode and 0.7802 for Kochi) which is relatively weak. Zn showed the highest incremental affinity to biofilms, as

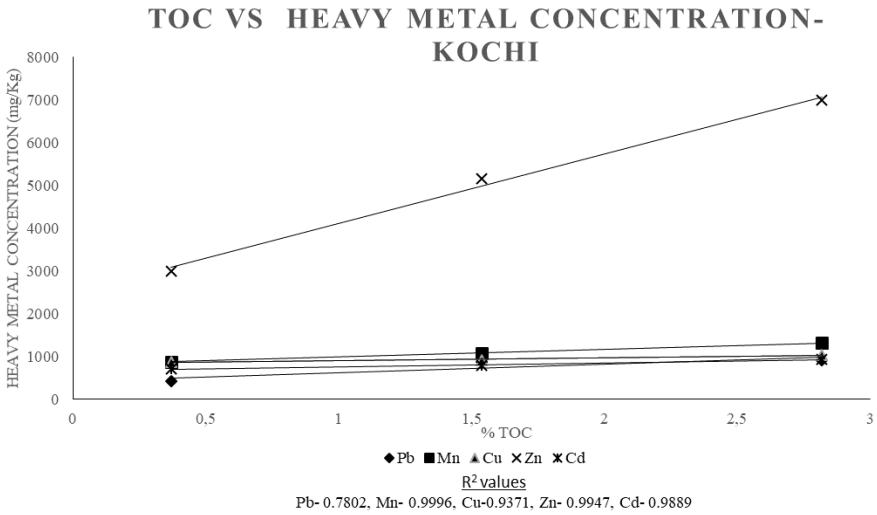


FIGURE 3: Variation of TOC with heavy metal concentration of Kochi samples.

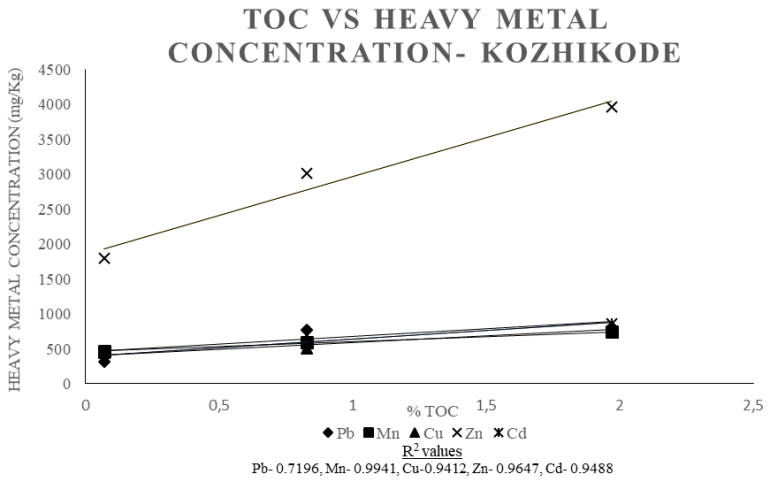


FIGURE 4: Variation of TOC with heavy metal concentration of Kozhikode samples.

indicated by a steeper graph. The intercepts of the graphs are given in Table 4.

The Y-intercept represent the theoretical concentration of heavy metals that adheres to the microplastics from the compost without biofilms (TOC=0%). The comparison of the heavy metal concentrations and the new unpolluted macro-plastics to the Y intercept values indicates that the adsorption of heavy metals onto the microplastics occurred via alternative mechanisms, rather than being solely adsorbed to biofilms. In the samples from Kochi, more than 80% of Cd and Cu remained directly adsorbed on the microplastic surface. The heavy metal adsorption on microplastics can depend on the polymer type, crystallinity, surface area, and also on the pH and temperature of the environment (Gao et al., 2021).

3.3 SEM results

The removal of biofilms adhered to the microplastic surfaces were visualized by the SEM images. The images obtained from the SEM analyses are shown as Figure 5.

The SEM analyses performed on the three microplastic samples revealed a noticeable decrease in the presence of biofilms adhered to the microplastic surfaces, progressing from Figure 5a to Figure 5c. The initial handpicked samples (Figure 5a) showed to have a thick layer of organic matter or biofilms. However, through subsequent treatments including thorough washing with distilled water (Figure 5b) and Fenton's reagent digestion (Figure 5c), the organic impurities were significantly reduced, as also shown by other authors (Pfohl et al., 2021). As a result, the surfaces of the microplastic samples appeared cleaner and less contaminated. The reduction in biofilm adherence can be correlated with a decrease in adsorption sites and functional groups present on the microplastics. These adsorption sites and functional groups have the potential to bind heavy metals to the microplastics. Therefore, the diminishing presence of organic matter suggests a corresponding reduction in the availability of sites that can facilitate the adsorption of heavy metals onto the microplastic surfaces. This observation reinforces the understanding that bio-films play a crucial role in the adsorption and retention of heavy metals by microplastics (Y. Li et al., 2022; Zheng et al., 2023).

TABLE 4: Y intercepts from the graphs.

Heavy Metal	Y intercept (mg/kg)	
	Kochi	Kozhikode
Lead	240.6	135.6
Manganese	655.3	330.0
Copper	778.0	225.3
Zinc	1045.0	760.3
Cadmium	591.6	248.3

4. CONCLUSIONS

The study showed that there is significant concentration of microplastics in the compost generated in MSW compost plants of Kochi and Kozhikode. It was also found that the concentration in the compost of some heavy metals exceeded the limits set by the US EPA for land application. Further, it was found that microplastic can act as vectors of heavy metals from compost to other environments. The biofilm formed on the microplastic surface was found to be the most influential factor for the heavy metal accumulation, although, the microplastic surface also adsorbs lower quantities of heavy metals directly. This finding highlights the importance of source segregated collection of MSW, where organic matter is not allowed to mix with plastic waste. Analyses showed that the heavy metal concentration adsorbed on microplastics is directly proportional to the amount of biofilm present over the microplastic, for a given concentration of heavy metal in the environmental matrix. The normal methods adopted for separation of microplastics from an environmental matrix influence the heavy metal analysis results. Analysis after chemical separation results in the underestimation of heavy metals concentrations in microplastics and consequent impacts.

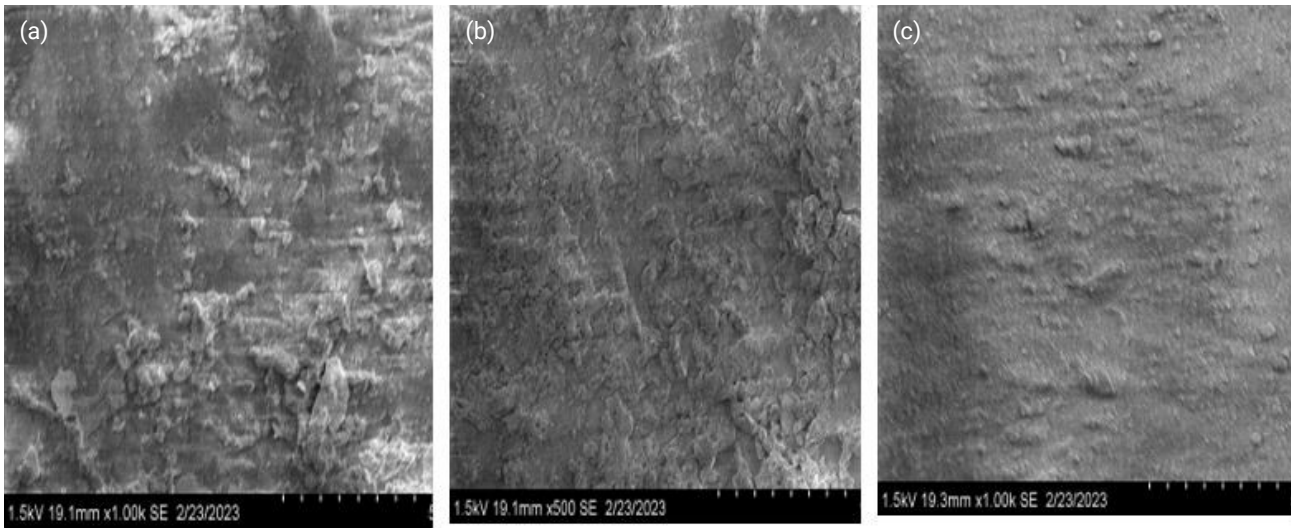


FIGURE 5: SEM images of Hand-picked samples, Distilled water washed samples and chemically separated microplastics.

Nevertheless, plastics act only as vectors (that may transport the pollution to other, more fragile environments) for the heavy metals that are anyways present in the waste. Therefore, a reduction of the heavy metal inflow is also an important measure that has to be taken into account.

REFERENCES

Aendo, P., Netvichian, R., Thiendedsakul, P., Khaodhiar, S., & Tulayakul, P. (2022). Carcinogenic Risk of Pb, Cd, Ni, and Cr and Critical Ecological Risk of Cd and Cu in Soil and Groundwater around the Municipal Solid Waste Open Dump in Central Thailand. Journal of Environmental and Public Health, 2022. https://doi.org/10.1155/2022/3062215

Andresen, E., Peiter, E., & Küpper, H. (2018). Trace metal metabolism in plants. Journal of Experimental Botany, 69(5), 909–954.

Auta, H. S., Emenike, C. U., & Fauziah, S. H. (2017). Distribution and importance of microplastics in the marine environment: A review of the sources, fate, effects, and potential solutions. Environment International, 102, 165–176. https://doi.org/10.1016/j.envint.2017.02.013

Borrelle, S. B., Ringma, J., Law, K. L., Monnahan, C. C., Lebreton, L., McGivern, A., Murphy, E., Jambeck, J., Leonard, G. H., Hilleary, M. A., Eriksen, M., Possingham, H. P., De Frond, H., Gerber, L. R., Polidoro, B., Tahir, A., Bernard, M., Mallos, N., Barnes, M., & Rochman, C. M. (2020). Predicted growth in plastic waste exceeds efforts to mitigate plastic pollution. Science (New York, N.Y.), 369(6510), 1515–1518. https://doi.org/10.1126/science.aba3656

Bożym, M. (2017). Heavy metal content in compost and earthworms from home composters. Ochrona Srodowiska i Zasobów Naturalnych, 28, 1–4. https://doi.org/10.1515/oszn-2017-0022

Conversio Market & Strategy GmbH (2018). Bericht Stoffstrombild Kunststoffe in Deutschland 2017 [Report material flow picture plastics in Germany 2017]. https://www.bkv-gmbh.de/infothek/studien.html

Cutroneo, L., Reboa, A., Geneselli, I., & Capello, M. (2021). Considerations on salts used for density separation in the extraction of microplastics from sediments. Marine Pollution Bulletin, 166, 112216. https://doi.org/10.1016/j.marpolbul.2021.112216

Dobrikova, A., Apostolova, E., Hanć, A., Yotsova, E., Borisova, P., Sperdouli, I., Adamakis, I.-D. S., & Moustakas, M. (2021). Tolerance Mechanisms of the Aromatic and Medicinal Plant Salvia sclarea L. to Excess Zinc. Plants, 10(2), Article 2. https://doi.org/10.3390/plants10020194

Dong, D., Li, Y., Zhang, J., & Hua, X. (2003). Comparison of the adsorption of lead, cadmium, copper, zinc and barium to freshwater surface coatings. Chemosphere, 51(5), 369–373. https://doi.org/10.1016/S0045-6535(02)00835-4

Gao, X., Hassan, I., Peng, Y., Huo, S., & Ling, L. (2021). Behaviors and influencing factors of the heavy metals adsorption onto microplastics: A review. Journal of Cleaner Production, 319, 128777. https://doi.org/10.1016/j.jclepro.2021.128777

Geyer, R., Jambeck, J. R., & Law, K. L. (2017). Production, use, and fate of all plastics ever made. Science Advances, 3(7), e1700782. https://doi.org/10.1126/sciadv.1700782

Gross, R. A., & Kalra, B. (2002). Biodegradable polymers for the environment. Science (New York, N.Y.), 297(5582), 803–807. https://doi.org/10.1126/science.297.5582.803

Guan, J., Qi, K., Wang, J., Wang, W., Wang, Z., Lu, N., & Qu, J. (2020). Microplastics as an emerging anthropogenic vector of trace metals in freshwater: Significance of biofilms and comparison with natural substrates. Water Research, 184, 116205. https://doi.org/10.1016/j.watres.2020.116205

Hernández-Sánchez, C., Pestana-Ríos, Á. A., Villanova-Solano, C., Domínguez-Hernández, C., Díaz-Peña, F. J., Rodríguez-Álvarez, C., Lecuona, M., & Arias, Á. (2023). Bacterial Colonization of Microplastics at the Beaches of an Oceanic Island, Tenerife, Canary Islands. International Journal of Environmental Research and Public Health, 20(5), 3951.

Huang, W., Song, B., Liang, J., Niu, Q., Zeng, G., Shen, M., Deng, J., Luo, Y., Wen, X., & Zhang, Y. (2021). Microplastics and associated contaminants in the aquatic environment: A review on their ecotoxicological effects, trophic transfer, and potential impacts to human health. Journal of Hazardous Materials, 405, 124187. https://doi.org/10.1016/j.jhazmat.2020.124187

Huerta-Lwanga, E., Mendoza-Vega, J., Ribeiro, O., Gertsen, H., Peters, P., & Geissen, V. (2021). Is the polylactic acid fiber in green compost a risk for Lumbricus terrestris and Triticum aestivum? Polymers, 13(5), 703.

Jones, F., Bankiewicz, D., & Hupa, M. (2014). Occurrence and sources of zinc in fuels. Fuel, 117, 763–775. https://doi.org/10.1016/j.fuel.2013.10.005

Kanmani, S., & Gandhimathi, R. (2013). Assessment of heavy metal contamination in soil due to leachate migration from an open dumping site. Applied Water Science, 3, 193–205.

Karamanlioglu, M., Preziosi, R., & Robson, G. D. (2017). Abiotic and biotic environmental degradation of the bioplastic polymer poly(lactic acid): A review. Polymer Degradation and Stability, 137, 122–130. https://doi.org/10.1016/j.polymdegradstab.2017.01.009

Khare, S., Singhal, A., Rai, S., & Rallapalli, S. (2023). Heavy metal remediation using chelator-enhanced washing of municipal solid waste compost based on spectroscopic characterization. Environmental Science and Pollution Research, 30(24), 65779–65800. https://doi.org/10.1007/s11356-023-26970-x

Li, P., Lai, Y., Li, Q., Dong, L., Tan, Z., Yu, S., Chen, Y., Sharma, V. K., Liu, J., & Jiang, G. (2022). Total Organic Carbon as a Quantitative Index of Micro- and Nano-Plastic Pollution. Analytical Chemistry, 94(2), 740–747. https://doi.org/10.1021/acs.analchem.1c03114

Li, Y., Zhang, Y., Su, F., Wang, Y., Peng, L., & Liu, D. (2022). Adsorption behaviour of microplastics on the heavy metal Cr(VI) before and after ageing. Chemosphere, 302, 134865. https://doi.org/10.1016/j.chemosphere.2022.134865

Loizia, P., Voukkali, I., Zorpas, A. A., Navarro Pedreño, J., Chatziparaskeva, G., Inglezakis, V. J., Vardopoulos, I., & Doula, M. (2021). Measuring the level of environmental performance in insular areas, through key performed indicators, in the framework of waste strategy development. Science of The Total Environment, 753, 141974. https://doi.org/10.1016/j.scitotenv.2020.141974

Long, Y., Shen, D.-S., Wang, H.-T., Lu, W., & Zhao, Y. (2011). Heavy Metal Source Analysis in Municipal Solid Waste (MSW): Case Study on Cu and Zn. Journal of Hazardous Materials, 186, 1082–1087. https://doi.org/10.1016/j.jhazmat.2010.11.106

Masura, J., Baker, J., Foster, G., & Arthur, C. (2015). Laboratory Methods for the Analysis of Microplastics in the Marine Environment: Recommendations for quantifying synthetic particles in waters and sediments. [Report]. NOAA Marine Debris Division. https://doi.org/10.25607/OBP-604

OECD. (2022). Global Plastic Outlook- Economy Drivers, Environmental Impacts and Policy Options- (accessed July 26, 2023)- OECD Library. https://www.oecd- ilibrary.org/environment/data/global-plastic-outlook_c0821f81-en

Pal, M. S., & Bhatia, M. (2022). Current status, topographical constraints, and implementation strategy of municipal solid waste in India: A review. Arabian Journal of Geosciences, 15(12), 1176. https://doi.org/10.1007/s12517-022-10414-w

Pani, T., Das, A., & Osborne, J. W. (2017). Bioremoval of zinc and manganese by bacterial biofilm: A bioreactor-based approach. Journal of Photochemistry and Photobiology B: Biology, 175, 211–218.

Pfohl, P., Roth, C., Meyer, L., Heinemeyer, U., Gruendling, T., Lang, C., Nestle, N., Hofmann, T., Wohlleben, W., & Jessl, S. (2021). Microplastic extraction protocols can impact the polymer structure. Microplastics and Nanoplastics, 1(1), 8. https://doi.org/10.1186/s43591-021-00009-9

Prata, J. C., da Costa, J. P., Girão, A. V., Lopes, I., Duarte, A. C., & Rocha-Santos, T. (2019). Identifying a quick and efficient method of removing organic matter without damaging microplastic samples. Science of The Total Environment, 686, 131–139. https://doi.org/10.1016/j.scitotenv.2019.05.456

Qadir, S., Jamshieed, S., Rasool, S., Ashraf, M., Akram, N. A., & Ahmad, P. (2014). Modulation of Plant Growth and Metabolism in Cadmium-Enriched Environments. In D. M. Whitacre (Ed.), Reviews of Environmental Contamination and Toxicology (pp. 51–88). Springer International Publishing. https://doi.org/10.1007/978-3-319-03777-6_4

Rillig, M. C., & Lehmann, A. (2020). Microplastic in terrestrial ecosystems. Science, 368(6498), 1430–1431.

Rotter, V. S., Kost, T., Winkler, J., & Bilitewski, B. (2004). Material flow analysis of RDF-production processes. Waste Management, 24(10), 1005–1021. https://doi.org/10.1016/j.wasman.2004.07.015

Schwinghammer, L., Krause, S., & Schaum, C. (2020). Determination of large microplastics: Wet-sieving of dewatered digested sludge, co-substrates, and compost. Water Science and Technology, 84(2), 384–392. https://doi.org/10.2166/wst.2020.582

Shah, H. H., Amin, M., & Pepe, F. (2023). Maximizing resource efficiency: Opportunities for energy recovery from municipal solid waste in Europe. Journal of Material Cycles and Waste Management. https://doi.org/10.1007/s10163-023-01733-5

Tagg, A. S., Harrison, J. P., Ju-Nam, Y., Sapp, M., Bradley, E. L., Sinclair, C. J., & Ojeda, J. J. (2016). Fenton's reagent for the rapid and efficient isolation of microplastics from wastewater. Chemical Communications, 53(2), 372–375. https://doi.org/10.1039/C6CC08798A

Tang, Z., Liu, M., Yi, L., Guo, H., Ouyang, T., Yin, H., & Li, M. (2019). Source Apportionment and Health Risk Assessment of Heavy Metals in Eastern Guangdong Municipal Solid Waste. Applied Sciences, 9, 4755. https://doi.org/10.3390/app9224755

USEPA. (1994). A plain English guide to the EPA part 503 biosolids rule. EPA832-R-93- 003.

Valadez-Vega, C., Zúñiga-Pérez, C., Quintanar-Gómez, S., Morales-González, J. A., Madrigal-Santillán, E., Villagómez-Ibarra, J. R., Sumaya-Martínez, M. T., & García-Paredes, J. D. (2011). Lead, Cadmium and Cobalt (Pb, Cd, and Co) Leaching of Glass-Clay Containers by pH Effect of Food. International Journal of Molecular Sciences, 12(4), Article 4. https://doi.org/10.3390/ijms12042336

Vithanage, M., Ramanayaka, S., Hasinthara, S., & Navaratne, A. (2021). Compost as a carrier for microplastics and plastic-bound toxic metals into agroecosystems. Current Opinion in Environmental Science & Health, 24, 100297. https://doi.org/10.1016/j.coesh.2021.100297

Wang, J., Guo, X., & Xue, J. (2021). Biofilm-developed microplastics as vectors of pollutants in aquatic environments. Environmental Science & Technology, 55(19), 12780–12790.

Wang, Q., Zhang, Y., Chen, H., Chen, S., & Wang, Y. (2023). Effects of humic acids on the adsorption of Pb(II) ions onto biofilm-developed microplastics in aqueous ecosystems. Science of The Total Environment, 882, 163466. https://doi.org/10.1016/j.scitotenv.2023.163466

Weithmann, N.; Möller, J.N.; Löder, M.G.J.; Piehl, S.; Laforsch, C.; Freitag, R. Organic fertilizer as a vehicle for the entry of microplastic into the environment. Sci. Adv. 2018, 4, eaap8060.

Zafiu, C., Binner, E., Beigl, P., Vay, B., Ebmer, J., & Huber- Humer, M. (2023). The dynamics of macro-and micro- plastic quantity and size changes during the composting process. Waste Management, 162, 18–26.

Zheng, R., Li, Q., Li, P., Li, L., & Liu, J. (2023). Total organic carbon content as an index to estimate the sorption capacity of micro- and nano-plastics for hydrophobic organic contaminants. Chemosphere, 313, 137374. https://doi.org/10.1016/j.chemosphere.2022.137374

detritus | Multidisciplinary Journal for Circular Economy and Sustainable Management of Residues

CISA

DEVELOPMENT OF A SIMULATION MODEL TO CARRY OUT TECHNICAL-ECONOMIC ANALYSIS OF A FOOD WASTE VALORIZATION PROCESS

Luca Preite *, Giovanni Paolo Carlo Tancredi, Arianna Paini and Giuseppe Vignali

Department of Engineering and Architecture, University of Parma, Parco Area delle Scienze 181/A, 43124 Parma, Italy

Article Info:
Received:
14 September 2023
Revised:
25 January 2024
Accepted:
5 February 2024
Available online:
20 March 2024

Keywords:
Food Waste
Waste Valorization
Circular Economy
Process Simulation
Technical – economic analysis

ABSTRACT

Worldwide interest in food waste has been grown over the years. According to the FAO about one third of all food produced for human consumption in the world is lost or wasted each year, amounting to about 1,6 billion tons per year. Food waste can become a source of valuable compounds which may be used as ingredients in cosmetics, pharmaceuticals, or food products. This study aims to evaluate the use of a process simulation software, specifically SuperPro Designer®, to carry out a technical-economic analysis of an orange waste valorization process. Specifically, the extraction of free sugars, essential oils, antioxidant phenolic compounds and pectin were digitally replicated by reproducing the corresponding material and energy balances. An economic and environmental assessment were carried out to evaluate the feasibility of the biorefinery modeled. The amount of orange peel processed, utilities and raw material costs were identified as significant parameters in the analyses performed. A sensitivity analysis was carried out to evaluate the profitability patterns under different operating conditions. Meanwhile, the aim of the environmental assessment is to define a disposal inventory, which is the starting point for a life cycle assessment. As a result, SuperPro Designer® can be a valuable tool in the designing and optimizing food waste treatment systems, providing detailed descriptions of the process performance, and enabling cost-effective and sustainable waste management practices. Indeed, the simulation accurately reproduced all the steps involved, identifying the total investment and the related economic parameters, as well as the outputs and the resulting disposal inventory.

1. INTRODUCTION

Food waste (FW) has become a problem of global concern that requires sustainable management strategies (Caldeira et al., 2020; Santagata et al., 2021). Valorization of FW through various processes is gaining attention to minimize waste and create valuable products (Dahiya et al., 2018). FW causes significant environmental impacts, including greenhouse gas emissions and resource depletion (J. Banerjee et al., 2017). The valorization of FW offers the potential to reduce these impacts by converting waste into valuable products, such as biofuels, bio-based chemicals, and animal feed (Bhatia et al., 2023; Imbert, 2017).

Circular economy can lead to economic benefits through the creation of new markets, job opportunities, and reduced disposal costs (Otles et al., 2015). Indeed, in Europe, the cost to dispose 1 ton of solid waste or 1 cubic meter of liquid waste ranged from 5 to more than 100€, for the period 2021-2023, including the landfill taxes (CEWEP, 2023). An effective techno-economic analysis is essential to identify economically viable circular processes and optimize resource allocation (Ginni et al., 2021). In the context of food waste valorization, a simulation software can assess the economic feasibility, energy consumption, and environmental impact of various valorization processes (Moncada B et al., 2016). Simulation software has emerged as a powerful tool to perform techno-economic analysis of food waste valorization processes (Li et al., 2022).

Orange peels and fruit peels contain bioactive compounds that have potential applications in the pharmaceutical, cosmetic, and food industries (Maqbool et al., 2023). Indeed, simulation software can help optimize extraction processes for maximizing yield and purity of these compounds.

Anaerobic digestion is commonly employed to convert food waste into biogas (Leung et al., 2016). In this perspective, simulation software can be used to model and optimize key parameters, such as substrate composition, temperature, and hydraulic retention time to improve the efficiency of the biogas production.

* Corresponding author:
Luca Preite
email: luca.preite@unipr.it

https://doi.org/10.31025/2611-4135/2024.18354

Orange peels and fruit peels can be used as feedstocks to produce bioethanol and biobutanol through fermentation processes (Sánchez et al., 2021). Moreover, for this application, the economic feasibility and process optimization of these biofuel production pathways can be evaluated using simulation software.

Simulation models heavily rely on accurate input data, which may be challenging to collect for food waste valorization processes, since they involve numerous interrelated variables Developing accurate simulation models requires comprehensive data validation and verification against real-world operating conditions. For this reason, setting a standardized methodology for data monitoring, data collection and data reporting becomes a matter of primary importance before the implementation of the analysis on a real case study based on primary data. In this regard, the present study, based on secondary data derived from the scientific literature, may also provide a framework for future analyses on real applications.

The purpose of this study is to investigate the application of a simulation software for evaluating the feasibility of an orange peel biorefinery, providing insights into its effectiveness and potential. Specifically, the details of the valorization processes and substrate characterization were taken from the data available in the scientific literature. Thus, the process flow diagram was digitally replicated by modeling the equipment required to simulate the extraction techniques involved. As a result, economic and environmental parameters were evaluated through various scenarios by implementing a sensitivity analysis.

Section 2 describes the methodology used by first introducing the software used for the investigation, the details of the orange peel and process characterization, and the framework used to set up the economic, sensitivity and environmental analysis. For the latter, the result will be an environmental inventory to perform a life cycle assessment. Section 3 highlights the results achieved by the analyses performed and finally section 4 outlines the conclusions and future developments.

2. MATERIAL AND METHOD

2.1 Process Simulation Software

In this research SuperPro Designer® (v. 12, Intelligen, Inc., Scotch Plains, NJ, USA) was used with the aim of developing a simulation model to perform a technical-economic analysis of a suitable orange peel valorization process.

The first step in creating the simulation model was to define the physical, chemical, and environmental properties to characterize raw materials and input streams. Next, a digital flow diagram was designed by modeling all the equipment and operations involved in the process. Meanwhile, the economic and financial parameters of the biorefinery were defined as a final step. Following these stages, the software can evaluate the output streams by solving the energy and mass balances. In this way, the equipment sizing can be adjusted to define the resulting purchase cost and thus carry out the economic analysis.

The effectiveness of this simulation process lies in the fact that the economic analysis and the evaluation of the disposal inventory were carried out by combining manufacturing, energy, and environmental operations models in the same tool.

2.2 Substrate characterization

Global orange production in the period 2022-2023 is estimated to be 5% lower at 47.5 million tons due to a lower production in the European Union (EU) and the United States (US). The EU production is forecast to decline by 13% to 5.9 million tons due to dry and warm seasons in Spain and Italy (USDA, 2023).

In 2018, 6.5 million tons of oranges were harvested in the EU. Spain was the main producer with 3.6 million tons of oranges (56% of the EU total), while the other main producers were Italy with 1.6 million tons (24% of the EU total) and Greece with 14% of the EU total (EUROSTAT, 2020).

According to (Meneguzzo et al., 2019), in 2017-2018 an amount of 36% of the global orange production was used for orange juice production, with orange waste amounting for approximately 50-60% w/w of the processed fruit. Specifically, 65% of the orange waste was characterized by peels, while the remaining 35% was internal tissues and seeds (Meneguzzo et al., 2019; Negro et al., 2017).

Table 1 shows the data collected for the modeling of the orange by-product biorefinery, with reference to Italian production in 2018.

The substrate composition, shown in Table 2, and the detailed process description were retrieved from a previous study (Tsouko et al., 2020). In particular, the available feedstock was assumed to be 7560 tons of orange peel per year, which represents about 5% of the orange peel available in Italy. According to this assumption, a quantity of 24 tons per day was evaluated, considering an operating time of 315 days per year and 24 hours per day in a continuous mode.

2.3 Model and process description

The modeled process has six distinct sections:

- Orange peel pretreatment
- Free sugars extraction
- Essential oils extraction
- Total phenolic compound extraction
- Pectin extraction
- Water and ethanol recovery and reuse

Thus, the resulting value-added compounds can be used as substrate in the cosmetic, pharmaceutical or food industries.

TABLE 1: Data collected to model the orange by-product biorefinery.

Component	Stream [tons/year]	Reference
Orange production	1 600 000	(EUROSTAT, 2020)
Orange processed in juice production	576 000	(Meneguzzo et al., 2019)
Orange waste	288 000	(Negro et al., 2017)
Orange peels	187 200	(Negro et al., 2017)
Orange peels processed by the modelled biorefinery	7560	Author's Data

TABLE 2: Orange peel composition.

Component	Percentage	Stream [kg/h]
Moisture (%wet basis)	79.1 ± 0.01	791
Solid components (%dry basis)	20.9 ± 0.01	209
Ash	3.3 ± 0.20	6.93
Protein	6.6 ± 0.30	13.86
Free sugars	50.0 ± 2.01	107.1
Essential oils	0.7 ± 0.01	1.47
Phenolics	0.6 ± 0.07	1.26
Pectin	22.0 ± 0.02	46.2
Lignin	1.2 ± 0.05	2.52
Hemicellulose	5.4 ± 0.19	11.34
Cellulose	9.2 ± 0.21	19.32

The process flow diagram used to develop the simulation model is reported in Figure 1.

2.3.1 Orange peels pre-treatment

The first step was to pretreat the orange peels to improve the efficiency of the extraction process. For this purpose, the orange peels were ground using a professional grinder referred to as GR-101 in the simulation model developed. Indeed, the extraction efficiency is closely related to the particle size of the raw material, since the contact surface area between the solvent and the matrix was increased (Alsaud et al., 2020; M'hiri et al., 2015; Tsouko et al., 2020).

2.3.2 Free sugar extraction

Free sugar extraction was carried out via aqueous extraction at 40°C for 1 h and with an appropriate solid-liquid ratio (1:20, w:v). Assuming an extraction yield of 90%, 115,93 kg/h of extract with 83% of free sugar was obtained (96,39 kg/h).

2.3.3 Essential oils extraction

Several authors have assessed different technologies for the extraction of essential oils (EO) from orange by-products. Specifically, EO were mainly represented by D-Limonene. For this reason, D-Limonene properties were used to model EO properties in the software database (National Center for Biotechnology Information, 2023).

Conventional EOs extraction techniques include mechanical cold pressing, water-based distillation or steam explosion, microwave steam distillation or solid-liquid extraction using conventional or organic solvents (Giwa et al., 2018; Sahraoui et al., 2011; Siddiqui et al., 2022).

In this research, the extraction of the EOs was performed by steam distillation. Specifically, 22.8 kg/min of steam (ratio 1:50 w:w) was assumed to carry out the EOs extraction for 120 minutes, obtaining 1.57 kg/h of EOs (removing up to 90% of the D-Limonene present in the peels) (Bustamante et al., 2016; Sahraoui et al., 2011).

2.3.4 Total phenolic compounds extraction

Various methods have been reported in the literature for the extraction of phenolic compounds from orange by-products. These extraction processes are very changeling to perform since phenols are very sensitive to certain conditions of high temperature and pressure (Xu et al., 2010).

Conventional solvent extraction based on ethanol was the most widely used extraction technique. There were also some interesting methods such as ultrasound assisted extraction, microwave assisted extraction, supercritical and subcritical extraction, and high hydrostatic pressure extraction, which can improve the yield of the bioactive compounds and the energy efficiency of the extraction process (M'hiri et al., 2014).

To this investigation, conventional solvent extraction was performed by using 80% ethanol. A mixture of peel powder and solvent, with a suitable ratio of 1:10 (w:v) was shaken at 200 rpm in the darkness using a mechanical stirrer for 30 minutes at 35°C (M'hiri et al., 2015). This process achieves an extraction rate of 2,19 kg/h, with 51,83% of total phenolic compounds.

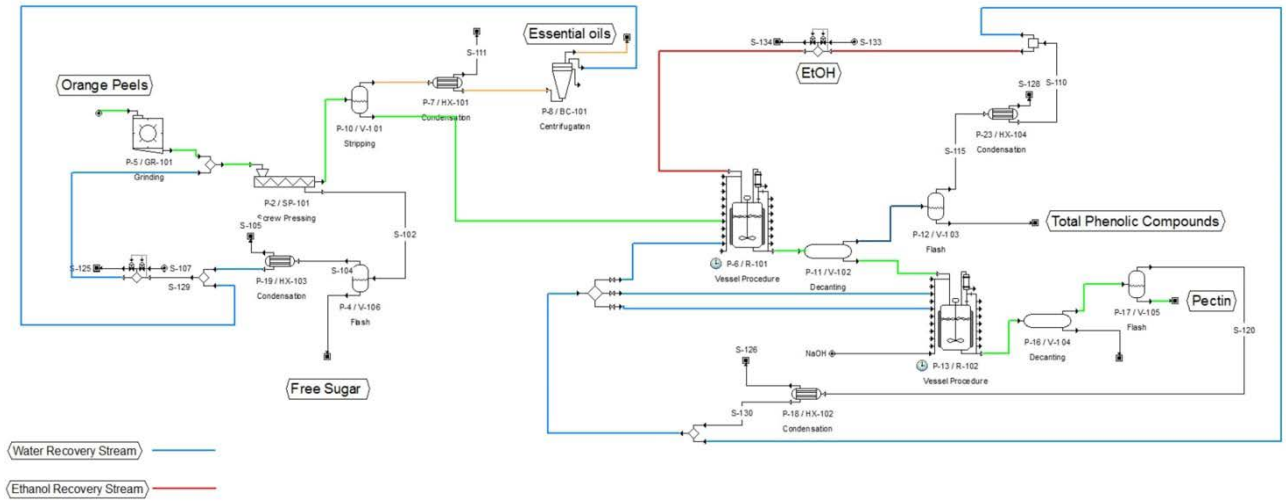


FIGURE 1: Process flow diagram of the modeled biorefinery.

2.3.5 Pectin extraction

Pectin extraction is a process that has already been consolidated at an industrial scale (May et al., 1990). In this model, the resulting stream was diluted with 2 M HCl solution with a suitable ratio of 1:20 (w:v) at 100°C for 1 hour. Subsequently, 1,5 M NaOH solution was added to adjust the pH of the resulting slurry to 4. The solid residue was separated from the mixture via decanter and the pectin-rich liquid stream was concentrated under vacuum to perform efficient concentration at low temperature to avoid pectin degradation. According to the evaluation performed, the residual solid (79,1 kg/h) were considered as a resource for other biorefineries involving hydrolysis processes of the cellulose and hemicellulose (Kulkarni et al., 2010; Tsouko et al., 2020). The extraction rate achieved is 562,20 kg/h, with 6,16% of pectin.

2.3.6 Water and ethanol recovery and reuse

A water and ethanol recovery and reuse system were simulated to reduce operating costs and to minimize the use of these valuable resources.

2.4 Economic analysis

SuperPro Designer® carries out technical-economic analysis by performing capital cost analysis, operating cost analysis, and cash flow analysis.

2.4.1 Capital cost analysis

According to (Rajendran et al., 2022), Direct Fixed Capital (DFC) should be estimated as a linear function of the equipment purchase cost (PC), considering also unlisted purchase cost. Direct cost (DC) such as piping, instrumentation, insulation, electrical facilities, buildings, yard improvement, auxiliary facilities and unlisted equipment purchase cost were expressed as a fraction of the section's total equipment PC. While side, indirect cost (IC), i.e., engineering, and construction were expressed as fraction of the section's total DC. Other cost (OC) such as contractor's fee and contingency cost were the fraction of the section's sum of DC and IC.

Capital cost analysis performed by the simulation software included other cost, such as the working cost, start-up cost and the validation cost. In this analysis, possible cost of R&D and royalties was not considered.

$$DFC = DC + IC + OC \quad (1)$$

2.4.2 Economic analysis parameters

Time evaluation and financial parameters had to be set based on the investment costs.

Specifically, the time required for the project realization and the related inflation was important to characterize the first topic.

The annual inflation rate and the net present value interest have been evaluated by considering the new European forecast. In addition, the construction and start-up period were set to 24 months, while the project lifetime was assumed to be 20 years. Construction and start-up costs were estimated to be 5% of DFC (Herrera Barragán et al., 2022).

The second issue was the financial aspect. In this case, the depreciation time was set at 10 years, the DFC outlay was defined as 30% of the DFC for the first three years, and the loan period was 10 years for the DFC and 6 years for the working capital (Kwan et al., 2018).

2.4.3 Operating cost analysis

The annual operating cost (AOC) included the cost of the raw materials, labor, consumables, quality control, quality assurance, waste treatment or waste disposal, maintenance, and utilities.

For this analysis, 10 people were assumed (including 8 operators, 1 QC analyst and 1 supervisor) to work 1720 hours per year. The total labor cost for each operator was determined by multiplying the European average labor cost, based on the European Qualifications Framework (EQF), by a lumped rate factor (it includes labor benefits or administrative costs of labor) (European Union, 2023). Furthermore, 15% of the total labor cost was allocated to cover quality control and assurance cost (Nguyen et al., 2020).

Asit can be seen in Table 3, the cost of the raw material has been set individually for each material. The cost of waste disposal or waste treatment was also evaluated individually according to the material balances and the required treatment specifications.

The utilities costs were investigated by defining the contribution of each energy source. Specifically, the cost of the electricity was set at 0,51 €/kWh and the cost of producing 1 ton of steam was assumed to be 95 €/ton (Global Petrol Prices, 2023).

To cover the cost of insurance, local taxes, and factory expenses, an amount of 1%, 2%, and 5% of the DFC was assumed, respectively. Finally, the cost of maintenance has been set individually for each equipment while the depreciation cost was determined considering a depreciation period of 10 years (Herrera Barragán et al., 2022).

2.4.4 Profitability analysis

The cash flow analysis was an assessment of the annual net cash flow over the life of the project. This evaluation involved several calculations, and the results were reported in the Cash Flow Analysis Report (CFR).

Three different parameters were examined to carry out the profitability assessment. Specifically, they were:

$$Gross\ Margin\ (\%) = \frac{Gross\ Profit\ [€\ years^{-1}]}{Revenues\ [€\ years^{-1}]} x100 \quad (2)$$

$$Return\ on\ Investment\ (ROI\ \%) = \frac{Net\ Profit\ [€\ years^{-1}]}{Revenues\ [€\ years^{-1}]} x100 \quad (3)$$

$$Payback\ time\ (years) = \frac{Total\ Investment\ \ [€]}{Net\ Profit\ [€\ years^{-1}]} \quad (4)$$

The Gross margin is a direct measure of profit, describing the percentage of the revenues that are actual profit (2).

Return on investment is another profitability measure used to assess the feasibility of an investment or to compare the profitability of different investments (3). If an investment does not have a positive ROI, or if there are other opportunities with a higher ROI, the investment should not be undertaken.

Finally, the payback time is the inverse measure of ROI. Indeed, it is a measure of the time needed to receive the cu-

mulative net profits that exactly balances the total capital investment (4).

To perform the profitability analysis, the resulting revenues were evaluated by defining the selling price according to the references and considering the purity level achieved by the processes modeled. Assumed selling prices are reported in Table 3.

2.4.5 Sensitivity analysis

A sensitivity study has been performed to assess the predicted biorefinery performance under various operating circumstances. Based on the outcomes of the system designed using the procedure outlined in (Tsouko et al., 2020), a few significant variables were determined by considering their influence on the profitability analysis outputs. These were the demands for orange peels (kg/h) and the costs of utilities (water and steam) (€/Smc). A factorial experiment has been implemented to evaluate how these combined factors impact on the profitability outcomes. Specifically, a variation between 0 and 100 percent with a step of 25 percent has been assumed for each factor, yielding 192 potential combinations of each element. The 50 percent value of each element has been selected as the baseline. To solve the corresponding materials and energy balances, every combination has been imported into the model using the SuperPro Designer COM library. The resulting profitability metrics were compiled together into a unique data frame with the aim to provide three-dimensional graphs that illustrate the results patterns (IRR, ROI Gross Margin) with different factors.

2.5 Environmental analysis

In SuperPro Designer®, several input properties can be set to generate a disposal inventory to perform an environmental impact analysis. Specifically, the information on the disposal streams have been reported in two reports, the Environmental Impact Report (EIR) and the Emission Report (EMS).

The first defines the environmental impact of the process output streams, identifying all chemicals that are either regulated by the US Environmental Protection Agency (EPA) or marked as hazardous by the user. Each waste stream can be categorized as aqueous, organic, and solid waste or such as emissions. In addition, environmental load properties (including TOC, COD, NH_3, and others) concentrations were assessed during the analysis and an appropriate treatment or disposal cost was assumed for each category.

To assess the effect of the chemicals, two different regulations required by US government were considered, EPCRA Section 313 and 33/50 Program. According to the first regulations, facilities were required to report annually a Toxic Chemical Release Inventory, which includes all the releases to the environment and other waste management of toxic chemicals that occurred during the previous calendar year (EPA, 2023).

Pollution indices were reported in the last section of the EIR report. These indices are representative of the environmental performance of the developed process:

$$Y1 = \frac{Total\ Waste\ [kg]}{Main\ Revenue\ Stream\ [kg]} \quad (5)$$

$$Y2 = \frac{Total\ Waste\ [kg]}{Raw\ Material\ [kg]} \quad (6)$$

The first index represents the ratio of the total amount of waste generated per kg of the main revenue stream processed, which is in this case the pectin rich liquid due to the large volume. The second index considers the same amount of waste generated but related to kg of raw material used. The analysis carried out provides also specific index to assess the ratio between the single stream waste (i.e, solid, aqueous, and pollutant) generated and the kg of main revenue stream or raw material.

The second report generated (EMS) provides information on the air pollutant impacts related to the whole process or individual procedure. For each air pollutant identified, the procedure/operation averaged component rates, the time-averaged component rates, and the total amounts have been assumed.

As a result, the outputs of this analysis can be used to perform a life cycle assessment with the aim of assessing the sustainability of the processes involved.

3. RESULTS AND DISCUSSION

3.1 Capital Costs Analysis Result

The results of capital cost analysis carried out by using the equation (1) are reported below. As can be seen, the amount of the DFC is more marginal than the annual operating cost.

- DFC = 7 129 000 €
- AOC = 38 855 000 €

TABLE 3: Raw material cost and revenue for each by – product expressed as €/kg.

Raw Material	Purchase Cost [€/kg]	Reference	Revenue	Selling price assumed [€/kg]	Reference
Orange peels	0,0025	(S. Banerjee et al., 2022)	Free sugars	1	(Foodcom, 2023)
HCl (37%)	0,3	(MERCK, 2023)	Essential oils	10	(Cbi, 2023)
NaOH	0.3	(MERCK, 2023)	Total phenolic compound	20	(Fisher scientific, 2023)
Ethanol	0.62	(Trading Economics, 2023)	Pectin rich liquid	10	(MERCK, 2023)
Water	1.5E-3	(ARERA, 2023)	Solid residual to Hydrolise	3	(MERCK, 2023)

3.2 Operating Costs Analysis Result

The value of the annual operating cost (AOC) based on the analysis carried out by the simulation software is 38 855 000 €. Figure 2 shows the distribution of the different item cost related to the AOC to identify the main cost item, which is the cost of utilities (78%), followed by the cost of the raw materials (17%), the labor-dependent cost (2%), the cost of the depreciation (2%), and the other facility – dependent cost (2%).

3.3 Profitability Costs Analysis Result

The modeled process gave a high ROI and a very short payback time. These highlight the profitability of the process which recovers over 60% of the initial investment in 1.57 years with a gross margin of 17.91%. As reported below:

- Gross margin (%) = 17,91%
- ROI (%) = 63,69%
- Payback time (years) = 1.57 years

3.4 Sensitivity Analysis Result

The annual operating cost section highlights how the utilities and raw materials are the major operating cost items. Indeed, the high influence of the former is due to the large amount of steam and water required to perform the heat transfers throughout the process. Similarly, the costs of the raw materials are also significant due to the large amount of water required to process the orange peels. According to the capital cost section, the DFC is linearly dependent on the equipment purchase cost, which is influenced by the volume of orange peel processed by the biorefinery.

As a result, the orange peels demand, the steam production costs, and the water supply and distribution costs were assumed as significant factors to carry out the sensitivity analysis. Figures 2 (a-b-c) show the patterns of gross margin, ROI, and payback time related to the combination between the identified factors.

3.5 Environmental Analysis Result

The performed environmental analysis highlights different indices, reported below, which show how much waste has been generated in relation to the main product of the biorefinery and the raw materials processed. The results show that 1.33 kg of waste was generated to produce 1 kg of pectin rich liquid. At the same time, according to the equation 6, total waste represents the 50% of the processed raw material. As it can be seen below, the main waste stream is represented by the aqueous stream.

$$Y1 = 1.33 \frac{kg\ of\ waste}{kg\ of\ main\ revenue\ stream}$$

$$Y2 = 0.50 \frac{kg\ of}{kg\ of\ raw\ material}$$

4. CONCLUSIONS

Waste management and waste valorization are the key drivers for reducing the environmental impact and increasing the economic growth. Indeed, several value-added products can be produced by valorizing the FW such as

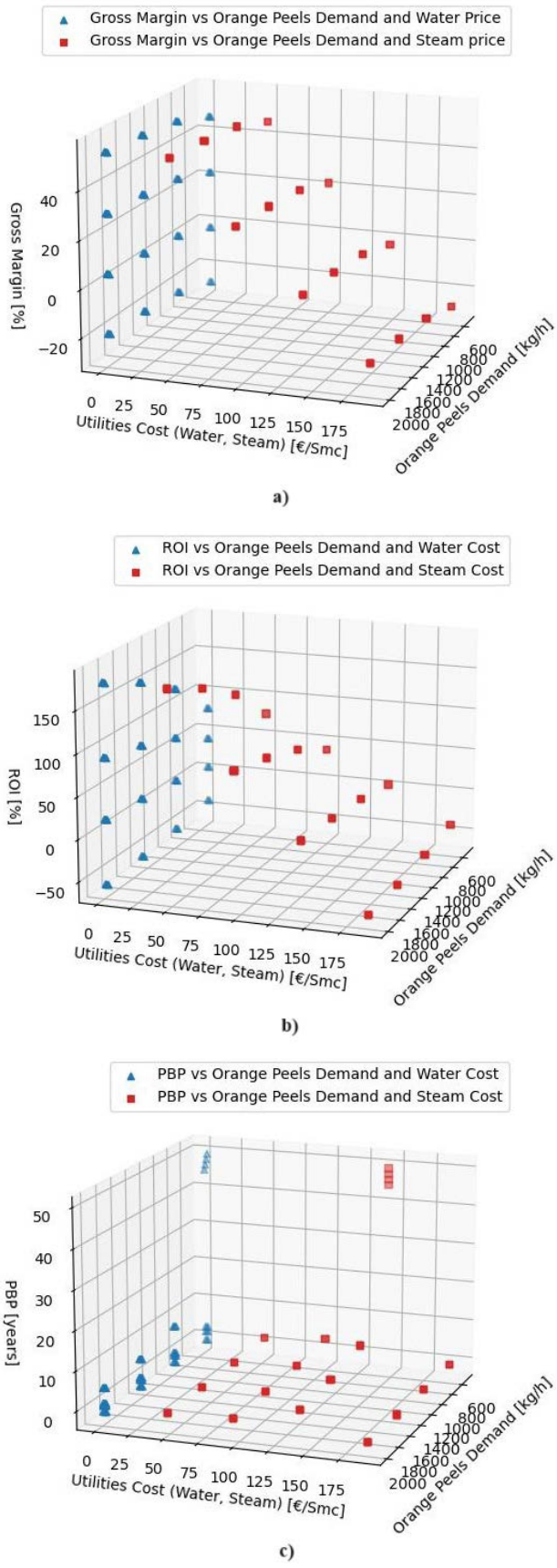


FIGURE 2: a) Gross margin vs. orange peel demand, water, and steam costs; b) ROI vs. orange peel demand, water, and steam cost; c) Payback time vs. orange peel demand, water, and steam costs.

biofuels, bio – based chemicals, and animal feed. Specifically, the attention on the bioactive compounds contained in fruits and agri-food products has grown over the years since they have potential applications as ingredients in the pharmaceutical, cosmetic and food industries. The scientific literature shows how several strategies for the extraction of these substances from FW have been investigated on a laboratory scale. With the aim of scaling up these processes to a pilot plant or industrial level, a technical-economic analysis had to be carried out to assess their feasibility. At the same time, the evaluation of some environmental parameters related to the processes involved is an essential step for the optimal design of a valorization process. The mentioned evaluations can be performed by using the simulation software to produce a digital replica capable of reliably reproducing the characteristics of the real processes.

The aim of this study is to investigate the application of a simulation software, SuperPro Designer®, to assess the feasibility of an orange peels valorization biorefinery, providing insight into its effectiveness and potential. Specifically, scientific evidence highlights how the substrate investigated can be a source of free sugars, essential oils, antioxidant phenolic compounds, pectin, cellulose, and hemicellulose. The modeled biorefinery was able to produce all the mentioned compounds by involving a series of extraction strategies.

As the first step, all the raw material and stream properties (physical, chemical, economic, and environmental properties) were initialized. In addition, all the economic, financial, and environmental parameters were defined with the aim of performing the technical-economic analysis and generating the disposal inventory. Next, all the equipment involved in the process was modeled to replicate the corresponding process flow diagram. At this point the software can evaluate the output streams by solving the energy and mass balances. As a result, the sizing of the equipment can be adjusted to define the resulting purchase cost and thus perform the economic evaluation. The latter was based on the direct fixed capital cost and annual operating cost. In particular, the former was characterized by the direct and indirect costs, which were a linear function of the equipment's purchase cost. Meanwhile, the most influential annual operating costs were raw materials and utilities costs. Three different parameters, gross margin, return on investment, and payback time, were examined to evaluate the profitability performance. Furthermore, a sensitivity analysis was performed to evaluate the patterns of the profitability indices by varying the parameters that have a relevant influence on the economic evaluation.

The simulation software provided the environmental impact and emission reports. From these, two different indices were identified to preliminary quantify the waste generated. Specifically, the first described the ratio between the amount of waste and the stream with the highest mass flow, while the second showed the ratio between the amount of waste and the raw material processed. In addition, the resulting reports provided an environmental inventory useful for further analysis focused on a life cycle assessment.

Digging deeper into the results, valorization processes represent a sustainable strategy to address the pressing issue of the FW. In this perspective, simulation software has emerged as a valuable tool for technical-economic analysis of food waste valorization processes. Potential assessments include economic viability, resource optimization, and environmental inventory management.

Despite some limitations, ongoing advances in simulation software and data availability hold promising prospects for further improving the effectiveness and accuracy of such analysis. Future research should focus on refining simulation models and integrating advanced technologies to support sustainable food waste valorization practices. Data collection and reporting on waste recovery processes also needs to be improved and standardized.

ACKNOWLEDGEMENTS

This study was carried out within the Agritech National Research Center and received funding from the European Union Next-GenerationEU (PIANO NAZIONALE DI RIPRESA E RESILIENZA (PNRR) – MISSIONE 4 COMPONENTE 2, INVESTIMENTO 1.4 – D.D. 1032 17/06/2022, CN00000022). This manuscript reflects only the authors' views and opinions, neither the European Union nor the European Commission can be considered responsible for them.

REFERENCES

Alsaud, N., & Farid, M. (2020). Insight into the influence of grinding on the extraction efficiency of selected bioactive compounds from various plant leaves. Applied Sciences (Switzerland), 10(18). https://doi.org/10.3390/app10186362

Banerjee, J., Singh, R., Vijayaraghavan, R., MacFarlane, D., Patti, A. F., & Arora, A. (2017). Bioactives from fruit processing wastes: Green approaches to valuable chemicals. In Food Chemistry (Vol. 225, pp. 10–22). Elsevier Ltd. https://doi.org/10.1016/j.foodchem.2016.12.093

Banerjee, S., Munagala, M., Shastri, Y., Vijayaraghavan, R., Patti, A. F., & Arora, A. (2022). Process Design and Techno-Economic Feasibility Analysis of an Integrated Pineapple Processing Waste Biorefinery. ACS Engineering Au, 2(3), 208–218. https://doi.org/10.1021/acsengineeringau.1c00028

Bhatia, L., Jha, H., Sarkar, T., & Sarangi, P. K. (2023). Food Waste Utilization for Reducing Carbon Footprints towards Sustainable and Cleaner Environment: A Review. In International Journal of Environmental Research and Public Health (Vol. 20, Issue 3). MDPI. https://doi.org/10.3390/ijerph20032318

Bustamante, J., van Stempvoort, S., García-Gallarreta, M., Houghton, J. A., Briers, H. K., Budarin, V. L., Matharu, A. S., & Clark, J. H. (2016). Microwave assisted hydro-distillation of essential oils from wet citrus peel waste. Journal of Cleaner Production, 137, 598–605. https://doi.org/10.1016/j.jclepro.2016.07.108

Caldeira, C., Vlysidis, A., Fiore, G., De Laurentiis, V., Vignali, G., & Sala, S. (2020). Sustainability of food waste biorefinery: A review on valorisation pathways, techno-economic constraints, and environmental assessment. Bioresource Technology, 312. https://doi.org/10.1016/j.biortech.2020.123575

Cbi, Ministry of Foreign Affairs, 2023. Exporting essential oils for aromatherapy to Europe. Available at: https://www.cbi.eu/market-information/natural-ingredients-cosmetics/essential-oils-aromatherapy

CEWEP. (2023). Retrieved from CEWEP - Confederation of the European Waste-to-Energy Plants: https://www.cewep.eu/wp-content/uploads/2021/10/Landfill-taxes-and-restrictions-overview.pdf

Dahiya, S., Kumar, A. N., Shanthi Sravan, J., Chatterjee, S., Sarkar, O., & Mohan, S. V. (2018). Food waste biorefinery: Sustainable strategy for circular bioeconomy. In Bioresource Technology (Vol. 248, pp. 2–12). Elsevier Ltd. https://doi.org/10.1016/j.biortech.2017.07.176

EUROSTAT, 2020. EU production and trade in oranges Available at: https://ec.europa.eu/eurostat/en/web/products-eurostat-news/-/ddn-20200103-1

Fisher scientifc, 2023. Available at: https://www.fishersci.it/shop/products/phenol-99-extra-pure-thermo-scientific/10479803

Foodcom, 2023. Available at: https://foodcom.pl/en/products/dextrose-monohydrate/?gclid=Cj0KCQjwsIejBhDOARIsANYqkD0s-3Mg1_7HnpqIxSRhqmTvg8Zjd4UrYjFz2XSYBkODdf1HFRO2kT-T4aAspOEALw_wcB

Ginni, G., Kavitha, S., Yukesh Kannah, R., Bhatia, S. K., Adish Kumar, S., Rajkumar, M., Kumar, G., Pugazhendhi, A., Chi, N. T. L., & Rajesh Banu, J. (2021). Valorization of agricultural residues: Different biorefinery routes. Journal of Environmental Chemical Engineering, 9(4). https://doi.org/10.1016/j.jece.2021.105435

Giwa, S. O., Muhammad, M., & Giwa, A. (2018). UTILIZING ORANGE PEELS FOR ESSENTIAL OIL PRODUCTION. 13(1). Retrieved from www.arpnjournals.com

Global Petrol Prices. (2023). Italian fuel prices, electricity prices, natural gas prices. Available at: https://www.globalpetrolprices.com/Italy/

Herrera Barragán, J. A., Olivieri, G., Boboescu, I., Eppink, M., Wijffels, R., & Kazbar, A. (2022). Enzyme assisted extraction for seaweed multiproduct biorefinery: A techno-economic analysis. Frontiers in Marine Science, 9. https://doi.org/10.3389/fmars.2022.948086

Imbert, E. (2017). Food waste valorization options: Opportunities from the bioeconomy. Open Agriculture, 2(1), 195–204. https://doi.org/10.1515/opag-2017-0020

Kulkarni, S. G., & Vijayanand, P. (2010). Effect of extraction conditions on the quality characteristics of pectin from passion fruit peel (Passiflora edulis f. flavicarpa L.). LWT, 43(7), 1026–1031. https://doi.org/10.1016/j.lwt.2009.11.006

Kwan, T. H., Hu, Y., & Lin, C. S. K. (2018). Techno-economic analysis of a food waste valorisation process for lactic acid, lactide and poly(-lactic acid) production. Journal of Cleaner Production, 181, 72–87. https://doi.org/10.1016/j.jclepro.2018.01.179

Leung, D. Y. C., & Wang, J. (2016). An overview on biogas generation from anaerobic digestion of food waste. International Journal of Green Energy, 13(2), 119–131. https://doi.org/10.1080/15435075.2014.909355

Li, J., Suvarna, M., Li, L., Pan, L., Pérez-Ramírez, J., Ok, Y. S., & Wang, X. (2022). A review of computational modeling techniques for wet waste valorization: Research trends and future perspectives. Journal of Cleaner Production, 367. https://doi.org/10.1016/j.jclepro.2022.133025

Maqbool, Z., Khalid, W., Atiq, H. T., Koraqi, H., Javaid, Z., Alhag, S. K., Al-Shuraym, L. A., Bader, D. M. D., Almarzuq, M., Afifi, M., & Al-Farga, A. (2023). Citrus Waste as Source of Bioactive Compounds: Extraction and Utilization in Health and Food Industry. In Molecules (Basel, Switzerland) (Vol. 28, Issue 4). NLM (Medline). https://doi.org/10.3390/molecules28041636

May, C. D., & Pectin, H. P. B. (1990). Industrial Pectins: Sources, Production and Applications. In Carbohydrate Polymers (Vol. 12). https://doi.org/10.1016/0144-8617(90)90105-2

Meneguzzo, F., Brunetti, C., Fidalgo, A., Ciriminna, R., Delisi, R., Albanese, L., Zabini, F., Gori, A., Nascimento, L. B. dos S., De Carlo, A., Ferrini, F., Ilharco, L. M., & Pagliaro, M. (2019). Real-scale integral valorization of waste orange peel via hydrodynamic cavitation. Processes, 7(9). https://doi.org/10.3390/pr7090581

Merck,2023.Available at: https://www.sigmaaldrich.com/IT/it/product/sigma/p9135?gclid=Cj0KCQjwsIejBhDOARIsANYqkD0f-h7K-wKyo_VL1h7PcSGi8QiRCpxI8gdTeHMAXrZAlpx4xx07F6-4aAiKvEALw_wcB&gclsrc=aw.ds

M'hiri, N., Ioannou, I., Ghoul, M., & Boudhrioua, N. M. (2014). Extraction Methods of Citrus Peel Phenolic Compounds. In Food Reviews International (Vol. 30, Issue 4, pp. 265–290). Taylor and Francis Inc. https://doi.org/10.1080/87559129.2014.924139

M'hiri, N., Ioannou, I., Mihoubi Boudhrioua, N., & Ghoul, M. (2015). Effect of different operating conditions on the extraction of phenolic compounds in orange peel. Food and Bioproducts Processing, 96, 161–170. https://doi.org/10.1016/j.fbp.2015.07.010

Moncada B, J., Aristizábal M, V., & Cardona A, C. A. (2016). Design strategies for sustainable biorefineries. Biochemical Engineering Journal, 116, 122–134. https://doi.org/10.1016/j.bej.2016.06.009

National Center for Biotechnology Information (2023). PubChem Compound Summary for CID 22311, Limonene. Retrieved May 12, 2023 from https://pubchem.ncbi.nlm.nih.gov/compound/Limonene.

Negro, V., Ruggeri, B., Fino, D., & Tonini, D. (2017). Life cycle assessment of orange peel waste management. Resources, Conservation and Recycling, 127, 148–158. https://doi.org/10.1016/j.resconrec.2017.08.014

Nguyen, T. T., & Zhang, W. (2020). Techno-economic feasibility analysis of microwave-assisted biorefinery of multiple products from Australian lobster shells. Food and Bioproducts Processing, 124, 419–433. https://doi.org/10.1016/j.fbp.2020.10.002

Otles, S., Despoudi, S., Bucatariu, C., & Kartal, C. (2015). Food waste management, valorization, and sustainability in the food industry. In Food Waste Recovery: Processing Technologies and Industrial Techniques (pp. 3–23). Elsevier Inc. https://doi.org/10.1016/B978-0-12-800351-0.00001-8

Rajendran, N., & Han, J. (2022). Integrated polylactic acid and biodiesel production from food waste: Process synthesis and economics. Bioresource Technology, 343. https://doi.org/10.1016/j.biortech.2021.126119

Sahraoui, N., Vian, M. A., El Maataoui, M., Boutekedjiret, C., & Chemat, F. (2011). Valorization of citrus by-products using Microwave Steam Distillation (MSD). Innovative Food Science and Emerging Technologies, 12(2), 163–170. https://doi.org/10.1016/j.ifset.2011.02.002

Sánchez, M., Laca, A., Laca, A., & Díaz, M. (2021). Value-Added Products from Fruit and Vegetable Wastes: A Review. In Clean - Soil, Air, Water (Vol. 49, Issue 8). John Wiley and Sons Inc. https://\doi.org/10.1002/clen.202000376

Santagata, R., Ripa, M., Genovese, A., & Ulgiati, S. (2021). Food waste recovery pathways: Challenges and opportunities for an emerging bio-based circular economy. A systematic review and an assessment. In Journal of Cleaner Production (Vol. 286). Elsevier Ltd. https://doi.org/10.1016/j.jclepro.2020.125490

Siddiqui, S. A., Pahmeyer, M. J., Assadpour, E., & Jafari, S. M. (2022). Extraction and purification of d-limonene from orange peel wastes: Recent advances. In Industrial Crops and Products (Vol. 177). Elsevier B.V. https://doi.org/10.1016/j.indcrop.2021.114484

Tsouko, E., Maina, S., Ladakis, D., Kookos, I. K., & Koutinas, A. (2020). Integrated biorefinery development for the extraction of value-added components and bacterial cellulose production from orange peel waste streams. Renewable Energy, 160, 944–954. https://doi.org/10.1016/j.renene.2020.05.108

United States Department of Agriculture Foreign Agricultural Service Record Exports Forecast for South Africa Mandarins. (2023). Retrieved from https://public.govdelivery.com/accounts/USDAFAS/subscriber/new

United States Environemntal Agency, 2023. Summary of the EPCRA Section 313 Reporting Requirements and the National Mining Association (NMA) Lawsuit. Available at: https://www.epa.gov/toxics-release-inventory-tri-program/summary-epcra-section-313-reporting-requirements-and-national

Xu, C., Zhang, Y., Wang, J., & Lu, J. (2010). Extraction, distribution and characterisation of phenolic compounds and oil in grapeseeds. Food Chemistry, 122(3), 688–694. https://doi.org/10.1016/j.foodchem.2010.03.037

detritus | Multidisciplinary Journal for Circular Economy and Sustainable Management of Residues

CISA

WHICH FOOD PARTS ARE CONSIDERED EDIBLE AND SHOULD BE INCLUDED IN FOOD WASTE REDUCTION TARGETS

Tomoko Okayama [1,*], Kohei Watanabe [2] and Hajime Yamakawa [3]

[1] *Taisho University, 3-20-1 Nishisugamo, Toshima-ku, Tokyo, 170-8470, Japan*
[2] *Teikyo University, 359 Otuska, Hachioji, 192-0395, Japan*
[3] *Kyoto Prefectural University, 1-5 Shimogamo-Hangi-cho, Sakyo-ku, Kyoto, 606-8142, Japan*

Article Info:
Received:
16 September 2023
Revised:
18 February 2024
Accepted:
28 February 2024
Available online:
25 March 2024

Keywords:
SDG target 12.3
Avoidable food waste
Tokyo Method
Questionnaire survey
Japan

ABSTRACT

SDG target 12.3 aims to reduce household avoidable food waste by half by 2030. This study introduces the "Tokyo Method," designed to quantify and categorize household food waste for reduction. The method divides avoidable food waste into three groups: A: unused ingredients, B: unused ready-to-be-eaten foods, and C: leftovers, with a goal of reducing their volume. Edible parts intentionally removed from the main food are placed in a separate category "De", while inedible parts like seeds and bones have their own classification "Di". An internet survey involving 1,254 participants in Japan assessed perceptions of 65 food items and their parts. Most respondents considered peels, cores, seeds, and stems of fruits as inedible, but there were exceptions like apple peels. Regarding vegetable parts like potato peels and cabbage leaves, a good number of respondents are aware that they could be eaten, but it is only a minority that believe they should be eaten, or they actually eat those parts. In conclusion, the study suggests excluding the "De" category from the primary food waste reduction target, as forcing the consumption of intentionally removed food parts is not a priority. This research sheds light on the complexities of food waste reduction, considering cultural and individual preferences regarding edible food parts.

1. INTRODUCTION

Level 2 of Food Waste Index for SDG target 12.3 recommends classifying food waste into edible (avoidable) and inedible (unavoidable) parts wherever possible, and reducing waste of edible parts. However, even in societies with homogeneous food cultures, it is difficult to clearly distinguish edible and inedible parts. Therefore, the separation of edible and inedible parts is not mandatory and remains as a recommendation. The Japanese authorities designated the "edible portion of food" as the target of household food waste that should be halved by 2030. However, it is difficult to clearly classify household food waste into "edible food waste" and "inedible food waste". Under these circumstances, we developed the "Tokyo Method," a classification method that enables quantification of household food waste through waste sorting analyses. Our objective was to develop a method that is internationally agreeable and adoptable, and that (1) generates useful information for policymaking and for tackling with reduction of food waste, (2) makes clear the concept of avoidable food waste, and (3) is practical and does not overcomplicate the work of grasping the situation of food wastage (Okayama et al 2021).

In the household, food is input, used and eaten, and the remainder is output, as shown in Figure 1. Food inputs are divided into two categories. The first are ingredients that are to be prepared (cooked), such as vegetables, meat, and fish, and the second are prepared foods or (almost) ready-to-eat foods, such as instant foods and frozen foods, or ready-to-eat items sold at takeaways.

Based on our discussion above, we define "unused food" and "leftovers" as "avoidable food waste" from households. Under our definition, avoidable food waste does not include intentionally removed parts in cooking (preparation residues), even if they are potentially edible. Unused food can be further divided into two categories: A: unused food ingredients (ingredients for cooking) and B: unused ready-to-be eaten (prepared) food (food that has not yet been placed on the table, or one unit of food that has been prepared to the last stage before consumption). A third category of avoidable food waste is C: leftovers, that is plate residues excluding parts that are deemed inedible and removed while eating. Thus, avoidable food waste consists of categories A, B, and C.

Apart from this, intentionally removed parts of food falls under category D, which has two subcategories. Removed parts that are potentially edible but not always consumed

* Corresponding author:
Tomoko Okayama
email: t_okayama@mail.tais.ac.jp

Detritus / Volume 26 - 2024 / pages 44-53
https://doi.org/10.31025/2611-4135/2024.18359

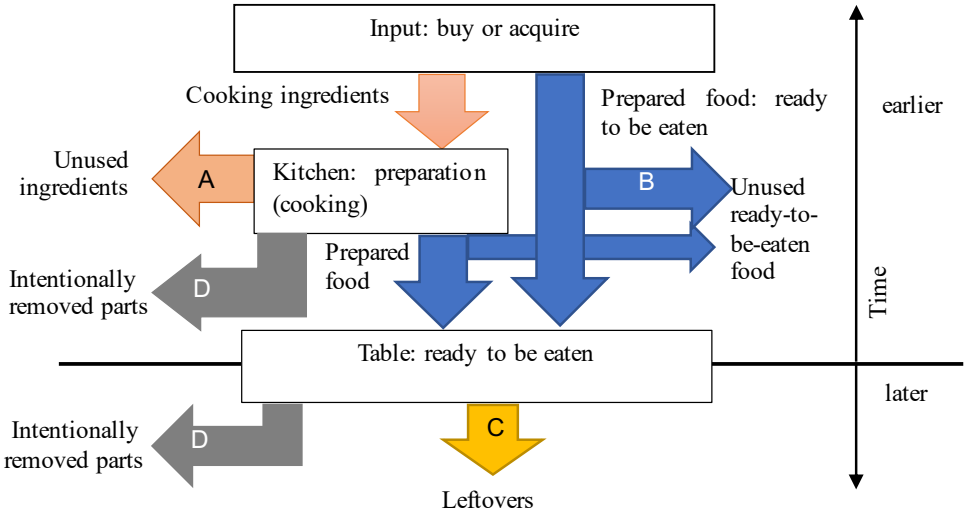


FIGURE 1: Generation of waste in the flow of food in households.

are classified as "De" (e.g. potato peel, fish skin), while physically (biologically) inedible parts such as seeds and bones belong to a separate classification "Di". Category De can be a margin for food waste reduction, but at the time being we do not include this as target for reduction. This classification D is quantifiable but difficult to reduce. As such wastes are inevitable when consuming the major (intended) part of food, we consider that they do not deserve to be included in the priority target items for reduction. Table 1 shows the classification of the Tokyo Method*. This classification of the Tokyo Method has been validated by multinational participants at Sardinia 2019, UN workshops

TABLE 1: Detailed categories of the classification system and the levels system of the Tokyo Method.

			Level			Definition
			1	2	3	
Food waste	Avoidable food waste	A/B Unused food	A Unused ingredients	A1 Unopened ingredients		Unopened ingredients in packaging
				A2w Whole unused ingredients		Whole unused ingredients not in/without packaging
				A2wf Home-grown vegetables		Large amounts of harvest that appears to be home-grown such as with irregularities and extensive stems.
				A2p Partly used ingredients		Partly used ingredients in or without packaging
			B Unused ready-to-be-eaten food	B1 Unopened ready-to-be-eaten food		Unopened ready-to-be-eaten food in packaging including in unopened individual packages
				B2 Uneaten ready-to-be-eaten food		Whole unused ready-to-be-eaten foods without packaging, and partly unused ready-to-be-eaten foods in packaging, including food in plastic wrap assumably intended for storage, such as steamed rice wrapped in cling film. However, obvious leftovers such as remains in disposable lunchbox are classified into leftovers even in packaging.
				B' Unopened drinks		Unopened drinks in packaging
			C Leftovers	C Leftover food		Ready-to-be-eaten or cooked food that appears to have been disposed after being served and partially eaten. In principle, without packaging. However, partially eaten food left in packaging that is designed to serve as plate/bowl (food that is designed to be eaten directly from the packaging) also qualifies as leftover food.
				C' Leftover drinks		Leftover drinks in bottles or packaging
	Non-avoidable food waste		D Intentionally removed parts		De Possibly avoidable	Intentionally removed parts that are physically edible such as vegetable scraps, meat fat, fish skin, cooking oil, bread crust and kelp for soup stock. However, vegetable waste such as corn cores, which are clearly inedible and may have a significant quantity, are classified into "inedible parts".
					Di Inedible parts	Intentionally removed parts that are physically difficult to eat such as fruit scraps, seeds, bones, eggshells, shells, used coffee grounds and bagged soup stock. However, fruit scraps which are clearly edible and may have a significant quantity such apple peels, are classified into "possibly avoidable".
			E Unclassifiable		E Unclassifiable	Very fine food waste that gets caught in kitchen sink strainers, or food waste blended with non-food waste that is difficult to sort further.

etc., and has been confirmed to have a low margin of error in international understanding (Okayama et al 2021).

Note that formally, the United Kingdom addressed the complexity of the definition of edible /inedible by classifying food waste into three categories (Nicholes et al 2019):

i) Avoidable: food and drink that was edible at the time before it was discarded (e.g., bread slices, apples, meat).
ii) Possibly avoidable: food and drink that some people eat and others do not (e.g., bread crusts), food and drink that is edible in one preparation but not in another (e.g., potato skins).
iii) Unavoidable: food or drink that is not and could not be eaten under normal conditions (e.g., eggshells, meat bones, pineapple peels).

If we apply the Tokyo Method classification to this WRAP classification, "A & B": unused food and "C": Leftovers fall under "i) Avoidable", while De falls under "ii) Possibly avoidable" and Di under "iii) Unavoidable".

Nicholes et al (2019) specifically reclassified "ii) Possibly avoidable" into either edible or inedible in order to eliminate the grey zone between avoidable and unavoidable. They conducted a large-scale questionnaire survey in the whole UK asking whether people consider the items should be eaten, and whether they actually eat them. As a result, most of the items previously classified as "possibly avoidable", such as bread crusts and potato peels, were reclassified as edible.

On the other hand however, we decided to maintain the "De" classification. This is a part of food that may be edible, but the person who disposed of it did not want to eat or did not eat for whatever reason, and was intentionally removed. We do not intend to add De to the categories of Avoidable food waste, as we consider it a low priority as a reduction target. Category "De" was set up to indicate possibilities for the next step, to secure comparability with other sorting categorisation schemes, and for operational clarity of sorting under the Tokyo Method. By defining "De", it becomes clearer what falls under categories A, B, and C, that are priority items for food waste reduction. Hence we decided to look into depths on people's behaviour and attitudes towards items that tend to be removed at preparation and thrown away.

The methodology of this study is similar to that of Nicholes et al (2019), which is so far the only literature geared to the international audience with a focus on drawing a line between avoidable and unavoidable food waste. This paper is in response to it, describing an adaptation of their method applied in the UK to Japan, with a modified concept of categorisation.

As with Nicholes et al, we have conducted a questionnaire survey to the general public on the extent to which food parts are generally considered by the public as "edible" or "inedible". In our survey, the list of food items are modified to fit the current Japanese culinary custom, and their number was increased to 65 from Nicholes et al's 16, to designate more specific parts of food items. Also we adopted different criteria for deciding whether avoidable or unavoidable. Nicholes et al only asked about self-reported consumption and general perception of edibility, We asked about perceptions of normative, physical, and conditional edibility, as well as actual consumption. This paper reports the results of the survey and adds some discussion on the implications and relevance of categorisation of avoidable (edible) versus unavoidable (inedible).

2. MATERIAL AND METHODS

We have conducted a survey to the general public, utilising the internet survey panels of Intage inc*. The detail of the survey is as follows:

- Survey method: Internet survey
- Survey area: Nationwide (any region) in Japan
- Survey period: March 15 to 17, 2021
- Screening: We limited the respondents to those that eat regularly at home, are in charge of cooking dinner at least twice a week, and deal with disposing of food waste.
- Sample size: males and females in 6 age groups from 20s to 70s and over: quota was set at 100 per each stratum. Total 1,254 valid responses, including a few extra responses for each stratum in case of removing responses of doubtful quality. We found no objectionable responses, and treated all 1,254 responses as valid.
- Number of food (parts) items: 65.
- Questions and options: Please select all options that apply to your situation of eating /not eating the following foods (parts).

1) I think this food/part should be eaten
2) I think I could eat this food/part if I wanted to
3) I usually (most of the time) eat this food/part
4) I may or may not eat this food/part, depending on the type
5) I may or may not eat this food/part depending on how it is prepared
6) This food/part does not fall into any of the above categories

The 65 items (parts) are foods (parts) commonly found as Category D when sorting household waste according to the Tokyo Method. For example, tomatoes are the most commonly eaten vegetable in Japan, but were excluded from this survey because discarded tomatoes and tomato peels are rarely seen in household waste. We purposely included "tricky items"; those items that triggered a discussion among the researchers while devising the initial version of Tokyo Method, as well as those that the sorting staff found puzzled while conducting the sorting analysis.

The 65 items (parts) included 6 seafood items such as fish peels and shrimp tails; 10 fruits (parts) such as apple peels and banana peels; 39 vegetables (parts) for example peels of potatoes, carrots, and radishes, outer leaves and cores of cabbage, spinach and *komatsuna* stubble (stump), base of enoki and shiitake mushrooms, cucumber and bell pepper stems, and broccoli stalks. Finally, there are three incidental items such as burnt toast.

Options 1-5 asked whether the item was objectively (physically) or subjectively (normatively) considered edible, as well as the circumstances under which it was or could be eaten (conditional edibility); option 6 is for an item that none of option 1-5 applies. Basically they are items that the survey respondents consider inedible in all circumstances, or the food itself was unknown to them or they had never been eaten it. In other words, foods (parts) with an dominantly high value of option 6 compared to 1-5 should in theory fall into category "Di" in the Tokyo Method.

3. RESULTS AND DISCUSSION

Table 2 lists the 65 items in the order of "inedibility" (% of those who chose option 6). Through cross tabulation by gender and age, we found little gender difference. We limited the respondents to only those who are regularly engaged in meal preparation, and this condition may have contributed to the lack of difference. Regarding age, for some items, there was a higher recognition of potential edibility (response option 2) as age progressed (e.g., leaves of root vegetables). Older generations may be more knowledgeable on traditional ways of making use of the whole ingredient, or through experience they have come across methods to utilise parts that are usually not eaten (for example, watermelon rind could be pickled: more than 17% of those over 70 chose that this part could be eaten). However, there was not a big difference by age in actual consumption of items (option 3: e.g., hardly anybody regularly eat watermelon rind, less than 1% in almost every age group). For some items, the younger age groups were higher in actual consumption.

Regional differences were hard to detect. For example, it is being said that people in East Japan favours the white part of leek (negi) while those in West Japan do not mind eating the green part towards the top. However, there was no statistically significant difference in the proportion of any of the responses (options 1-6) regarding this part of leek.

Comparing the results of Nicholes et al (2019) with ours, both UK and Japanese consumers agree that crusts of sliced bread can be and is being eaten. Apple peel also turned up high in the edibility list for both countries, but while in the UK both actual consumption (78%) and perception (86%) are high, not many Japanese usually eat this item (response option 3: 18%) although they consider it can or should be eaten (options 1-5: 83%). UK consumers are more positive about eating potato skins (5th item in the ranking of edibility. Perception: 77%) than those in Japan (options 1-5: 52%). In Japan stems (e.g. that of broccoli) and outer leaves (e.g. cabbage) of vegetable are considered more edible than potato skin (see table 2), while in the UK it is the opposite.

TABLE 2: List of items in the order of "inedibility" (% of option 6).

92,7%	Shellfish shell	56,4%	Bottom of onion	24,8%	Pumpkin skin
92,0%	Corn husk	54,4%	Carrot petiole	24,6%	Shrimp tail
91,9%	Strawberry calyx	51,0%	Contents of the tip of banana	24,4%	Sudachi citrus (garnish)
90,5%	Corn cob	50,6%	Top of onion	23,8%	Fish bones
90,1%	Banana peel	48,5%	Potato peel	23,5%	Fresh parsley (garnish)
86,4%	Enoki stem (bottom 1 cm)	45,1%	Cabbage core	22,7%	Burnt food/dishes
86,0%	Edamame pods	44,1%	Lettuce core	21,9%	Shiitake stem
85,1%	Nut shells	40,4%	Fish guts	20,3%	Broccoli stems
82,5%	Brown skin of onion	39,7%	Komatsuna stubble	19,1%	Cut or sliced lemon (garnish)
81,6%	Watermelon seeds	38,7%	Food dropped on the floor	16,7%	Apple peel
77,6%	Apple core	38,4%	Leek stubble	15,0%	Inner membrane of mandarin
76,7%	Pumpkin wad	37,3%	Cut surface of daikon radish	13,6%	Enoki stem (3-5cm above the bottom)
74,4%	Green pepper calyx	36,2%	Daikon petiole	13,0%	Daikon leaves
73,7%	Mandarin orange peel	35,3%	Spinach stubble	12,6%	Tsuma (shredded radish, garnish)
73,4%	Peach peel	32,3%	Chive stubble	10,4%	Top green part of leek
72,2%	Watermelon rind	32,1%	Cabbage leaf core	10,1%	Fish skin
70,2%	Green pepper seeds	31,6%	Enoki stem (1-3cm above the bottom)	5,4%	Pizza crust edge
70,2%	Cucumber calyx	30,2%	Outer leaves of cabbage	5,3%	Rice grains left in cooker or bowl
68,9%	Pumpkin seed	30,1%	Daikon peel	3,3%	Bread crust
65,5%	Oil after deep frying	29,8%	Confectionery dropped on the floor		
63,1%	End of shiitake stem	29,7%	Carrot peel		
		29,4%	Outer leaves of Chinese cabbage		
		27,0%	Outer leaves of lettuce		
		26,2%	Chinese cabbage stubble		
		26,1%	Sweet potato peel		

The discrepancy between actual consumption and perceived normative and physical edibility varied depending on items. Notable results are mentioned in the analyses of each item in the sections below. Looking into the results of each item, we found that the food parts could be clustered into three groups: "Undoubtedly inedible group (Di)", "De and Di borderline group", and "Rather avoidable De (almost A or C) group. The reason why there was not a distinct "De" group is probably because of the intentional selection of the food parts.

3.1 Undoubtedly inedible group (Di)

This group consists of the following items (% of option 6): Shells of shellfish (92.7%), apple cores (77.6%), banana peels (90.1%), peach peels (73.4%), mandarin orange peels (73.7%), watermelon peels (72.2%), watermelon seeds (81.6%), strawberry calyx (green leaves attached to strawberry) (91.9%), brown onion skins (82.5%), pumpkin seeds (68.9%) pumpkin wads (soft part surrounding the seed) (76.7%), bell pepper seeds (70.2%), bell pepper calyx (74.4%), edamame pods (Figure 2A, 86.0%), cucumber calyx (70.2%), corn husks (92.0%), corn cobs (90.5%), nut shells (85.1%), bottom of enoki mushroom (86.4%), bottom of shiitake mushroom stem (63.1%), and used cooking oil (65.5%).

The peels, cores, and seeds of fruits, and seeds, calyxes, and roots of vegetables tend to be considered almost physically inedible, since less than 5% of the respondents answered "1 should eat" and more than 70% answered "6 other" with few exceptions.

Of the above, for apples, the core (Figure 2B) is classified as Di, but the peel (Figure 2C) is considered physically edible by 29.2% of the respondents who say it should be eaten and 17.6% who say it is usually eaten. In Tokyo Method, as a general rule fruit peels are classified as Di, with the exception of apple peels, which are classified as De.

It is not surprising that an overwhelming proportion (90.1%) chose option 6 for banana peels. However, we often find bananas discarded in waste sorting analysis with about 3-5 cm of the contents remaining with the peel (Figure 3A). Therefore, we asked about that portion as well (Figure 3B). While 20.0% responded that this portion should be eaten, 51.1% chose option 6. This means that more than half of the respondents answered that this part is not to be eaten. When we have found such items in the sorting analyses, we have been classifying them as "De" in the Tokyo Method. There was a discussion this part could even be considered as category C (unfinished leftovers) i.e., count them as avoidable. The results showed that many Japanese are rather surprisingly wasteful in eating bananas.

As for mandarin oranges, we often find in sorting analyses that only the juice inside the fruit is sucked out and the soft membrane of the sections inside is discarded (Figure 3C). We asked about this part, and found that many people eat the section membrane and consider that it should be eaten. In other words, if this part is discarded after absorbing the juice, it would be classified as De considering that the membrane is intentionally removed, while if the mandarin sections was discarded as is, it may be considered as B2 (whole fruit) or C (partly eaten).

For onions, its outer brown skin (Figure 3D) is designated as Di together with skin of corn cobs in the Tokyo Method as an exception to the general rule that vegetable skins are De. The bottoms of onions (56.4%, Figure 3E) and the tips of onions (50.6%, Figure 3F) are also designated as Di, however the survey results suggested it is difficult to say that they are absolutely inedible, since around 10% of the respondents answered, "1 should eat them" and "3 I generally eat them".

Regarding enoki mushrooms, we asked about three parts (Figure 4A). Enoki mushrooms are sold in bags each containing a bunch. The bags are often coloured or printed towards the bottom, and some consumers use the edge of printing as a guideline for cutting off the bottom part. Probably this is the reason why we find in sorting analysis bottom part of enoki cut off at line 3. Only the bottom-most part about 1 cm from the root was considered inedible by the respondents (Figure 4B), while the part above that, people consider edible and actually do eat (Figure 4C and 4D). Shiitake mushrooms, as with enoki mushrooms, which are both popular mushrooms in Japan, the bottommost part is considered inedible (Figure 4E) and the stem as edible and eaten (Figure 4F). These trends agree with the De / Di demarcation in the Tokyo Method.

3.2 De and Di borderline group

This corresponds to the group of food items with 30%~50% of the respondents choosing option 6 in the questionnaire. Category D is food (parts) that were intentionally removed and not eaten, and as mentioned earlier,

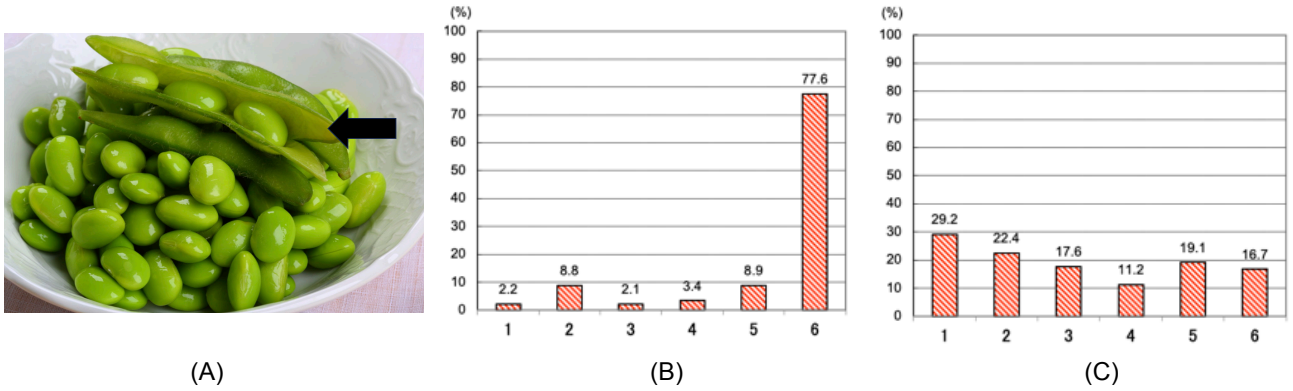


FIGURE 2: (A) Edamame Pod, (B) Apple Core, (C) Apple Peel.

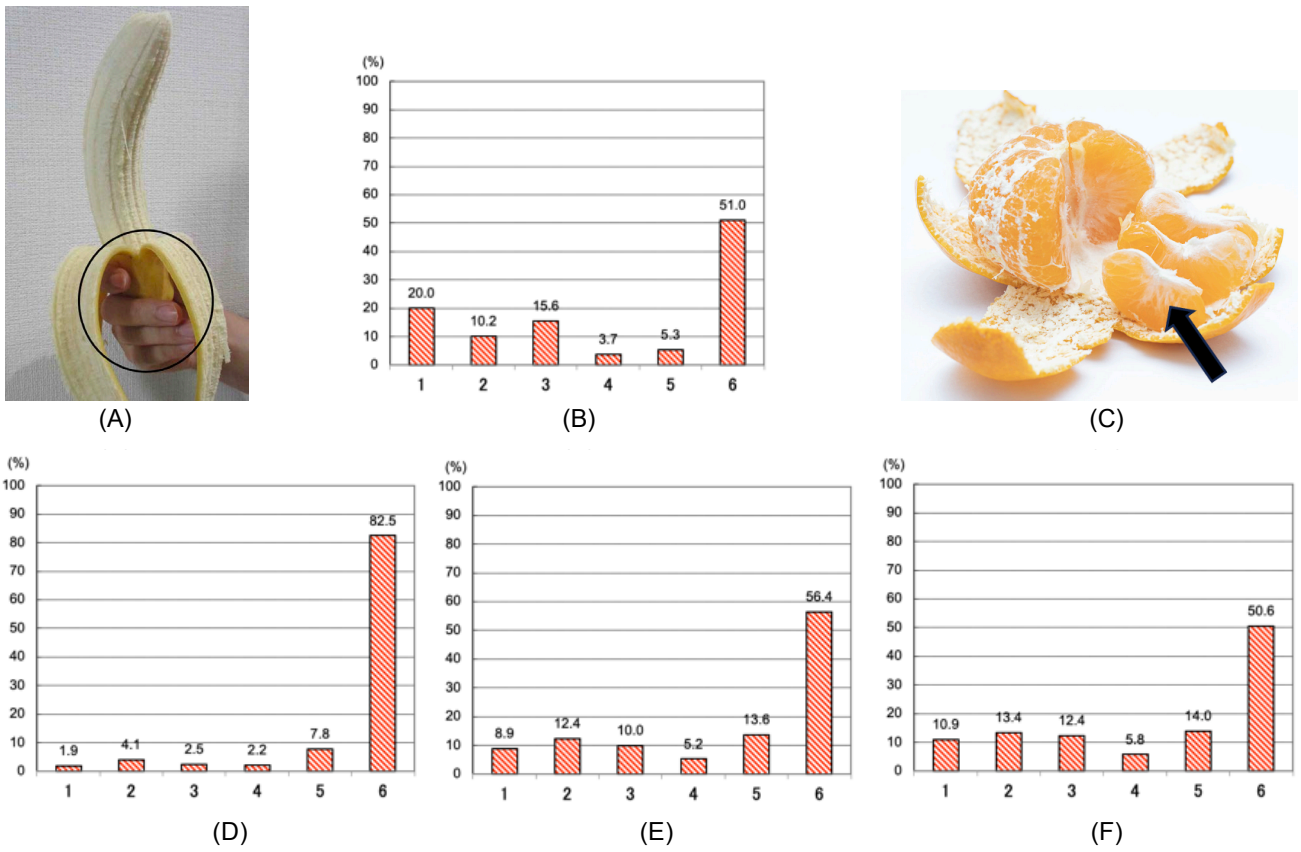


FIGURE 3: (A) Banana "handle", (B) Contents of the end of the banana, the part you were holding when you peeled and ate it, (C) Mandarin Sections, (D) Outer Onion Skin, (E) Bottom of Onion, (F) Tip of Onion.

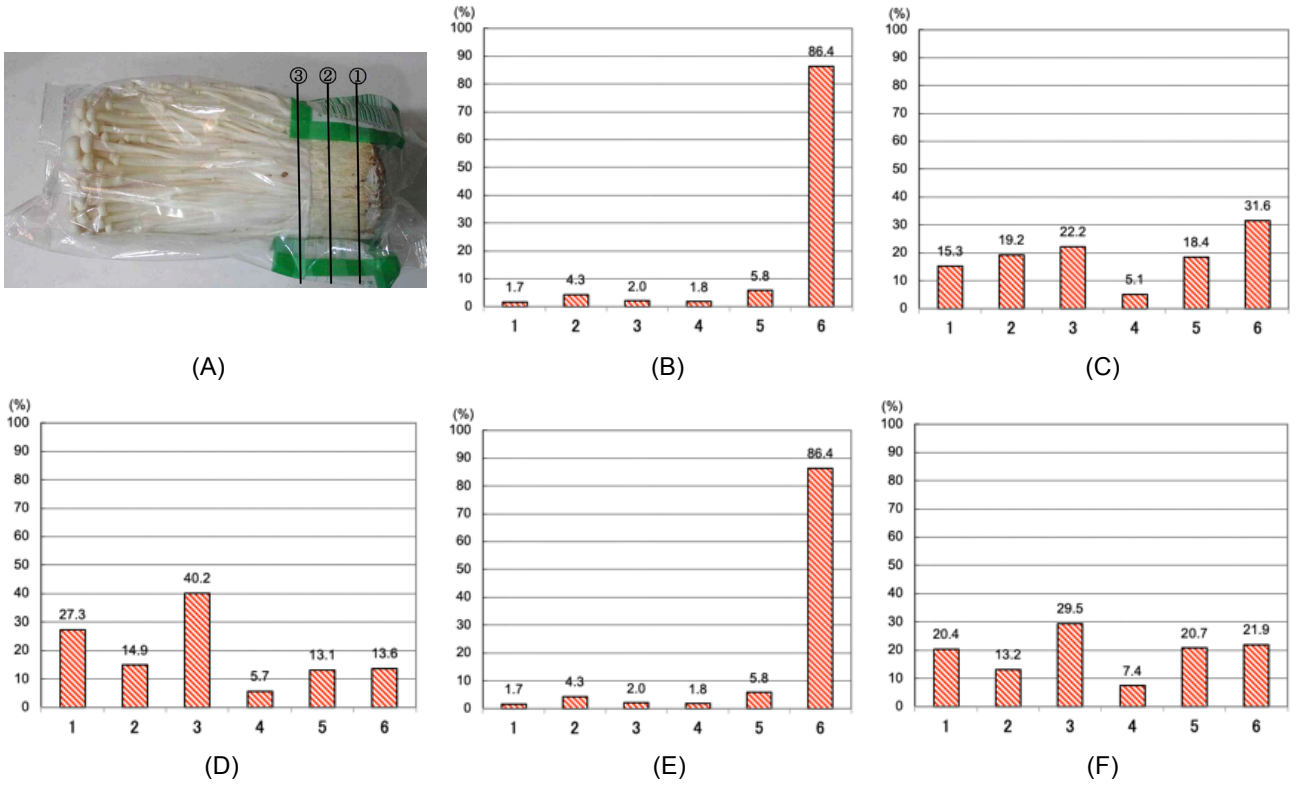


FIGURE 4: (A) Enoki Mushroom Sections, (B) Enoki cut at line (1), (C) Enoki cut at line (2), (D) Enoki cut at line (3), (E) End of Shiitake Stem, (F) Shiitake Stem.

Di is the part of a food item that is physically most difficult to eat. On the other hand, this group is understood as foods (parts) that are De (possibly edible) but near to Di.

The following food items are in this group: fish entrails, potato peels, carrot petioles (junction of carrot leaves and carrot), radish petioles, cut surface of partly used daikon, outer leaves of cabbage, outer leaves of Chinese cabbage, outer leaves of lettuce, lettuce core, cabbage leaf core, cabbage body core, Chinese cabbage stubble (stump), *komatsuna* stubble, spinach stubble, chive stubble, leek stubble, and the inner part of the tip of a banana (as mentioned earlier) also fall in this borderline group.

Regarding fish, we asked about entrails or internal organs (Figure 5A), bones (Figure 5B), and skin (Figure 5C). Fish skin was considered rather as an edible part. Fish bones were also considered to be an edible part of fish depending on the type of fish and the way it is cooked. This result may be attributed to the fact that many types of small fish are eaten whole, as a wide variety of fish is consumed in Japan. The same applies for shrimp tails (Figure 5D). Therefore, in the Tokyo Method, fish skin and small shrimp tails were considered De, while fish bones and large shrimp tails were considered Di.

As for potato peels (Figure 5E), 48.5% of respondents chose option 6, 6.3% was of the opinion "should eat," 4.8% said "usually eat," and 10.8% said "could eat if I wanted to," making it the part of the potato that "I could eat if I wanted to, but I don't eat much. The same tendency can be seen for the core of cabbage (Figure F), petiole of Japanese white radish - daikon (Figure G), petiole of carrot (Figure 5H), and the inner part of the end of a banana (mentioned in Section 3.1). The reason why carrot petiole is more "inedible" than the petioles of other root vegetable is probably due to their shape and toughness (Figure 5I). The outer leaf of cabbage (Figure 6A) was selected by 30.2% of respondents as "6", 14.1% as "should eat," 24.0% as "could eat if I wanted to,"

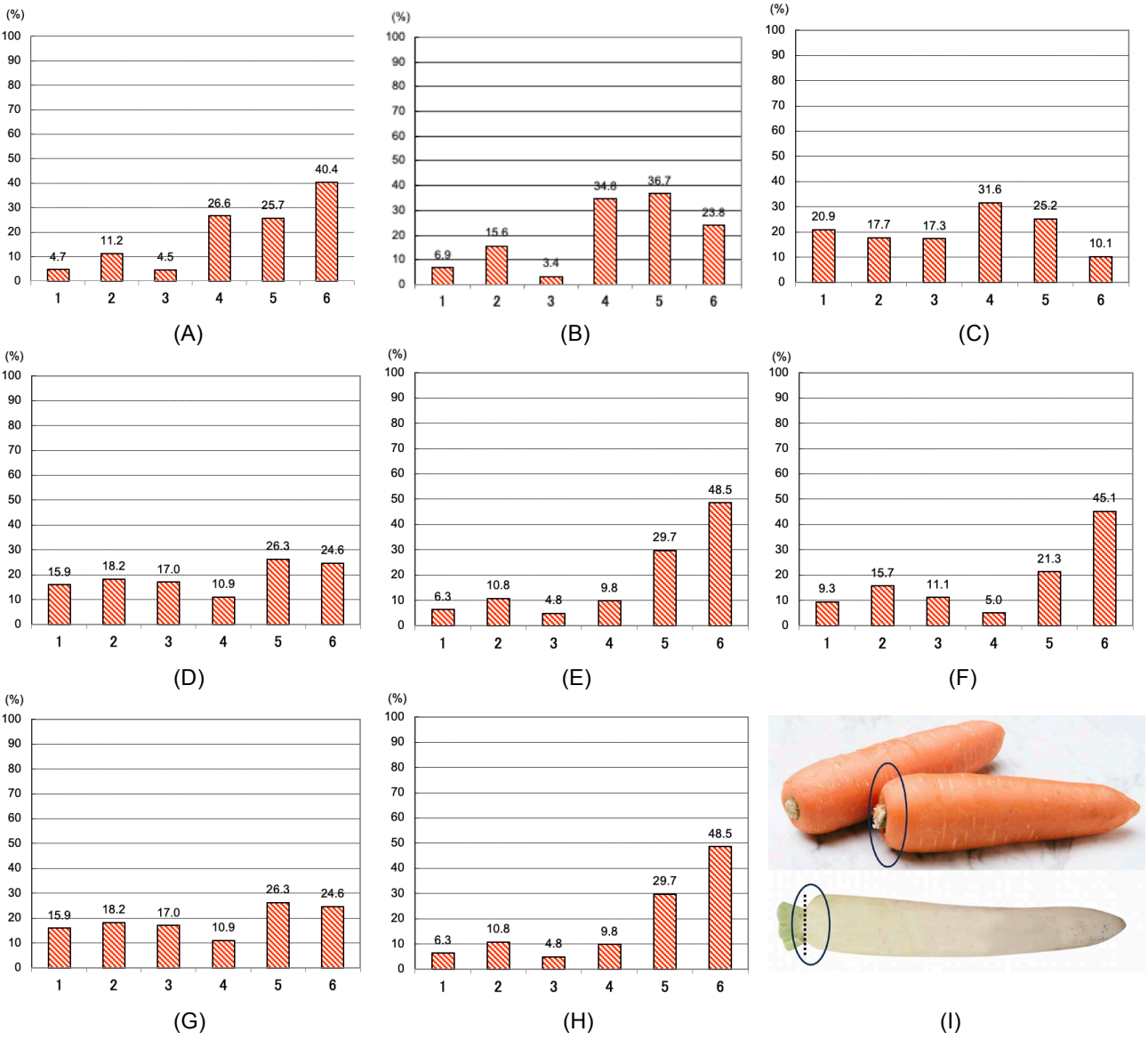


FIGURE 5: (A) Fish Entails, (B) Fish Bones, (C) Fish Skin, (D) Shrimp Tail, (E) Potato Peel, (F) Cabbage Core, (G) Petiole of Daikon, (H) Petiole of Carrot, (I) Petioles.

and 12.4% as “I generally eat”, indicating that it they are also parts that are perceived as edible but not eaten very often. The same tendency is observed for the outer leaves of lettuce (Figure 6B) and Chinese cabbage (Figure 6C). In general, we can say that the outer leaves of tuberous vegetables are perceived as the part of the vegetable that can be eaten but not very often in practice. At some supermarkets, these outer leaves are collected on the spot to be composted (Figure 6D). The results conform with our categorisation of these items as “De” in the Tokyo Method.

Daikon (Japanese radish) peels (Figure 6E) and carrot peels (Figure 6F) as well as sweet potato peels (Figure 6G), share a similar trend with that for shrimp tails (Figure 5D). Apparently, this is understood as a part of the food that may be eaten depending on the cooking. The pattern of responses for stubble of *komatsuna* (leaf vegetable similar to spinach), spinach (Figure 6H), stubble of thin green onion (chive) - Figure 6I, all fit into category “De”. In summary, this confirms the general principle in the Tokyo Method where vegetable peels and cores are considered De, with the exception of the brown peels of onions and corn cobs, which are considered Di.

3.3 Rather avoidable “De” (almost “Avoidable”) group

In the Tokyo Method, De is intentionally removed parts that could potentially be eaten. For many items in this

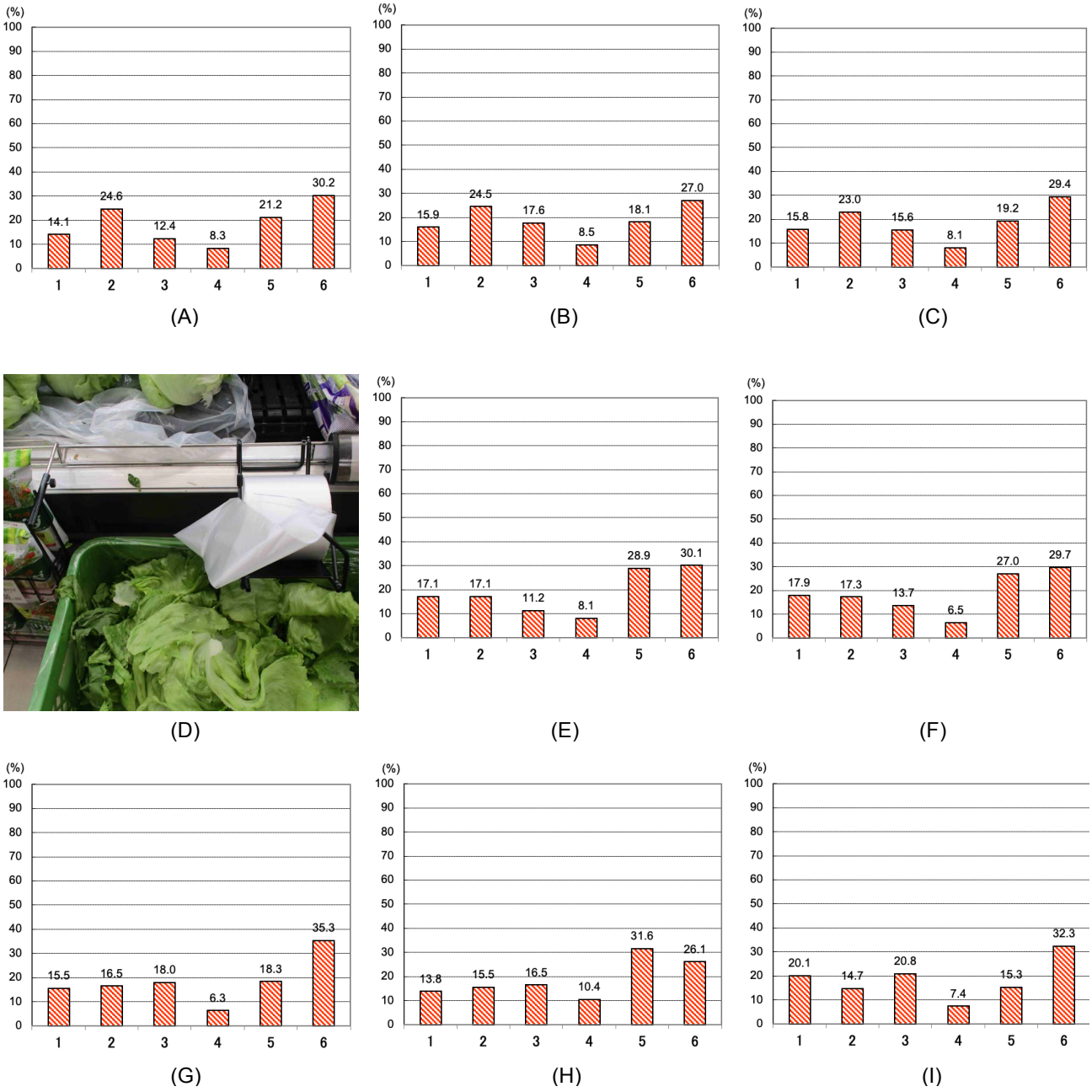


FIGURE 6: (A) Outer Leaves of Cabbage, (B) Outer Leaves of Lettuce, (C) Outer Leaves of Chinese Cabbage, (D) Collection of Outer Leaves at Supermarket, (E) Daikon Peel, (F) Carrot Peel, (G) Peel of Sweet Potato, (H) Spinach Stubble, (I) Chive Stubble.

group, it is often difficult to demarcate whether it is De or either partly used A (ingredients), B (prepared food) or C (unfinished items).

As accidental food items, dishes (cooked foods) dropped on the floor (Figure 7A) and confectionery dropped on the floor (Figure 7B) are considered edible, with just over 20% saying they could eat them if they tried to, while 13.9% said they would eat the item, and 38.7% said "6: none of the above". In other words, in the composition survey, such food will be classified as "C" leftovers, and sweets will be classified as "B2" both in the avoidable category, but the awareness of those who throw them away is De (intentionally not eaten). In Japan, shoes are usually not worn at inside the house. Therefore, it is thought that the number of people who will pick up and eat what was accidentally dropped on the floor at home is larger than that of those doing the same in a restaurant (homes with pets may be an exception). Accidentally dropped items had a higher value for actual consumption compared to normative edibility. People do not say they should be eaten, but they do sometimes eat them. For the accidentally burnt dishes (Figure 7C), 12.2% of the respondents answered "1) should be eaten", 25.6% answered "2) can eat if I want to", and 22.7% answered "6 none of the above (do not eat)", making them slightly more likely to be eaten than the dishes accidentally dropped on the floor (Figure 7B), but they are not actively eaten. In Tokyo Method, burnt dishes are classified as C uneaten or B2 cooked food, as such wastage (accident) could be avoided.

While developing the Tokyo Method, we had a good discussion on whether garnishes such as fresh parsley (Figure 7D) or cut /sliced lemon (Figure 7E)) found in waste sorting analyses should be classified as A: ingredients, C: plate leftovers, or De: intentionally removed. In the ques-

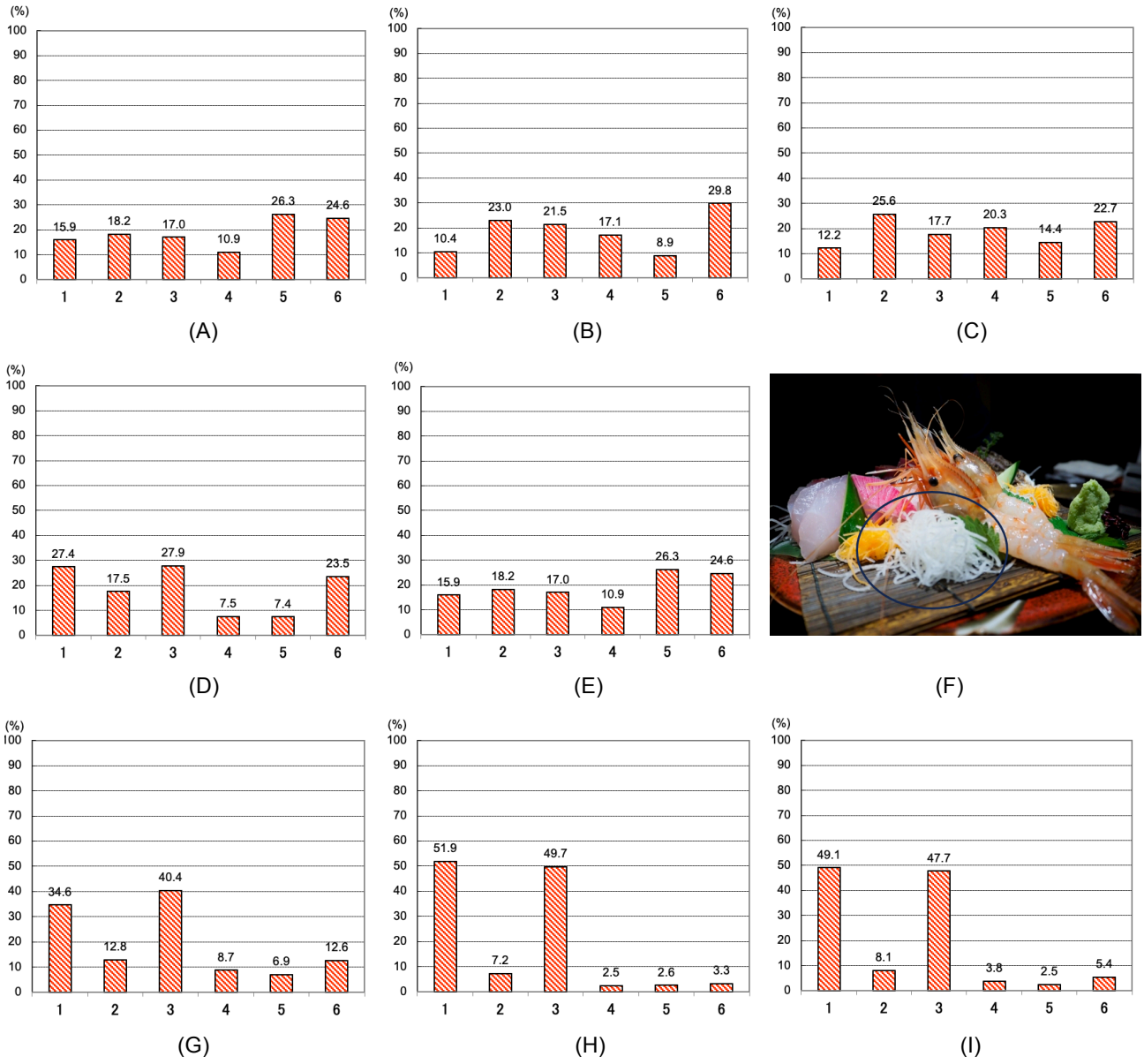


FIGURE 7: (A) Food Dropped on Floor, (B) Confectionery Dropped on Floor, (C) Burnt Dish, (D) Fresh Parsley, (E) Cut /Sliced Lemon, (F) Tsuma for Sashimi (photo), (G) Tsuma for Sashimi, (H) Bread Crusts, (I) Pizza Crust.

tionnaire survey there was not much difference between the responses of "rather should be eaten" and "I usually eat it", and "6 (do not eat it)". These foods were designated as De in the Tokyo Method.

Tsuma for Sashimi (Figure 7F) is thin slices of daikon (Japanese radish) that is mainly served with Sashimi (slices of fish to be eaten raw). Probably "tsuma" in packages of Sashimi sold in supermarkets is what Japanese people think of when they think of sashimi "tsuma". Japanese respondents were more conscious of eating tsuma for sashimi (Figure 7G), with 34.6% saying "1) they should eat it", 40.4% saying "3) they usually eat it", and 12.6% saying "6) not any of the above" (do not eat it). In the Tokyo Method this garnish is assumed generally as "De", however if it is evident that this tsuma was purchased specifically (e.g. a package of tsuma only, not as a garnish in a package of sashimi) it will be categorised as avoidable (category B).

Bread crusts were initially classified as possibly avoidable in the United Kingdom, and were reclassified as edible (Avoidable). In our survey, crusts of a slice of bread (Figure 7H)) were also recognized as a normally eaten part, with 51.9% of respondents saying "1) they should be eaten, 49.7% saying "3) I usually eat them", and only 3.3% saying "6) none of the above (do not eat them)".

From this result, bread crusts could be classified as unutilized food (A2p in Tokyo Method), however as in the initial stance of WRAP, we considered that bread crust that was cut off and discarded is De as it was intentionally removed (but potentially edible). On the other hand, pizza crust edge was considered as "C: leftovers", as in the preliminary workshops almost all participants expressed that pizza as a dish is served with the intention that the whole including the crusty edge is to be eaten. In the survey, pizza crust edge (Figure 7I) showed the same tendency as bread crusts, with 49.1% saying "1) should eat it", 47.4% saying "3) I usually eat it," and 5.4% saying "6 none of the above (do not eat)". Grains of cooked rice left in rice cookers and bowls showed exactly the same trend, and these were classified as "C: leftovers".

4. CONCLUSIONS

Nicholes et al. (2019) re-classified "possibly avoidable" items mostly as edible (avoidable), while we decided to classify those as unavoidable. This is because we believe that when actually considering measures to reduce avoidable food waste by half by 2030, the initial priority should be to encourage people to reduce readily avoidable food waste, for example, eat up fruits that are thrown away as whole, use up vegetables and meat that are half used and thrown away, avoid wastage of frozen foods and leftovers, etc., rather than to encourage people to eat chicken skin and potato skin.

It is possible to consider the "De" classification in the "Tokyo Method" as physically edible, and include it in the reduction target. However, that will make the message of reduction to the general public more complicated and can be confusing. It may be counterproductive to request too much and raise the hurdle for the less-aware consumers. In food waste reduction campaigns, often recipes are distributed that make use of often uneaten parts, but in most cases these are adopted by only those who are already aware and rather committed to reducing food waste. Such aspects may be part of the reason why some campaigns ended up with little impact. At this stage, at least in Japan, probably a focused approach on items that are obviously intended to be eaten would be more effective.

Although it is known from previous sorting analyses that category "De" has a significant percentage in total food waste, we cannot expect people to always eat these parts. For some dishes, people will need or want to peel potatoes, and people will not always want *kinpira* (a dish that could be made from daikon peel) whenever they have a daikon dish. For some removed parts, even if they may be potentially edible, it may be reasonable enough as an environmental behaviour if they were separately disposed of and directed to animal feed or composting.

Telling people to eat parts that they customarily remove intentionally is not a priority for food waste reduction measures, and this can be set aside as a secondary target for those who are already highly aware and committed, and for indicating the potential for future initiatives on making people aware that some parts that they regularly remove may actually be used for certain recipes.

One of the objectives of the Tokyo Method is to generate useful information for policymaking and for tackling with the reduction of food waste. As our results show, for many of the "marginally edible" items, there is a variety on actual consumption as well as perceived normative, physical and conditional edibility, and it is rather difficult to draw an accurate line between what should be considered edible and inedible. This also differs by geographical regions and cultures. It would still be useful when adopting the "Tokyo Method" in other regions, to investigate how a specific population categorises /comprehend different food items /parts. There is still room to improve the survey questions, for example which response options to be offered, which food items to ask, and how to indicate accurately which part of the food is in question - many of the often removed parts are difficult to be expressed in words, a visual expression may help as in the case of enoki mushroom this time. In assessing the results of such investigation, probably it is more useful to consider what should be included as priority targets for reduction of avoidable food waste, rather than trying to accurately assess the edibility of food items.

ACKNOWLEDGEMENTS

This research was funded by the Environment Research and Technology Development Fund (JPMEERF 20183005).

REFERENCES

Nicholes, Miranda J.; Quested, Tom E.; Reynolds, Christian; Gillick, Sam; and Parry, Andrew D. (2019) Surely you don't eat parsnip skins? Cartegorising the edibility of food waste, Resources, Conservation & Recycling 147 179-188

Okayama, Tomoko; Watanabe, Kohei; and Yamakawa, Hajime (2021) Sorting Analysis of Household Food Waste - Development of a Methodology Compatible with the Aims of SDG12.3, Sustainability 13(15) 8576; https://doi.org/10.3390/su13158576

detritus | Multidisciplinary Journal for Circular Economy and Sustainable Management of Residues

CISA

MATHEMATICAL MODELLING OF QUANTIFYING BIOETHANOL FUEL PRODUCTION FROM PINEAPPLE WASTE

Monzur Alam Imteaz [1,*], A.B.M. Sharif Hossain [2], Amimul Ahsan [3] and Parminder Kaur [4]

[1] *Department of Civil and Construction Engineering, Swinburne University of Technology, Melbourne, Australia*
[2] *Department of Biology, Imam Mohammad Ibn Saud Islamic University, Riyadh, Kingdom of Saudi Arabia*
[3] *Department of Civil and Environmental Engineering, Islamic University of Technology, Gazipur, Bangladesh*
[4] *Circular Economy Solutions, Geological Survey of Finland, 0210 Kuopio, Finland*

Article Info:
Received:
27 September 2023
Revised:
23 January 2024
Accepted:
26 February 2024
Available online:
20 March 2024

Keywords:
Climate change
Reuse
Waste reduction
Greenhouse gas
Bioethanol

ABSTRACT

Wider-scale implementations of bioethanol production from different wastes are not happening mainly due to lack of confidence on potential production and net benefit. With the aim of accelerating real-life implementations of more bioenergy productions, this paper presents development of a simple mathematical model, which can be used to evaluate potential bioethanol production capacity from pineapple waste under different input conditions. Based on an earlier experimental study, the mathematical model was developed depending on three contributing factors; pH, temperature and substrate concentration as considered in the earlier experimental study. Results from the developed mathematical formulation were compared with the experimental data from the earlier study. It is found that the developed model is quite capable to estimate potential bioethanol productions from pineapple waste. Model estimated results are having a coefficient of correlation of 0.84 with the measured data. Standard errors of the model's estimations are also quite low; RMSE = 0.49, MAE = 0.39 and RAE = 0.06. To facilitate a wider industrial generation, a basic mathematical model framework for economic analysis is proposed involving evaluation of net present values of future yields, as well as costs (initial and maintenance). Such mathematical model of economic analysis will help stakeholders on selecting optimum input parameters through optimised energy consumption.

1. INTRODUCTION

In the process of combating imminent climate change impacts energy sector plays a significant role. Due to the excessive usage of fossil fuel, the increase of CO_2 level in the atmosphere causing to global warming (Rudolph et al., 2015). It is well-established that bioethanol is one of the significant alternatives in abating greenhouse gas emissions (Hossain and Fazliny, 2010; Hossain et al., 2010). Conversion of waste product, feedstock or lignocellulosic residues into biofuel is a crucial choice for global potential of bioenergy. Bioethanol was used as a fuel in vehicles, either in a neat form or in a mixture with gasoline (Demirbas, 2007; Rosenfeld et al., 2018). Biofuel is renewable, could reduce petroleum imports, improve national energy security and reduce the reliance on petroleum from unstable areas of the world (Arijana et al., 2018). It has been a growing interest for many years because of its alternative green energy sources, consequently minimizing greenhouse gas (GHG) emission and finally help alleviate the rise of fuel prices (Rudolph et al., 2015). Any feedstock containing sugar can be used to produce ethanol. The main feedstock, sugar cane or molasses in Brazil and starch crops was used to produce bioethanol (Arijana et al., 2018). However, in the future, the most promising could be from cellulosic materials. Basically, ethanol can be obtained from three main groups of raw materials (feedstock). These are sugars like sugar cane, molasses and fruits (pineapple, banana and rambutan) (Fazliny et al., 2010, Hadeel et al. 2011, Imteaz et al. 2022) which can be converted to ethanol through fermentation, starches like corn and cassava which hydrolysed into fermentable sugar, and cellulose like wood and straw which can be converted to sugar by the action of mineral acid (Rosillo-Calle and Walter, 2006).

Bioethanol production can be obtained from renewable resource and different kind of sources including household waste, lignocellulosic biomass, waste crop and fruit wastes. Sugar, starch and lignocellulosic components are potentially converted into ethanol. These components are from biomass resources such as agriculture residues, herbaceous crops, forestry wastes, wastepaper, food waste, fruits wastes and other wastes (Fazliny et al., 2010). The

* Corresponding author:
Monzur Alam Imteaz
email: mimteaz@swin.edu.au

https://doi.org/10.31025/2611-4135/2024.18356

main potential feedstock for bioethanol yield was carbohydrate, which included starch sugar, cellulose and hemicellulose. A major potential feedstock for bioethanol was the waste crops (McAlloon et al., 2000). Much research has been done on the production of bioethanol from different sources including the main source, sugar cane, either in form of cane juice which is mostly produced in Brazil (Wilkie et al., 2000) or molasses in India (Ghosh and Ghose, 2003), fruit waste in Malaysia (Hossain, 2017).

Tiwari et al. (2014) studied the productions of ethanol from five different fruits (apple, berry, grapes, papaya and sapota) with inoculation of bacteria and reported that among the five fruits, rotten sapota (Manilkara Zapota) produced highest amount (9.4%) of bioethanol after 5th day of incubation. Productions of bioethanol including different forms of sugars from the peels of mango, papaya, pineapple and banana were studied by Jahid et al. (2018), who reported that although simple soaking of the peels in water and steaming can result the recovery of free sugars, however enzymatic hydrolysis using cellulase and xylanase enzymes resulted very good yields of different forms of sugars. They also reported that among the studied fruits, banana and pineapple are the potential ones to produce ethanol. Ingale et al. (2014) reported that pre-treated banana waste can be economically utilized as a cheaper substrate for ethanol production. They also reported that the maximum ethanol yield was 17.1 g/l after 72 h of incubation period of fermentation. Gosavi et al. (2017) studied productions of bioethanol from Indian water chestnut, sweet potato, jackfruit and pineapple through acid hydrolysis, which yielded fermentable sugar. They have reported that among the studied fruits, pineapple waste produced highest amount (0.90 mg/ml) of ethanol. Recently, Wandono et al. (2020) reported that pineapple peel waste containing carbohydrate and reducing sugar is a good feedstock for bioethanol production and one ton of pineapple produced 250 kg waste, and 2.5 kg of pineapple peel produced 1 liter of bioethanol with 27% content. They also reported that 4,125 tons of pineapple peel waste produced 4,125 kg of bioethanol.

In fact, potential production of bioethanol from different fruits vary, also for a particular fruit it depends on several different factors. Experimental studies on bioethanol productions are based on experiments with varying different factors, which were different for different studies. As such widespread implementations of such bioethanol production is not happening due to the absence any generalised relationship on potential production. Most of the stakeholders are in dilemma regarding individual benefits from such bioethanol production, as in some cases such production may turn out to be costlier compared to traditional fuel production. Also, in some cases such production indirectly may cause more GHG emissions, if the energy used for the conversion of bioethanol is from traditional sources. Karmee (2016) presented prospects and limitations of adoption of bioethanol generation and recommended detailed economic analysis of any industrial production considering all the factors including difference in prices of bioethanol and other fuel, as well as costs of establishing and maintaining such facility. For such analysis, costs of productions need to be optimised so that adoption of bioethanol yields a net benefit.

For an optimisation analysis, a mathematical model is a useful and efficient tool, which compares the current value of output energy to the costs of production process, incorporating major contributing factors as independent variables. Such modelling was never attempted for the case of bioethanol production from pineapple. Objective of this study was to develop a simple data-driven modelling framework, which can be applied to perform economic analysis of bioethanol production through the optimisation of magnitudes of input parameters. To the best of authors knowledge, this is a pioneer study on such data-driven modelling on bioethanol production from pineapple.

2. MATERIALS AND METHODS

2.1 Theoratical Background

Fermentation is the traditional process, which is used for the production of ethanol, and this is a common practice to use yeast as chemical precursors in the process of fermentation. The chemical equation of conversion of ethanol from sugar/glucose is as follows, details of which was provided by Maicas (2020):

$C_6H_{12}O_6$(glucose)/Fruits $\longrightarrow$ $2C_2H_5OH$(ethanol) / bioethanol fuel + CO_2 (carbon dioxide)

Hossain and Fazliny (2010) presented an in-depth experimental study on bioethanol generation from pineapple waste. They have experimented the influence of three salient factors such as pH, temperature and substrate concentrations on the generation of bioethanol from pineapple. This study develops a mathematical model for the quantification of bioethanol production based on the experimental results from Hossain and Fazliny (2010).

2.2 Methodology

Mathematical formulations were developed to expresses relationship between bioethanol general and each contributing factor studied in the study of Hossain and Fazliny (2010). The derived mathematical formulations were then integrated into a single equation as outlined shown Equation 1. Such type of mathematical function is commonly used for the predictions of algal/bacterial growth (Imteaz and Asaeda, 2000) and was recently successfully applied for the prediction of pollutants removal efficiency by Imteaz et al. (2021, 2020). Such formulation is based on the concept that there is a maximum level of achievable growth/removal/production for a certain process or system, which is affected and reduced by one or more limiting factor(s). Contributions of the factors to the maximum achievable magnitude can be amalgamated into the following single equation:

$$PEP=f(pH)*f(T)*f(SC)*MPP \quad (1)$$

Where, PEP is the potential ethanol production as weight % of biomass used, f(pH) is the factor for the influence of pH, f(T) is the factor for the influence of temperature, f(FP) is the factor for the influence of fermentation period and MPC is the maximum potential production. From

the experimental measured data of Hossain and Fazliny (2010), the relationships of f(pH), f(T), f(SC) were derived. Based on the study of Hossain and Fazliny (2010), the following expressions of f(pH), f(T), f(SC) are proposed:

$$f(pH) = \frac{(a_1 * pH^2 + b_1 * pH + C_1)}{Eth_{max}^{pH}} \quad (2)$$

$$f(T) = \frac{(a_2 * T^2 + b_2 * T + C_2)}{Eth_{max}^{T}} \quad (3)$$

$$f(SC) = \frac{(a_3 * SC + C_3)}{Eth_{max}^{SC}} \quad (4)$$

Where Eth_{max}^{pH}, Eth_{max}^{T} and Eth_{max}^{SC} are the maximum ethanol productions from individual experiments of varying pH, temperature and substrate concentration respectively. a_1, a_2, a_3 and b_1, b_2 are the coefficients. C_1, C_2, C_3 are the intercepts of the best-fit lines, when individual independent variable is zero. 'pH' is the pH of the solution, 'T' is the temperature in °C and 'SC' is the substrate concentration in 'gm/l'.

Potential ethanol production values for different combinations of independent parameters (pH, temperature and substrate concentration) were calculated using Equation 1. In the equation, the maximum potential production (MPP) was unknown. As such, MPP was calculated through trial assuming different values of MPP, until calculated PEP values closely matched with the corresponding measured values.

The following section describes final derived equation, its estimated values and comparison with the corresponding measured values. Performance of the developed model results were assessed with the common statistical measures such as Root Mean Squared Error (RMSE), Mean Absolute Error (MAE) and Relative Absolute Error (RAE), which are defined below. Also, a framework has been proposed for the proper analysis of benefit-cost ratio for such project considering time value of the money.

The RMSE of a predicted model with respect to the observed variable is defined with the equation.

$$RMSE = \sqrt{\frac{\sum_{i=1}^{n}(X_{obs,i} - X_{model,i})^2}{n}} \quad (5)$$

Where, X_{obs} is observed/measured values, X_{model} is modelled values at time i. 'n' is the number data.

The mean absolute error (MAE) is defined as the sum of the absolute value of the differences between all the measured values and modeled values, divided by the total number of predictions as outlined below:

$$MAE = \frac{\sum_{i=1}^{n}(X_{obs,i} - X_{model,i})}{n} \quad (6)$$

The Relative Absolute Error (RAE) is expressed as a ratio of cumulative errors to cumulative actual measured values, which is expressed as:

$$RAE = \frac{[\sum_{i=1}^{n}(X_{obs,i} - X_{model,i})^2]^{1/2}}{[\sum_{i=1}^{n}(X_{obs,i})^2]^{1/2}} \quad (7)$$

3. RESULTS

Experimental results of different bioethanol productions with varying pH, temperature and substrate concentration were extracted from Hossain and Fazliny (2010), which were the basis of current study on model development. In the study of Hossain and Fazliny (2010), there are nine sets of data with different combinations of input variables: pH, temperature and substrate concentration. As usual with other similar studies, for the assessment on the effect of a selected variable, the other variables were kept constant. Detailed derivations of f(pH), f(T) and f(SC) using the data from the experimental measurements of Hossain and Fazliny (2010) are described in the following section.

3.1 Derivation of Factors

While assessing the effect of varying pH, the temperature and substrate concentration were kept at 28°C and 1 gm/l respectively. Figure 1 shows the measured values of bioethanol production in % (v/v) for three different pH values. Figure 1 also shows the best-fit trendline with the pH values and corresponding bioethanol productions. From the trendline, the following best-fit equation of 2nd order polynomial is derived, which yields a coefficient of determination value of "1.0":

$$Eth_{pH} = -0.15*pH^2 + 1.7*pH + 2.68 \quad (8)$$

Where, Eth_{Sh} is the ethanol production in % (v/v) for any pH value under a temperature of 28°C with a substrate concentration of 1 gm/l.

Figure 2 shows the measured values of bioethanol production in % (v/v) under varying temperature, when pH and substrate concentration were kept as 5.5 and 3 gm/l

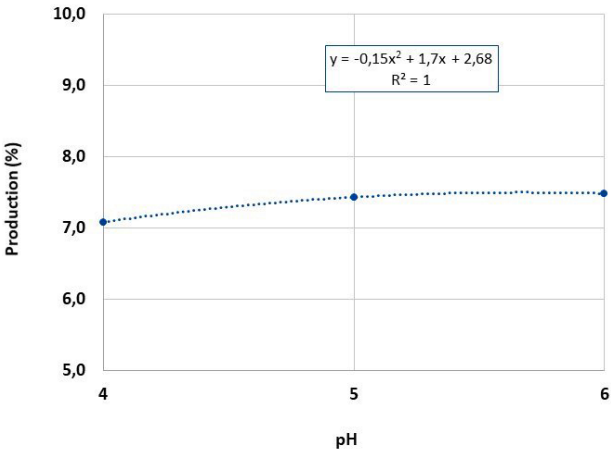


FIGURE 1: Effect of pH on bioethanol generation.

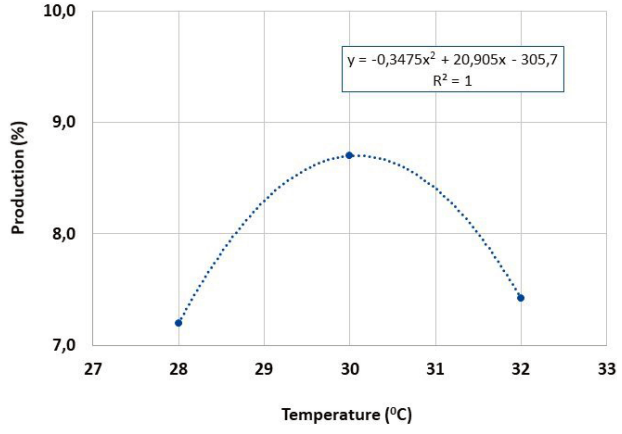


FIGURE 2: Effect of temperature on bioethanol generation.

respectively. Figure 2 also shows the best-fit trendline between the temperature and corresponding bioethanol production values. The best-fit trendline can be expressed with the following 2nd order polynomial, which yields a coefficient of determination value of "1.0":

$$Eth_T = -0.3475*T^2+20.905*T-305.7 \quad (9)$$

Where, Eth_T is the ethanol production in % (v/v) for any temperature (T) under a pH of 5.5 with a substrate concentration of 3 gm/l.

Figure 3 shows the measured values of bioethanol production in % (v/v) under varying substrate concentration, while pH and temperature were kept as 5.6 and 30°C respectively. Figure 3 also shows the best-fit trendline between the substrate concentrations and the corresponding bioethanol production values. The best-fit trendline can be expressed with the following liner equation, which yields a coefficient of determination value of "1.0":

$$Eth_{SC}=0.075*SC+7.735 \quad (10)$$

Where, Eth_{SC} is the ethanol production in % (v/v) for any substrate concentration (SC) under a temperature of 30°C with a pH of 5.6.

From the nine available measured values, replacing the derived functions for Eth_{pH}, Eth_T & Eth_{SC} into the Equations 2, 3 & 4 respectively, the corresponding values of f(pH), f(T) and f(SC) were evaluated. Eventually, replacing the calculated values of f(pH), f(T) and f(SC) into Equation 1, the potential bioethanol productions were calculated assuming the value of MPP (Maximum Production Production) through trials with the aim of achieving maximum correlation and least RMSE values between the measured and modelled values.

3.2 Developed Model

MPP value was determined through trial, assuming several reasonable values until a close fit between the measured ethanol productions and calculated productions was reached. Table 1 shows the calculated f(pH), f(T) and f(SC) values for different combinations of the selected independent variables; pH, temperature and substrate concentration. The table also shows the corresponding values of the model calculated potential productions, with the best 'MPP' value achieved of 9.0%.

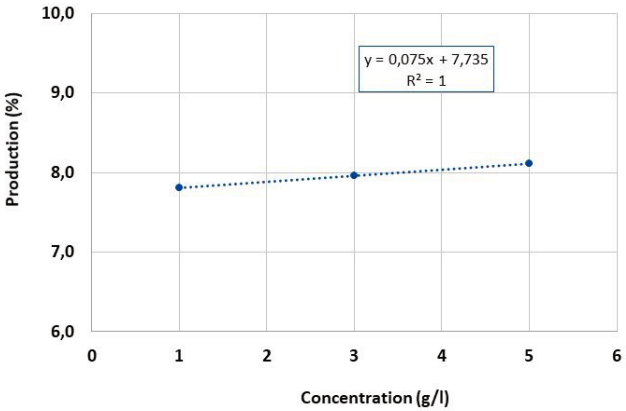


FIGURE 3: Effect of substrate concentration on bioethanol generation.

The usual practice of assessing such model results is to plot the model computed results with the experimental measured results on a single graph. Figure 4 shows the comparison between model calculated results and the experimental measured values. It is found that the model calculated values are having a correlation coefficient of 0.84 with the measured values. To evaluate the errors of the model calculated values the Root Mean Squared Error (RMSE), Mean Absolute Error (MAE) and Relative Absolute Error (RAE) values were calculated. The MAE, RMSE and RAE values evaluated for the model calculated values are "0.49", "0.39" and "0.06" respectively. All these values are quite low and can be considered as good achievement.

3.3 Framework for Economic Analysis

It is to be noted that in general the amount of yields from such bioethanol generation using fruit waste is not great and it is likely to take several years to achieve the payback of initial investment cost. Moreover, there will be ongoing operating and maintenance costs involved with such production. As the monetary benefit of the yields will be coming in future years, it is necessary to consider the present value of the future potential benefits which will be accumulated over the years using the Net Present Value (NPV) concept. Also, the future operation and maintenance costs need to be converted to net present values. Such eco-

TABLE 1: Calculated factors for different combinations of input variables.

Temperature (°C)	Substrate conc. (gm/l)	pH	f(T)	f(SC)	f(pH)	Estimated Production (%)
28	48	5.5	0.83	0.96	1.00	7.20
30	48	5.5	1.00	0.96	1.00	8.70
32	48	5.5	0.85	0.96	1.00	7.42
30	24	5.6	1.00	0.95	1.00	8.54
30	72	5.6	1.00	0.96	1.00	8.70
30	96	5.6	1.00	0.98	1.00	8.87
28	48	4.0	0.83	0.95	0.95	6.67
28	48	5.0	0.83	0.95	0.99	7.00
28	48	6.0	0.83	0.95	1.00	7.05

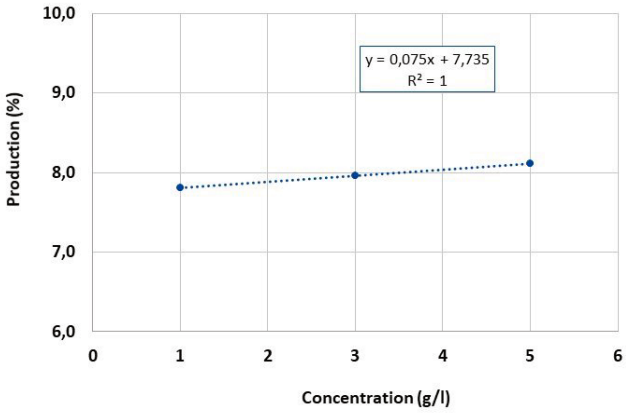


FIGURE 4: Comparison of model results with measured data.

nomic analysis is crucial for widescale implementations of bioethanol generation; without accurate estimations it may turn out to be not economically feasible. The total costs of the bioethanol generation can be calculated using following equation:

$$C = IC + \sum_{k=1}^{n} \frac{OM_k}{(1+r)^k} \quad (11)$$

Similarly, the accumulative benefits from the yields of the bioethanol production can be calculated considering variable price of bioethanol using the following equation:

$$B = \sum_{k=1}^{n} \frac{P_k}{(1+r)^k} \quad (12)$$

In the above equations, 'B' is the total accumulated benefit, 'C' is the total accumulated cost, r = internal rate of return (%/year), n = design life in years, 'P_k' is the variable future price of the bioethanol in in a year 'k', 'IC' is the initial investment cost of the system and 'OM_k' is the future annual operational and maintenance cost for a year 'k'. These equations should be considered simultaneously to evaluate total costs and return for a particular design life of the production system. Through comparing total costs and benefits the industries would be able to quantify actual benefits, which will encourage widespread implementations of such sustainable energy generations. For the current study, as no data was available on energy spent in the production process, as well as associated costs, the complete economic analysis was not performed.

4. CONCLUSIONS

With the aim of enhancing biofuel generation from different fruit/vegetable wastes, this paper presented development of a simple mathematical model for the estimation of potential bioethanol production from pineapple waste. The basic model was developed based on three contributing variables, which were extracted from an earlier experimental study on bioethanol productions from pineapple waste under different input conditions; pH, temperature and substrate concentration. For each of the studied variables, based on the earlier experimental measurement a contributing factor was derived. Then all the derived factors were multiplied with a maximum production capacity value to evaluate the potential bioethanol production. Model predicted values were compared with the experimental measurements and it is found that the model estimations are very close to the measured values having a good correlation coefficient of 0.84. Other standard statistical error parameters (RMSE, MAE and RAE) were also found to be low, revealing the fact on model's predictive capability. Such kind of model would be very useful for stakeholders of industrial-scale generation on their decision making while selecting appropriate magnitudes of the input variables related to the bioethanol production.

Such type of data-driven modelling approach was never explored for the generation of bioethanol from pineapple waste, although wider-scale implementations of such sustainable generation would help reducing carbon footprint through two ways; reducing waste and generating energy from sustainable source. From the experimental results it is clear that except substrate concentration, for other input variables there are certain optimum stages which yield maximum bioethanol productions. It is found that increasing temperature up to 30°C and a slightly acidic (pH<6) environment causes to maximise the production. Achieving such optimum conditions are associated with additional cost, which should be minimized to achieve a higher benefit-cost ratio. A framework for economic analysis incorporating net present values of the costs and yields is proposed. In the current study a complete economic analysis was not possible due to lack of data. It is recommended that future studies should incorporate a complete economic analysis with further data on cost and production amount.

It is to be mentioned that the proposed model was developed having three independent variables only, which was due to limited availability of the experimental data. One can explore to find additional factor(s) affecting the bioethanol production and if found the additional factor(s) can be easily incorporated in the existing model formulation. Nonetheless, the current model will be the foundation being a primitive effort in this data-driven model. More rigorous experimental measurements will be required to establish potential effect of any additional factor(s). Also, the proposed individual relationships of mentioned variables with the bioethanol generations are based on a single set of experiments with only 3 measurements for each variable. Validation of such relationships through more experiments warrants focus of any future study. Same methodology can be employed to develop similar data-driven models for other fruit/food waste.

REFERENCES

Arijana, B., Marđetko, N., Semjon, K., Galina, M., Halina, B., Mirela, Š., Draženka, K., Srđan, N., Božidar, Š., 2018. Bioethanol Production from Renewable Raw Materials and Its Separation and Purification: A Review. Food Technol. Biotechnol. 56(3): 289–311. https://doi.org/10.17113/ftb.56.03.18.5546

Demirbas, A., 2007. Progress and recent trends in biofuels. Prog. Energy Combus. Sci. 33, 1-18.

Ghosh, P., Ghose, T.K., 2003. Bioethanol in India: recent past and emerging future. Advances in Biochemical Engineering/Biotechnology 85, 1–27.

Gosavi, P., Chaudhary, Y., Durve-Gupta, A., 2017. Production of biofuel from fruits and vegetable wastes, European Journal of Biotechnology and Bioscience, 5(3), 69-73.

Hadeel, A., Hossain, A.B.M.S., Latifa, K., ALNaqeb, H., Abear, J., Norah, A., 2011. Bioethanol fuel production from rambutan fruit biomass as reducing agent of global warming and greenhouse gases, African J. Biotechnol. 10(50), 10157-10165.

Hossain, A.B.M.S., 2017. Fruit Biomass Derived Bio-ethanol production: Its Physical, Chemical, Biochemical Mechanical, properties and Bio-energy Generation. Adv. in Bioresearch 8 (5):238-244.

Hossain, A.B.M.S., Boyce, A.N., Salleh, A., Chandran, S., 2010. Impacts of alcohol type, ratio and stirring time on the biodiesel production from waste canola oil. African J. Agr. Res. 5: 1851-1859.

Hossain, A.B.M.S., Fazliny, A.R., 2010. Creation of alternative energy by bio-ethanol production from pineapple waste and the usage of its properties for engine. African J. Microbiology Res. 4: 813-819.

Imteaz, M.A., Ahsan, A., Kaur, P., 2020. Mathematical Modelling for predicting pollutants removal efficiencies of an electrolysis system, Water, Air, & Soil Pollution 231 (438). https://doi.org/10.1007/s11270-020-04809-2

Imteaz, M.A., Asaeda, T., 2000. Artificial mixing of lake water by bubble plume and effects of bubbling operations on algal bloom, Water Res. 34(6), 1919-1929.

Imteaz, M.A., Bayatvarkeshi, M., Kaur, P., 2021. Mathematical modelling for predicting Methylene Blue removal efficiency through adsorption using activated carbon of Parthenium Hysterophorus, Water, Air, & Soil Pollution, 232 (264). https://doi.org/10.1007/s11270-021-05216-x

Imteaz, M., Hossain, A.B.M.S., Maryam, B., 2022. A Mathematical modelling framework for quantifying production of biofuel from waste banana. Env., Dev. and Sust. 1-13. https://doi.org/ 10.1007/s10668-021-01517-7.

Ingale, S., Joshi, S.J., Gupte, A., 2014. Production of bioethanol using agricultural waste: Banana pseudo stem. Brazilian J. Microbiology 45(3), 885–892. https://doi.org/10.1590/s1517-83822014000300018.

Jahid, M., Gupta, A., Sharma, D.K., 2018. Production of Bioethanol from Fruit Wastes (Banana, Papaya, Pineapple and Mango Peels) Under Milder Conditions, J. Bioprocessing & Biotechniques 8(3), 1000327.

Karmee, S.K., 2016.) Liquid biofuels from food waste: Current trends, prospect and limitation, Renewable and Sust. Energy Rev. 53, 945–953.

Rosenfeld, J., Lewandrowski, J., Hendrickson, T., Jaglo, K., Moffroid, K., Pape, D., 2018. A Life-Cycle Analysis of the Greenhouse Gas Emissions from Corn-Based Ethanol. Report prepared by ICF under USDA Contract No. AG-3142-D-17-0161, Washington DC.

Rudolph, M., Antonio, D.R., Anna, A.C., Dela, C., Quinto, A.S, Paul, R.C., Maria, N., Dimaano, R., 2015. Bioethanol production from pineapple (Ananas comosus) peelings using Saccharomyces cerevisiae as fermenting yeast with ocus on fermentation pH. Int. J. Eng. Res. & Tech. 4 (50): 356-360.

Tiwari, S., Jadhav, S.K., Sharma, M., Tiwari, K.L., 2014. Fermentation of Waste Fruits for Bioethanol Production, Asian J. Biological Sciences 7 (1): 30-34, https://doi.org/10.3923/ajbs.2014.30.34.

Wandono, E.H., Endang, K. and Yanto, H. (2020). Analysis of potential bioethanol production from pineapple (Ananus commosus L. Merr) peel waste Belik district,Pemalang central java. AIP Conference Proceedings 2296, 020015, https://doi.org/10.1063/5.0030343.

Wilkie A.C., Riedesel, K.J., Owens, J.M., 2000. Stillage characterization and anaerobic treatment of ethanol stillage from conventional and cellulosic feedstocks. Biomass and Bioenergy 19, 63-102.

detritus | Multidisciplinary Journal for Circular Economy and Sustainable Management of Residues

CISA

RECYCLING OF POTENTIAL HAZARDOUS STONE WOOL INTO A NON-HAZARDOUS NEW STONE WOOL

Theresa Sattler [1,*], Klaus Doschek-Held [2], Anna Krammer [2], Roland Pomberger [1] and Daniel Vollprecht [3]

[1] *Department of Environmental and Energy Process Engineering, Montanuniversitaet Leoben, Franz-Josef-Straße 18, A-8700, Leoben, Austria*
[2] *Department of Environmental and Energy Process Engineering, Montanuniversitaet Leoben, Chair of Thermal Processing Technology, Franz-Josef-Straße 18, A-8700, Leoben, Austria*
[3] *Institute of Materials Resource Management, University of Augsburg, Am Technologiezentrum 8, D-86159, Augsburg, Germany*

Article Info:
Received:
22 September 2023
Revised:
31 January 2024
Accepted:
9 February 2024
Available online:
20 March 2024

Keywords:
Mineral wool waste
Recycling
Stone wool
Hazardous waste
Leaching behaviour
Wool2wool

ABSTRACT

Mineral wool products are man-made vitreous fibres (MMVFs), such as glass wool and stone wool, mainly used for thermal and acoustic insulation. Demolition of buildings generates mineral wool (MW) waste. With regard to the intended recycling of materials, the European Union's circular economy package currently foresees a landfill ban for certain waste streams by 2030. As a result, Austria will have a landfill ban for MMVFs from 2027. This paper presents an investigated route for the recycling of MW waste into new mineral wool (wool2wool). The recycling route aims to conserve valuable and limited landfill volume and enables the reduction of primary resource consumption and CO_2 emissions. The investigation was based on pH-dependent leaching tests of the fibres according to ÖNORM EN 14429 and hydrogeochemical modelling using LeachXS/Orchestra to identify the solubility-controlling mechanisms. The next step was a thermochemical treatment using correction materials to adjust the chemical composition, followed by rapid cooling through a spinning process. Another focus was on the theoretical determination of the dynamic viscosity to ensure suitable flow behaviour during fibre production. The chemical composition of the mineral wool produced was analysed, and it was shown that the target formulation could not be achieved for all elements within the permitted variation. The variations were due to the dissolution of the kiln lining, which had a more significant influence on the experiment than expected. Overall, the recycling pathway showed a high potential for CO_2 savings, resource savings and other environmental benefits by recycling waste that is currently landfilled.

1. INTRODUCTION

The 2030 Agenda for Sustainable Development of the United Nations (UN) proclaimed 17 Sustainable Development Goals (SDGs) in addition to the Millennium Development Goals (MDGs) (United Nations 2015). The recycling of mineral wool waste can be expected to contribute to the achievement of some of these goals, as waste management is only indirectly addressed in the SDGs. It should also enable the implementation of the Austrian landfill ban for mineral wool waste from 2027 (DepVO 2021).

Mineral wool is the generic term for a man-made vitreous fibre made primarily from glass (glass wool), igneous rock (stone/rock wool) and slag (slag wool). Mineral wool products are used as insulation and in horticulture. Mineral wool waste causes waste management problems due to its high volume and low density. Currently, most of Austria's mineral wool waste is landfilled and not recycled (Sattler et al. 2020a). As it is mandatory to landfill mineral wool waste in big bags in separate landfill compartments, this results in a 400-fold difference in Young's modulus between the general Construction and Demolition (C&D) waste and the mineral wool compartments (Sattler et al. 2020b), causing serious accidents in the form of overturned vehicles due to sudden ground settlement when crossing the landfill and driving on the unstable mineral wool body (Huber 2019). The positive effect of briquetting mineral wool waste on density and strength was shown, where the bulk density of glass wool and stone wool was increased up to 100 times. Therefore, briquetted mineral wool waste is expected to be more stable in landfill than loose mineral wool waste (Sattler et al. 2019).

In line with the waste hierarchy, priority however should be given to recycling rather than landfilling. Studies have

* Corresponding author:
Theresa Sattler
email: theresa.sattler@unileoben.ac.at

https://doi.org/10.31025/2611-4135/2024.18355

shown that recycling mineral wool waste (glass wool waste and stone wool waste) in the cement industry can decrease production costs, saves primary raw materials and decreases CO_2 emissions in production, and can also save valuable landfill space (Sattler et al. 2020c). Another way in which mineral wool can be recycled is as supplementary cementitious material (SCM) (Doschek- Held et al. 2023), (Sattler et al. 2020d). It can also be used to produce alkali-activated materials (AAMs) (Yliniemi et al. 2016). AAMs are alternative binder systems, activated by alkaline solutions, such as water glass and alkali hydroxides and are used to create concrete-like structures (Tuorila et al. 2020), (Steindl et al. 2023).

From the point of view of the waste hierarchy, a recycling at the mineral wool plant is preferable. Currently, mineral wool manufacturers only take back their own new, non-hazardous mineral wool waste for recycling. This is because mineral wool fibres may have adverse health effects in case of low solubility in the human lung (Muhle et al. 1998), (Costa & Orriols 2012) which is generally not known for old mineral wool fibres in C&D waste. The carcinogenity of mineral wool fibres depend on their dimension, dosis and durability (Barly et al. 2019). A dimension with a length of more than 5 µm, a diameter of less than 3 µm and a length-to-diameter-ratio of 3 or more is considered as "critical" for lung dieseases according to the World Health Organization (WHO), so that such fibres are called WHO fibres (IARC 1988). However, even WHO fibres can be destroyed in the human lung by so-called clearing mechanisms. The dwell time of a fibre in the human lung is described by the biopersistance which is affected by mechanical clearance mechanisms and biochemical dissolution (IARC 1988). Therefore, since the 1990s many countries introduced compulsory biosolubility tests for newly produced mineral wool (97/69/EC 1997), (GefStoffV 2010) and the industry developed corresponding labels such as RAL (RAL 2023) and EUCEB (EUCEB 2023). The EUCEB (EUropean CErtification Board for mineral wool products) was established in 2000 to increase the confidence of authorities, customers, and consumers in the safety of mineral wool. The general purpose of these labels is to provide voluntary certification that the manufactured fibres have a chemical composition within the ranges of the approved reference fibres. In these in-vivo tests, mineral fibres are implanted into animals and after 40 days the animals are killed and the number of still existing fibres is compared with the initial amount. An alternative are in-vitro-tests in which the lung environment is modelled by experimental solutions. In this case the pH values of the extracelular environment (7.4) and within the macrophages (4.5) must be investigated (Oberdörster 1991). For stone wool, a mineral wool subgroup, the biosolubility increase was reached by a higher alumina content (Guldberg et al. 2000) but it has to be considered that the dissolution rates of the fibres are also influenced by the binder of the stone wool (Wohlleben et al. 2017). The relation between the Al content and the biosolubility is highly complex. For Al/(Al+Si) ratios below 0.1, which is typical for glass wool, the dissolution rate at pH 7.4 decreases with increasing Al content, whereas it increases with increasing Al content above ratios of 0.2 which are typical for stone wool (Guldberg et al. 2000). It has to be mentioned that the observed trend is only valid for pH 7.4 which is typical for the pleural fluid. In the macrophages at pH 4.5 also low-Al stone wool dissolves well which has to be considered in an overall health assessment. In consequence, for stone wool, "new" products with Al_2O_3 concentrations of 19 to 22 wt% and SiO_2-concentrations of 37 to 43 wt% compared to "old" products with Al_2O_3 concentrations of around 14 wt% and SiO_2 concentrations of about 46 wt% were produced. However, due to the landfill ban, demolition and waste management face a severe challenge and request manufacturers to recycle all mineral wool waste. For this purpose, it is necessary to investigate how old, hazardous mineral wool waste can be spun into new mineral wool. The adverse health effects of hazardous mineral wool are thought to be determined by certain fibre characteristics such as fibre length, fibre diameter and also in vivo durability and persistence (IARC 1988). In vivo tests (Eastes et al. 2000) and in vitro tests (Guldberg et al. 2001) found that an increasing aluminium content and decreasing silicon content increased the dissolution/degradation rate at an acidic pH in stone wool, which is preferable from a health point of view. However, beside the aspect of health, the chemical composition effects the properties of the melt. The implementation of the aforementioned EUCEB certificate led to an increase in the aluminium oxide content of stone wool products. This circumstance is essential for the chemical modification in a wool-to-wool recycling concept and influences the thermal behaviour of the melt, e.g. the dynamic viscosity, during the fibre production process.

This study aimed to investigate the recycling of low aluminium mineral wool in order to obtain new mineral wool with a higher aluminium content. The results of this work show that it is possible to recycle mineral wool waste by conditioning it with other correction materials.

2. MATERIALS AND METHODS

2.1 Sampling

In order to obtain a representative sample material of mineral wool waste, a staggered sampling was conducted at an Austrian landfill. The waste material was collected from each truck over the course of a month, and then placed in hermetically sealed bags. 13 stone wool waste samples were taken.

Seven mineral wool product samples were purchased from Austrian construction markets.

2.2 XRF analyses

The chemical composition of the mineral wool waste and mineral wool product samples, as well as the new mineral wool spun in this study, was determined by XRF. The fiber samples were milled and analysed for loss on ignition at 1025°C before producing melt-fused tablets. Subsequently, the chemical composition was determined using X-ray fluorescence spectroscopy (XRF) by a Panalytical XRF instrument (Axios PW2400) from CRB GmbH at a voltage of 60 kV.

2.3 Chemical composition and solubility of stone wool

Three stone wool samples (SW_1, SW_2 and SW_3) were selected from the 20 available (13 waste samples, 7 products) for further experiments based on their chemical composition. pH-dependent leaching tests based on ÖNORM EN 14429 were conducted to study the solubility of the samples (Bauer 2021). The shredded samples weighing 25 g were suspended in 1 L of ultrapure water and shaken for 48 hours using an overhead shaker at 6 rpm. To achieve the desired pH level, a predetermined amount of acid or base, determined in separate pre-tests, was added before the experiments. After completion of the experiments, the solutions were separated from the solids through filtration at 0.45 µm. In contrast to the study of Guldberg et al. (2000) who determined dissolution rates, i.e. kinetic constants, in this approach a thermodynamic equilibrium between solid and aqueous solutions should be achieved. Prior to the leaching tests, samples were comminuted using an Eirich mixer to maximum fibre lengths of 1 to 1.5 cm. In deviation to the standard, a liquid/solid (L/S) ratio of 15 instead of 10 was chosen to prevent complete absorption of the liquid by the solid, which had been observed for L/S = 10. The leachate was analysed after the experiment for pH, filtrated at 0.45 µm and analysed for cations using inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7500 CE) and for anions using ion chromatography (IC, Thermo Fisher Scientific ICS 2000). The leachable concentrations at all pH values were used as input for hydrogeochemical modelling which was done using LeachXS/Orchestra and the Minteqv4 database. The program uses the maximum leachable concentrations as "available" concentrations and predicts the precipitation of solid phases from this hypothetical solution as well as the sorption of dissolved species to sorbents such as hydrous ferric oxides (HFO). The modelling strategy was based on the inclusion of all phases possibly precipitating from the solution. If the model yielded lower concentrations than in equilbrium with these phases, the corresponding phases were excluded from the model. This procedure was applied iteratively until modelled and analysed leached concentrations matched each other. Since carbonate was not determined in the leachates due to the rapid interaction with the atmosphere, the available carbonate concentrations were fitted to the measured Ca concentrations since calcite saturation is suggested to be a leaching controlling mechanism. The corresponding values were 20,000 mg/kg dry matter (DM) for the Al-rich samples and 500 mg/kg DM for the Al-poor sample.

2.4 Wool2wool – Mineral wool recycling

The stone wool sample with the lowest aluminium content, i.e. 1.65 wt%, was selected as the conditioned sample due to its presumed low solubility. This value is far below the "old" stone wool composition given in the literature and rather suggests a high solubility (Guldberg et al. 2000). The target formulation in the experiment was the chemical composition of a new, non-hazardous mineral wool. The Urbain model was used to ensure comparability with the dynamic viscosity published by Peternelj et al. (2017). The dynamic viscosity was calculated for the chemical composition of the melt of the newly spun mineral wool and the target composition range using the EUCEB deviation criteria.

TABLE 1: Amount of stone wool and residual correction materials.

component	weight [g]
stone wool (SW_3)	17,500.0
dolomite slurry	7,001.6
corundum dust	7,001.1
SiO_2 (pure)	2,455.0
MgO (pure)	1,049.0

2.4.1 Chemical composition and dynamic viscosity

In order to achieve the target composition (Table 3), the appropriate amount of addition of waste and correction materials to be added to the stone wool was calculated, using a Microsoft Excel Solver Add-In; these correction materials were dolomite slurry and corundum dust, while SiO_2 and MgO were added as pure materials (Table 1). The chemical composition of the stone wool, dolomite slurry and corundum dust are shown in Figure 1.

To calculate dynamic viscosity, an aluminium oxide content of stone wool ranging from 14 to 18 wt% (Yliniemi et al. 2021) was anticipated. Peternelj et al. (2017) published a dynamic viscosity 1.88 Pa*s at 1400°C for his spinning wheel tests using a stone wool sample with an aluminium oxide content of about 17 wt%. The dynamic viscosity was calculated using the Urbain model which considers cations such as glass formers, modifiers and amphoteric cations (Urbain 1987).

2.4.2 Mechanical processing

The first step was to prepare the mineral wool using a forced action mixer to reduce particle size and homogenise the material with the other residual and pure materials (correction materials), followed by wet pelletising. Prior to the thermochemical treatment, the pellets were dried, preheated at 120°C and separated in 2 batches of 18 kg each.

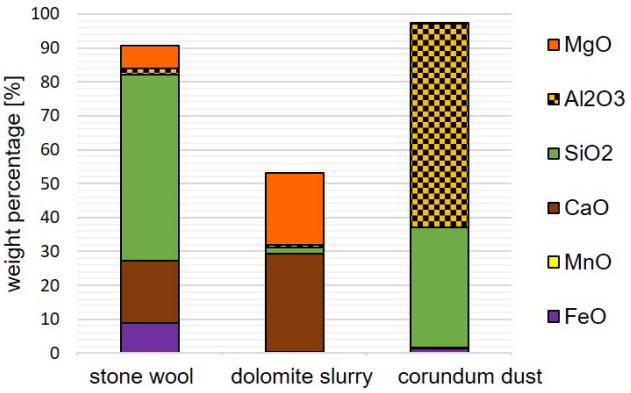


FIGURE 1: Chemical composition of stone wool and waste correction waste materials.

2.4.3 Thermochemical conditioning

A top blown rotary converter (TBRC) furnace was loaded with the preheated pellets. The material was then heated to a maximum temperature of 1500°C in the furnace. As the melting point of the pellets was exceeded, a melt was formed. When the target temperature was reached, the furnace was tilted and the melt stream was poured over a steel nose onto a 2-wheel spinner. At the spinner, the melt was defibred by compressed air and spun into conditioned, new mineral wool (Figure 2). The melting process of both batches was monitored and documented using a thermal imaging camera, a high-speed camera and several pyrometers.

3. RESULTS AND DISCUSSION

3.1 Chemical Composition of stone wool products and stone wool waste

The chemical composition of the stone wool products is shown in Figure 3 and the composition of the analysed stone wool waste is presented in Figure 4. Stone wool products tend to be richer in SiO_2, Al_2O_3, Na_2O and MgO, whereas values for CaO, K_2O and Fe_2O_3 tend to be slightly higher in stone wool waste. The variation in stone wool waste is explained by two factors. Firstly, the chemistry of old mineral wool waste has changed compared to new mineral wool waste after the EUCEB label for new mineral wool products

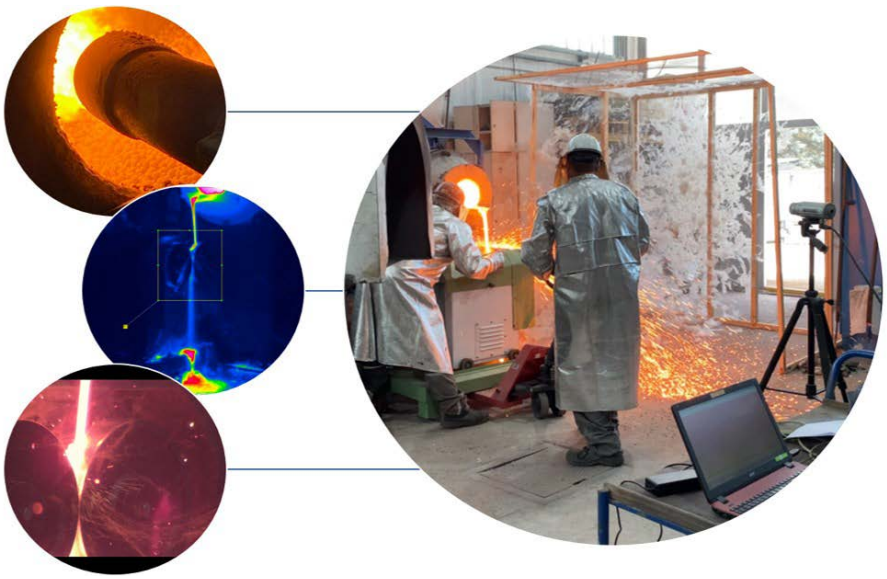


FIGURE 2: Overview of thermochemical conditioning and spinning process.

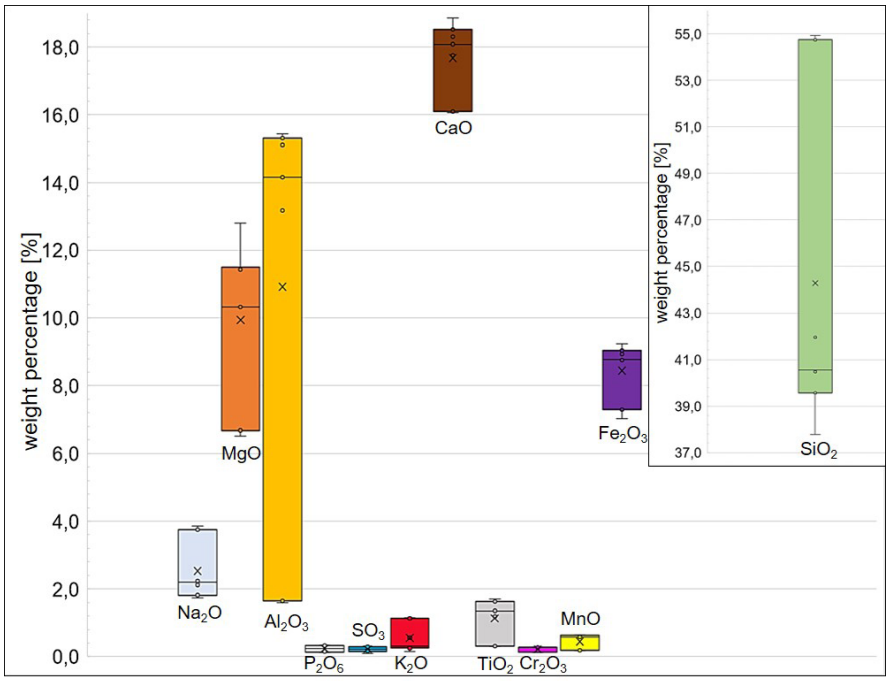


FIGURE 3: Chemical composition of the stone wool products (n=7).

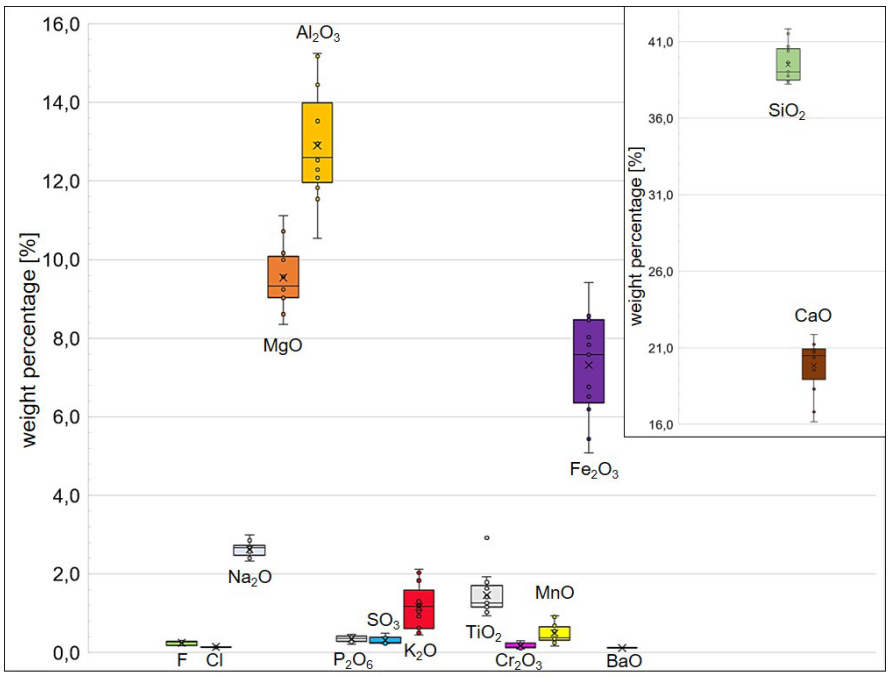


FIGURE 4: Chemical composition of the stone wool waste (n=13).

was achieved. This explains in particular the variation in Al_2O_3 content. Secondly, some impurities are introduced into the waste as a result of contamination during the demolition of buildings. Typical impurities in stone wool waste are gypsum adhesions, iron filings and aluminium facings. The presence of these materials results in increased levels of CaO and Fe_2O_3.

The full list of chemical analyses can be found as supplementary content alongside the electronic version of this article.

3.2 Solubility of Stone Wool

The chemical composition of the investigated samples within the solubility tests (Table 2) shows that one sample (SW_3) is significantly depleted in Al compared to the other two samples. The Al/(Al+Si) ratio of this sample is 0.03 compared to 0.23 and 0.26, respectively. According to the data of Guldberg et al. (2000), the Al-poor sample should have an increased biosolubility compared to the Al-rich samples, whereas even higher Al/(Al+Si) ratios of around 0.4 would also yield a high biosolubility.

The pH-dependent leachability of Si and the corresponding hydrogeochemical models of the investigated samples is displayed in Figure 5, modified after Bauer (2021).

Si can be considered as a proxy for stone wool dissolution as it is the network former of the glass structure. At first, the solubility at pH 4.5, the environment inside the macrophages, shall be compared. In this range, 150 mg/L Si are leached from sample SW_1, 18 mg/L from sample SW_2 and less than 1 mg/L from sample SW_3. In contrast to the results for the dissolution rates of Guldberg et al (2000), these equilibrium tests show the lowest leaching of Si for the lowest Al concentration and lowest Al/Si ratio. The sample with the highest Al concentration and highest Al/Si ratio plots, however, does not show the highest, but intermediate leaching. At pH 7.5, the environment outside the macrophages in the lung fluid, 30 mg/L Si are leached from sample SW_1, 6 mg/L from sample SW_2 and only 0.5 mg/L from sample SW_3. This means, that the order between the samples remains the same, but the overall leaching of Si is lower at neutral pH than in the acidic range. The overall pH-dependent trend of Si leaching shows an amphoteric behavior with lowest leaching in the neutral pH range and increasing leachability towards both acidic and alkaline pH. However, the low-leaching Al-rich sample SW_3 has the leaching maximum in the alkaline pH range - with similar values as the two other samples, whereas the higher-leaching samples have a leaching maximum in the acidic pH range. The main difference between the Al-rich

TABLE 2: Chemical composition of the stone wool samples chosen for solubility tests.

	SW_1 [wt%]	SW_2 [wt%]	SW_3 [wt%]
Na_2O	2.85	2.24	3.87
MgO	9.24	12.80	6.68
Al_2O_3	11.83	15.11	1.65
SiO_2	39.68	41.96	54.94
P_2O_5	0.28	0.09	0.05
SO_3	0.49	0.07	0.29
K_2O	1.83	0.14	0.32
CaO	20.71	18.86	18.31
TiO_2	1.42	1.70	0.31
Cr_2O_3	0.11	0.04	0.03
MnO	0.62	0.19	0.05
Fe_2O_3	6.19	7.30	8.93

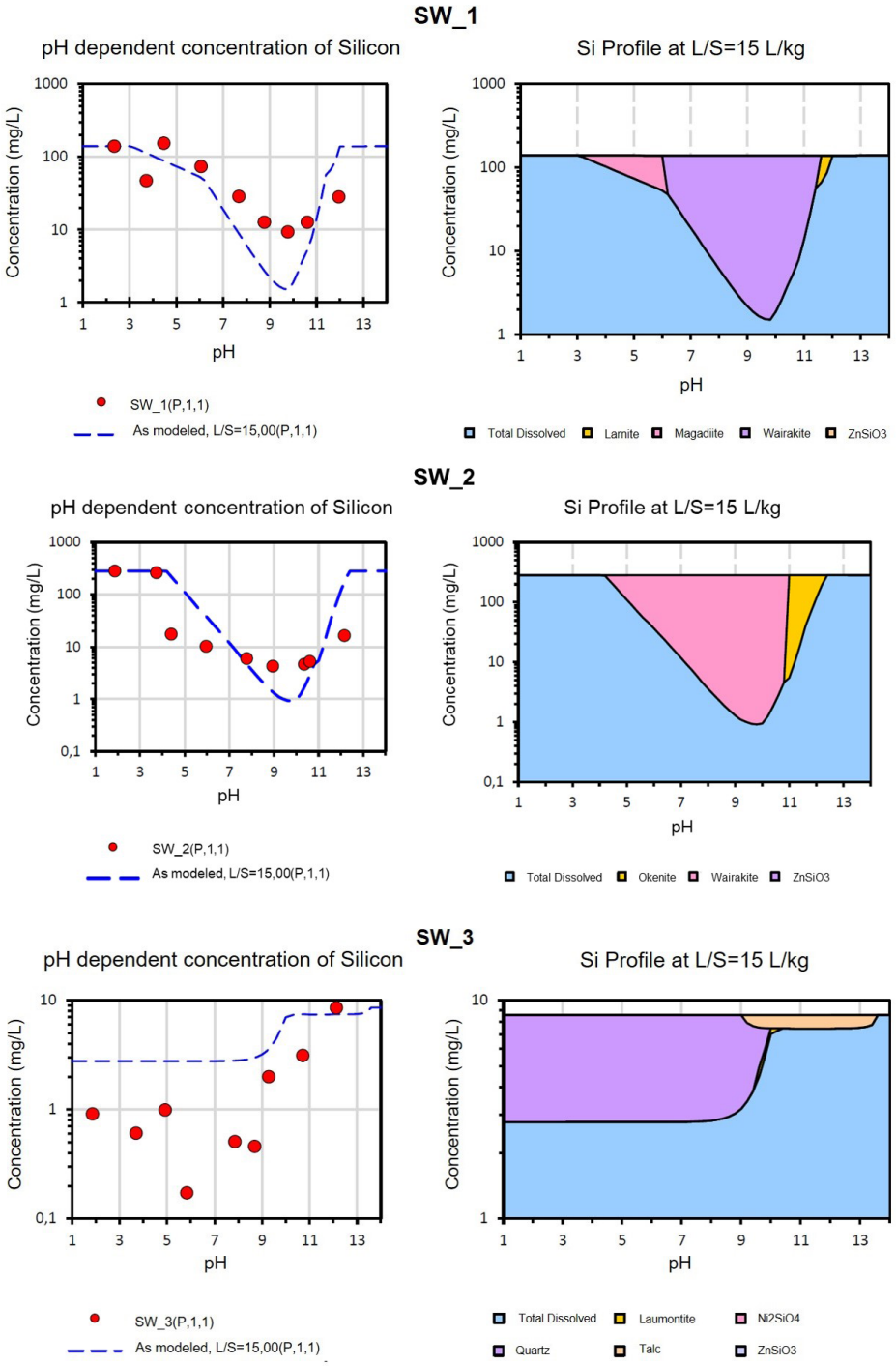


FIGURE 5: Hydrogeochemical models regarding the pH-dependent leachability of silicon for SW_1, SW_2 and SW_3 (modified after Bauer (2021)).

sample and the other two samples is the suppression of Si leaching in the acidic to neutral pH range. It has to be considered that the experimental approach in this study is a simplification of the actual conditions in the human lung, not considering organic species present and not accounting for kinetic effects or phagocytosis. However, this simplification allows to identify the effect of inorganic processes such as dissolution and precipitation of primary and secondary phases, respectively. In contrast, in the Al-rich sample, the entire available Si concentration, i.e. more than 100 mg/L, is leached at acidic pH and any leaching control mechanism is absent. It can be suggested that the presence of Al in the leachate yields to the formation of dissolved Al-Si species increasing the solubility of Al-rich stone wool and preventing precipitation of secondary mineral phases. In contrast, in the alkaline pH range, leaching control mechanisms are present. For the Al-rich samples, the precipitation of wairakite, $Ca(H_2O)_2[Al_2Si_4O_{12}]$, is suggested to control the leaching. For the Al-poor sample, the precipitation of talc, $Mg_3[(OH)_2|Si_4O_{10}]$, yields similar leach-

able concentrations of <10 mg/L Si at pH 10. Anyway, this pH range is not relevant to assess the health risks associate with stone wool waste.

Based on the chemical analyses and the solubility studies, the sample SW_3 was selected as a potentially hazardous material to demonstrate that such kind of wastes can be recycled into non-hazardous, highly soluble new stone wool. The composition of sample SW_2 was defined as a target composition which would be non-hazardous and could be sold under current legislation. This was done, because the even more soluble sample SW_1 was a waste sample, whereas the chosen SW_2 was indeed a "new" stone wool product with EUCEB certificate. The aim of the subsequent thermochemical treatment test was therefore to adjust the composition of SW_3 to the composition of SW_2 by adding Al-rich residues.

3.3 Recycling test

The XRF analysis of the newly spun mineral wool (Figure 6) showed that the target formulation within the permitted range of variation of the EUCEB quality label was not achieved for all elements (Table 3). The Al_2O_3 content after spinning was 2.73 wt% higher in batch 1 and 4.23 wt% higher in batch 2 than calculated using the composition and mixing ratio of the input materials. There were also deviations in the magnesium oxide and iron oxide contents. This can be explained by the fact that the refractory lining has dissolved and mixed with the melt. It was observed that all components detachable from refractory lining were raised in both batches of newly spun mineral wool.

3.4 Dynamic Viscosity

The determination of dynamic viscosity over a temperature range of 1000°C to 1700°C was effectively determined using the Urbain model (1987), with the chemical compositions serving as the controlling factor. Importantly, both batch 1 and batch 2 met the specified EUCEB deviation criteria for the desired target composition. Consequently, both batches are well within the specified dynamic viscosity thresholds. It should be emphasized that there is a high degree of consistency between the results of the two test batches, indicating a good reproducibility and methodological reliability. This consistency is evident in Figure 7, which shows not only the internal agreement but also the agreement with the dynamic viscosity results published by Peternelj et al. 2017. These agreements support the validity of the Urbain model and enhance its applicability in predicting the dynamic viscosity trends for similar compositions and conditions.

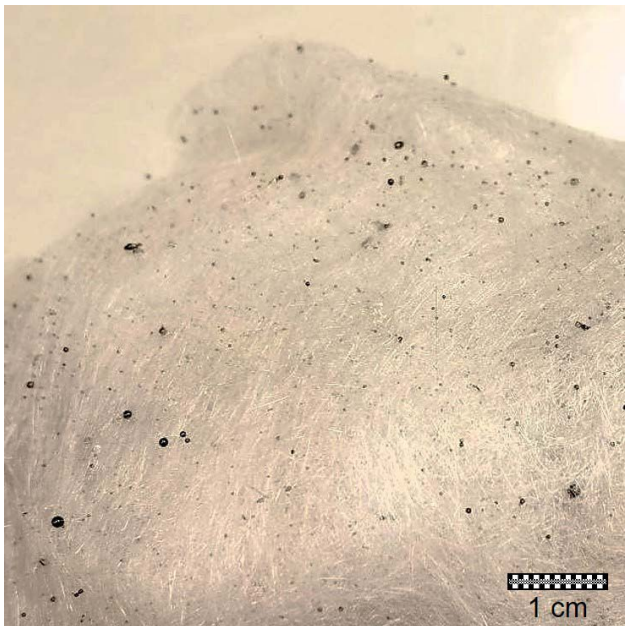


FIGURE 6: Newly spun mineral wool.

TABLE 3: Composition of the newly spun mineral wool (batch 1 and batch 2) compared to target composition.

	initial composition [wt%]	batch 1 [wt%]	batch 2 [wt%]	target composition [wt%]
Na_2O	3.87	2.1	2.2	1.72
MgO	6.68	12.5	12.5	9.77
Al_2O_3	1.65	18.6	20.1	15.87
SiO_2	54.94	43.4	42.8	41.09
P_2O_5	0.05	0.1	0.0	0.36
SO_3	0.29	<0.025	<0.025	0.33
K_2O	0.31	0.2	0.2	1.29
CaO	18.31	16.9	16.3	15.65
TiO_2	0.31	0.2	0.2	1.34
Cr	0.0	0.07	0.07	0.0
MnO	0.05	0.1	0.0	0.45
FeO	8.04	5.22	5.04	3.69

4. CONCLUSIONS

The feasibility of recycling post-consumer mineral wool waste of unknown origin and potential hazardous properties into safe, new mineral wool products is demonstrated by the recycling route (wool2wool) investigated. Post-consumer mineral wool waste from C&D activities is often lacking labels indicating health safety and is therefore considered hazardous. In-vitro and especially in-vivo tests for (bio)solubility are not feasible for mineral wool waste due to temporal and financial efforts. The relationship between chemistry and solubility generally allows to predict the health impact of mineral wool. However, mineral wool manufacturers and quality associations do often not disclose the chemical composition of their products and the outcome of (bio)solubility tests, excluding a scientific assessment of the complex relations between chemistry and solubility. pH-dependent leaching tests revealed that low-Al fibres (1.65 wt% Al_2O_3) are characterized by a low solubility in the biologically relevant acidic to neutral pH range (<1 mg/L Si), whereas high-Al fibres (11.83 wt% and 15.11 wt% Al_2O_3) exhibit more than one order of magnitude higher solubility (>10 mg/L Si). Hydrogeochemical modelling suggested reasons for the different leaching of Si from the three stone wool samples. Leaching is the property of a chemical element to be released from a sol-

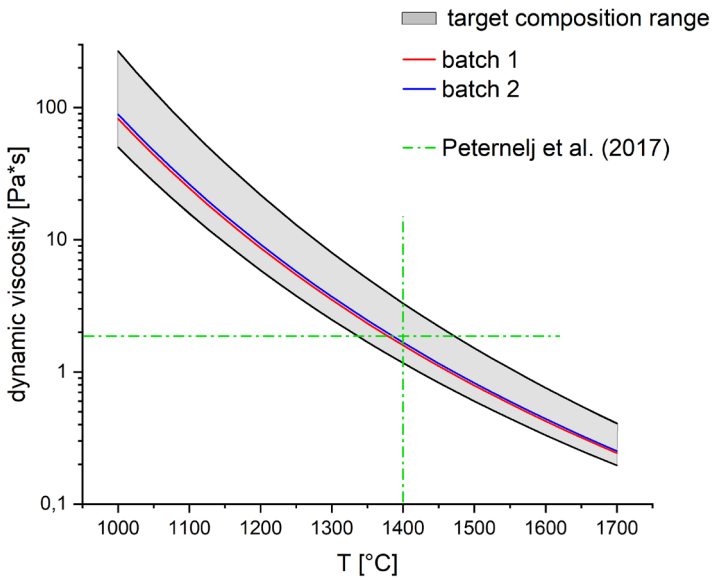


FIGURE 7: Hydrogeochemical models regarding the pH-dependent leachability of silicon for SW_1, SW_2 and SW_3 (modified after Bauer (2021)).

id to the liquid. Leaching is associated with solubility in thermodynamic equilibrium, if precipitation/dissolution reactions control the leaching. Solubility is the property of a solid phase to dissolve in an aqueous solution. Both the dissolution of a solid phase in an undersaturated solution and the precipitation of this phase from a supersatured solution yield the same equilibrium concentration of the dissolved species in the leachate. In both cases, the aqueous solution is saturated with respect to the coexisting solid phase. According to our model, in the Al-rich sample SW_3 the low leaching of Si in the acidic to neutral pH can be explained by the low solubility of quartz. Considering that quartz is not present in the mineral wool, which is amorphous, the model assumption is that the glassy phase dissolves, releasing Si species into solution. Then this solution gets supersaturated with respect to secondary mineral phases which may precipitate at the surface or in the free solution volume. Alternatively, and additionally, surface adsorption processes may take place which are also considered in the model. However, it seems unlikely that quartz precipitates from aqueous solutions at room temperature, but also the slightly higher solubility of amorphous silica would be a reasonable leaching control mechanism. In this context, leaching control mechanism means that the detected Si concentration in solution is the equilibrium concentration coexisting with amorphous silica. Assuming such a situation, it may still be the case, that the overall fibre dissolution continues, if the solubility of the glassy phase is above that of amorphous silica, but the excess Si released into the solution, would be precipitated as amorphous silica.

Hydrogeochemical modelling suggests that low solubility is due to the presence of amorphous pure silica, whereas the formation of dissolved alumino-silicate species fosters the dissolution of high-Al mineral wool fibres. Therefore, mixing Al-poor and therefore potentially hazardous mineral wool waste with Al-rich corundum dust and additional correction materials, and remelting the mixture to produce Al-richer mineral wool products is a feasible strategy to cope with the challenge of mineral wool waste management. In order to calculate the required mixing ratio, the dissolution of refractory material in the melt must also be considered. Further research is required to develop appropriate refractory concepts and to predict the dissolution of refractories in silicate melts obtained from multi-waste mixtures. In summary, thermochemical treatment of mineral wastes allows to destroy hazardous properties such as biopersistance or fibre geometry.

Since, unlike landfilling, thermo-chemical treatment can destroy the hazardous character, it should be further investigated for the recycling of other hazardous wastes such as asbestos.

ACKNOWLEDGEMENTS

This research was funded by the Austrian Research Promotion Agency (FFG) as part of the “RecyMin” and “UpcycSlag-Binder” projects and in the “Green Tech 100 – 1 Earth, 0 Carbon, 0 Waste” programme, which was supported by the “Zukunftsfonds Steiermark” (future fonds Styria) and the “Klimaschutzfonds der Stadt Graz” (climate protection fonds of the city of Graz). The authors would like to thank the company “Knauf Insulation GmbH”.

REFERENCES

Barly, S.H.Q., Okhrimenko, D.V., Solvang, M., Yue, Y., Stipp, S.L.S. (2021). Dissolution of Stone Wool Fibres with Phenol-urea-formaldehyde Binder in a Synthetic Lung Fluid. Chemical Research in Toxicology 32, 2398-2410. https://doi.org/10.1021/acs.chemrestox.9b00179.

Bauer, S. (2021). Zusammensetzung, Löslichkeit und löslichkeitsbestimmende Mechanismen von Mineralwollen. Master´s thesis. Montanuniversity Leoben.

Costa, R., Orriols, R. (2012). Man-Made Mineral Fibers and the Respiratory Tract. Archivos de Bronconeumología (English Edition). Volume 48, Issue 12, December 2012, Pages 460-468. https://doi.org/10.1016/j.arbr.2012.04.004.

DepVO (Deponieverordnung) (2021). Deponieverordnung 2008 – DVO 2008, Änderung der Deponieverordnung 2008, Verordnung der Bundesministerin für Klimaschutz, Umwelt, Energie, Mobilität, Innovation und Technologie (BMK).
Doschek-Held K., Krammer A., Steindl F., Sattler T., Juhart J. (submitted). Recycling of mineral wool waste as supplementary cementitious material through thermochemical treatment. Waste Management & Research, submitted for publication.
Eastes, W., Potter, R. M., Hadley, J. G. (2000). Estimation of dissolution rate from in-vivo studies of synthetic vitreous fibers. Inhal. Toxicol. 12, 1037–1054. https://doi.org/10.1080/08958370050164644
97/69/EC (1997). Commission Directive 97/69/EC of 5 December 1997 adapting to technical progress for the 23rd time Council Directive 67/548/EEC on the approximation of the laws, regulations and administrative provisions relating to the classification, packaging and labelling of dangerous substances.
EUCEB (European Certification Board for Mineral Wool Products) (2023). www.euceb.org, assessed on 2023/08/22.
GefStoffV (Gefahrstoffverordnung) (2010) Verordnung zum Schutz vor Gefahrstoffen, Bundesrepublik Deutschland, BGBl. I 2010, 1674 – 1676.
Guldberg, M. Jensen, S., Knudsen, T., Steenberg, T. Kamstrup, O. (2001). High-Alumina Low-Silica HT Stone Wool Fibers: A Chemical Compositional Range with High Biosolubility. Regulatory Toxicology and Pharmacology 35, 217–226 (2002), June 2001. https://doi.org/10.1006/rtph.2001.1523.
Guldberg, M.; de Meringo, Al; Kamstrup, Ol, Furtak, H, Rossiter, C. (2000) The Development of Glass and Stone Wool Compositions with Increased Biosolubility. Regulatory Toxicology and Pharmacology 32, 184-189. https://doi.org/10.1006/rtph.2000.1418.
Huber, C. (2019). Dämmstoffe (Glas- und Steinwolle) auf der Deponiedeponiebautechnische Aspekte. Powerpoint Präsentation. Wien: Erfahrungsaustausch Deponien.
Höllen, D.; Galler, R.; Pomberger, R., (2015). Möglichkeit des Schlackeeinsatzes als Untertageversatz. In: Mineralische Nebenprodukte und Abfälle. Aschen, Schlacken, Stäube und Baurestmassen, 2015, Bd. 2, S. 519-530.
IARC (1988). IARC Man-made Mineral Fibres and Radon, IARC Monographs on the evaluation of the carcinogenic risks to humans, Volume 43.
Muhle, H.; Bellmann, B.; Sebastian, K.; Barig, A.; Blome, H. (1998). Fasern - Tests zur Abschätzung der Biobeständigkeit und zum Verstaubungsverhalten, BIA-Report. HVBG, Sankt Augustin.
Oberdörster, G. (1991). Deposition, elimination and effects of fibres in the respiratory tract of humans and animals. VDI-Berichte 853, 17-37.
Peternelj, M., Bizjan, B., Širok, B. (2017). The Influence of Airflow Characteristics and Accumulation Grid Velocity on the Formation of a Stone Wool Primary Layer. Strojniški vestnik - Journal of Mechanical Engineering 63(2017)6, 405-414. 2017 Journal of Mechanical Engineering. https://doi.org/10.5545/sv-jme.2017.4503.
RAL (2023). www.ral-guetesiegel.de, accessed on 2023/08/22.
Sattler, T., Vollprecht, D., Schimek, J., Pomberger, R. (2019). Recycling künstlicher Mineralfasern, Deutsche Gesellschaft für Abfallwirtschaft e.V. DGAW, 9. Wissenschaftskongress, Abfall- und Ressourcenwirtschaft, Amberg-Weiden, innsbruck university press 2019, pp.215-219.
Sattler T, Pomberger R, Schimek J and Vollprecht D (2020a). Mineral Wool Waste in Austria, Associated Health Aspects and Recycling Options. Detritus(9): 174–180, 10.31025/2611-4135/2020.13904.
Sattler T, Sartori M, Galler R et al. (2020b). Effects of cement addition and briquetting of rock wool on its geomechanical stability in landfills. Waste management & research the journal of the International Solid Wastes and Public Cleansing Association, ISWA 38(4): 408–414, https://doi.org/10.1177/0734242X20906876.
Sattler, T. M., Höllen, D., & Pomberger, R. (2020c). Stoffliche Verwertung von Mineralwolleabfällen in der Zement- und Mineralwolleindustrie. in Mineralische Nebenprodukte und Abfälle 7: -Aschen, Schlacken, Stäube und Baurestmassen- (Band 7, S. 342-355).
Sattler, T. M., Vollprecht, D., Dietrich, V., Schimek, J. (2020d). Eignung ungefährlicher Mineralwolleabfälle als aufbereiteter hydraulisch wirksamer Zusatzstoff in der Zementindustrie. Recy&DepoTech. Band 15. S. 605-610.
Steindl RF, Doschek-Held K, Weisser K et al. (2023). Mineral residues and by-products upcycled into reactive binder components for composite cements or alkali-activated materials. In SynerCrete ‘23 (Synercrete (ed.)).
Tuorila, H., Luukkonen, T., Yliniemi, J., Ramaswamy, J., D’Hooghe, J., Kinnunen, P., Kaiser, A., Illikainen, M. (2020). Utilization of mineral wool from construction and demolition waste: sorting, pre-treatment, and alkali activation. https://www.wool2loop.eu/en/deliverables/ [20.06.2023].
United Nations (2015). Transformation unserer Welt: die Agenda 2030 für nachhaltige Entwicklung. Vereinte Nationen, New York, A / RES/70/1.
Urbain, G (1987). Viscosity estimation of slags. Steel research 58 (198) NO.3. March 1987. https://doi.org/10.1002/srin.198701513.
Yliniemi, J., Kinnunen, P., Karinkanta, P., Illikainen, M. (2016). Utilization of Mineral Wools as Alkali-Activated Material Precursor. Materials 2016, 9, 312; https://doi.org/10.3390/ma9050312.
Wohlleben, W., Waindok, H., Daumann, B., Werle, K., Drum, M., Egenolf, H. (2017). Composition, Respirable Fraction and Dissolution Rate of 24 Stone Wool MMVF with their Binder. Particle and Fibre Toxicology (2017). https://doi.org/10.1186/s12989-017-0210-8.
Yliniemi, J., Ramaswamy. R., Luukkonen, T., Laitinen, O., Nunes de Sousa, A., Huuhtanen, M. Illikainen, M. (2021). Characterization of mineral wool waste chemical composition, organic resin content and fiber dimensions: Aspects for valorization. Waste Management 131 (2021) 323–330. June 2021. https://doi.org/10.1016/j.wasman.2021.06.022.

detritus | Multidisciplinary Journal for Circular Economy and Sustainable Management of Residues

CISA

UTILIZATION OF RECYCLED AGGREGATES IN CONCRETE: CASE STUDY

Ariana C. Morales Rapallo [1,*], Janus zum Brock [1], Mahsa Doostdar [1] and Kerstin Kuchta [2]

[1] *Institute of Circular Resources Engineering and Management (CREM), Hamburg University of Technology (TU Hamburg), Germany*
[2] *Head of Institute for Circular Resource Engineering and Management (CREM), Hamburg University of Technology (TU Hamburg), Germany*

Article Info:
Received:
13 September 2023
Revised:
27 February 2024
Accepted:
22 March 2024
Available online:
31 March 2024

Keywords:
Recycled aggregate
Recycled concrete
Hamburger Mische
Concrete mixture

ABSTRACT

The increase in carbon emissions is a growing concern for the sustainability in our society, particularly as energy consumption rises, leading to annual CO_2 releases into the environment. The construction sector, responsible for utilizing a significant portion of the Earth's yearly extracted raw materials, significantly contributes to this issue. After the life cycle of a structure, this one is often transformed or demolished for new developments, generating large amounts of construction debris. Most concrete debris is further processed to create recycled aggregates, which are commonly used for road construction or as filling material. Nonetheless, efforts are underway to promote material circularity by reusing these aggregates back into concrete, reducing concrete downcycling and disposal in landfills. Hamburg's "Musterbude" project in 2022 stands as an example of material circularity, showcasing the sustainable use of recycled aggregates in concrete. Seven concrete mixes were formulated; two conforming to German recycled concrete standards with 45% and 35% recycled aggregate replacement. Others, including the so-called "Hamburger Mische," departed from these standards, incorporating varied recycled materials like crushed bricks and 100% mixed C&DW aggregates. The findings provided valuable insights for policymakers, engineers, and researchers, fostering a transition towards a more circular economy in the construction sector while minimizing environmental impact.

1. INTRODUCTION

In recent years, the interest in the utilization of recycled concrete within civil engineering projects has increased with the shift in industry focus driven by mounting concerns over global warming and the carbon footprint associated with construction activities. However, existing DIN standards have imposed strict regulations on the use of recycled aggregates for concrete production. Factors such as aggregate proportions, granulation sizes, exposure areas, and physical properties of recycled concrete are among the key characteristics subject to meticulous standardization and oversight by construction authorities.

1.1 State of the Art

Currently in Germany, two types of recycled concrete are permitted, namely Type I with a 45% volume of recycled aggregates, and Type II with a 35% volume of recycled aggregates, primarily intended for interior exposure. However, the allowable proportions of recycled aggregates decrease significantly for exterior exposure applications. Additionally, according to the standards outlined in DIN 4226-100 (Deutsche Institut für Normung, 2002) particles smaller than 2 mm generated during concrete demolition cannot be reused as recycled material, leading to substantial construction waste. Consequently, a significant portion of recycled concrete is currently used for road construction and filling materials, which can be classified as material downcycling.

To address the limitations in the country surrounding the production and use of recycled concrete, a sample booth called the "Musterbude" was developed in the city of Hamburg. The Musterbude is a small concrete cabin built to showcase different concrete mixes using recycled concrete. This cabin not only demonstrates recycled concrete recipes adhering to existing standards but also explores concrete structures incorporating varying proportions of recycled aggregates outside the standard.

1.2 Objectives

By developing recycled concrete that matches the performance of traditional concrete, the project aims to reduce carbon emissions during production, promote material circularity, and drive innovation in the construction

* Corresponding author:
Ariana C. Morales Rapallo
email: ariana.morales@tuhh.de

https://doi.org/10.31025/2611-4135/2024.18366

sector. By raising awareness among policymakers and the community, the showcase project aims to encourage collaboration and demonstrate the potential of using higher levels of recycled aggregates in different exposure categories. This initiative not only actively promotes circularity in construction, but also plays a key role in waste reduction by significantly reducing the amount of construction waste sent to landfills nationwide.

2. CHALLENGES AND LIMITATIONS

This section evaluates the prevailing challenges associated with acquiring, processing, and establishing the competitiveness of recycled materials in the construction industry, as the demand for sustainable alternatives continues to rise.

2.1 Demolition Preparation and Planning for Future Use

The limitations of recycled concrete extend beyond its usage and encompass the surrounding processes of acquisition, storage, transportation, and distribution. Insights gathered from demolition work in Hamburg revealed that successful concrete recycling requires careful preparation. Emphasizing the prioritization of on-site demolition, crushing, storage, and utilization of recycled concrete minimizes the need for transportation (Purchase, et al., 2021). However, this approach may not always be feasible in construction projects, needing additional collaborative efforts from various stakeholders to process the aggregates and provide temporary storage. Furthermore, it was observed that having a clear plan for the future utilization of crushed concrete before demolition work starts is advantageous to avoid potential delays and penalties (European Commission, 2018).

2.2 Recycled Concrete Price

Price challenges are a real barrier to the widespread adoption of recycled concrete in construction projects. Some of these challenges include obtaining the appropriate type of recycled concrete, which can be more expensive than extracting the raw material due to the process involved in demolition and C&D waste classification, such as metal extraction, ensuring concrete quality standards, and impurity content such as bituminous material. Once the material is collected from the demolition site, it must be transported to a recycling facility to be crushed and stored. This additional step adds cost to the recycled concrete, especially since the supply has not yet reached the level of the raw material (Holcim, 2023), and the recycled aggregate must be stored until enough production is reached and then can be sold and shipped to the new construction site. Therefore, the higher price of recycled concrete together with the potential delays in obtaining the material near future projects to decrease transportation emissions may discourage some stakeholders from completing the transition or seeking the recycled concrete route when it comes to concrete production. This reduces the motivation to adopt a circular economy in construction and the wider adoption of recycled concrete in the industry.

2.3 Production

During the demolition of concrete structures, the concrete scrap is separated from external materials such as steel and plastic to be further crushed and sieved into grain-size categories. Currently, only grain size larger than 2 mm and up to 16 mm is accepted to be reused in concrete based on industry standards for alkaline salt resistance (Memminger-Rieve, 2021), any rubble smaller than 2 mm becomes construction waste. After the separation of concrete, the granulated material is subjected to quality control tests in accordance with the DIN 12620 standard (Deutsche Institut für Normung, 2008). These tests evaluate various parameters, including conductivity, pH levels, and the presence of PAH (Polycyclic Aromatic Hydrocarbons), which are considered problematic due to long-term health effects after exposure (Abdel-Shafy & Mansour, 2016). While asphalt and gypsum may not be ideal, they are still accepted as recycled materials in certain cases, with a maximum allowable content of 1% (Jaawani, Franco, De Luca, Coppola, & Bonati, 2021).

3. MATERIAL AND METHODOLOGY

A total of eight specific recipes were formulated to construct the Musterbude, consisting of seven mixes that incorporated varying proportions of recycled aggregates as a replacement for conventional aggregates, and one mix that served as a reference using solely virgin aggregates for comparison purposes. The primary objective was to implement an environmentally sustainable approach in construction by developing recycled concrete that performs as conventional concrete, thereby minimizing carbon emissions during production and promoting material circularity.

In Figure 1, an aerial picture of the Musterbude is shown. From the building image, the simple design of the structure as well as the properly marked section with its corresponding concrete mixture can be seen. Additionally, two panels on each side of the Musterbude were constructed to further showcase the use and performance of recycled aggregate in concrete.

3.1 Concrete Recipes

This section describes the eight concrete mixes used in the Musterbude. In general, the concrete mixes are as follows: one reference mix using raw aggregates, two (2) Type I RC mixes adhering to German standards and utilizing size 2-16 mm aggregates, one (1) Type II RC mix following German standards with size 2-16 mm aggregates, and four (4) additional mixes incorporating varying proportions of recycled aggregates placed out of the current standards for recycled concrete mixtures.

3.1.1 Reference Concrete (RB- Reference Beton in German)

The reference concrete was developed with the specific intention of serving as a benchmark, not only for assessing the physical properties of the concrete but also for evaluating appearance-related aspects such as surface roughness, porosity, microorganism growth, and other visual characteristics.

FIGURE 1: Musterbude.

3.1.2 Type I Recycled Concrete 2-16 mm 45% (R1 and R8)

The R1 mixture, which was prepared following the guidelines for Type I recycled concrete as per DIN EN 206 and DIN 1045-2, was used in an exterior wall of the Musterbude. On the other hand, the R8 mixture, also following Type I recycled concrete specifications, was applied to an interior wall of the Musterbude.

3.1.3 Type II Recycled Concrete 2-16 mm 35% (R5)

This mix was prepared following the standard for Type II recycled concrete, utilizing coarse granulated aggregates with a size larger than 2 mm. The maximum allowable proportion of recycled aggregates used in this mix was 35% of the total volume of aggregates.

3.1.4 Fine and Coarse Recycled Concrete (R4 Not in the standard)

This particular mix was formulated outside the current standards for recycled concrete due to its composition, which includes 17% of fine aggregates ranging from 0-2 mm in size and 28% of 2-16 mm aggregates. The existing German standard does not currently permit the use of aggregate sizes smaller than 2 mm. However, in the upcoming update of the standards, the inclusion of particles smaller than 2 mm will be allowed.

3.1.5 Recycled Concrete using Bricks (R3 Not in the standard)

This mix was specifically formulated with a 60% by volume of crushed bricks as a replacement for traditional aggregate. Currently, no standards addressing the utilization of brick with such a high content as an aggregate substitute exist.

3.1.6 Recycled Concrete using 100% Mixed C&D Waste as Recycled Aggregates (R6 and R7 Not in the standard)

The unique "Hamburger Mische" mix was specifically designed with the complete replacement of aggregates (0-2 mm and 2-16 mm) using mixed demolition rubble, which includes clinker, brick, sand-lime brick, unbound natural stone grains, and concrete. This mixture does not conform to any standard for recycled concrete. However, it does meet the requirements of DIN 4226-101 (Deutsche Institut für Normung, 2017) concerning the types and regulated dangerous substances in recycled aggregate for concrete.

In Figure 2, the material composition of each concrete mix compared to the reference concrete is shown in a bar chart. In this chart, a clearer visualization of material usage and proportions by volume can be seen in comparison to the reference concrete. The percentage of recycled aggregate used in each mix is also shown including brick, processed recycled aggregate, or mixed construction and demolition waste depending on the mix design.

4. RESULTS

The result of the hardened concrete test is shown in Table 1. In this table, the laboratory results obtained from the density and compressive strength test done on each concrete mix can be seen.

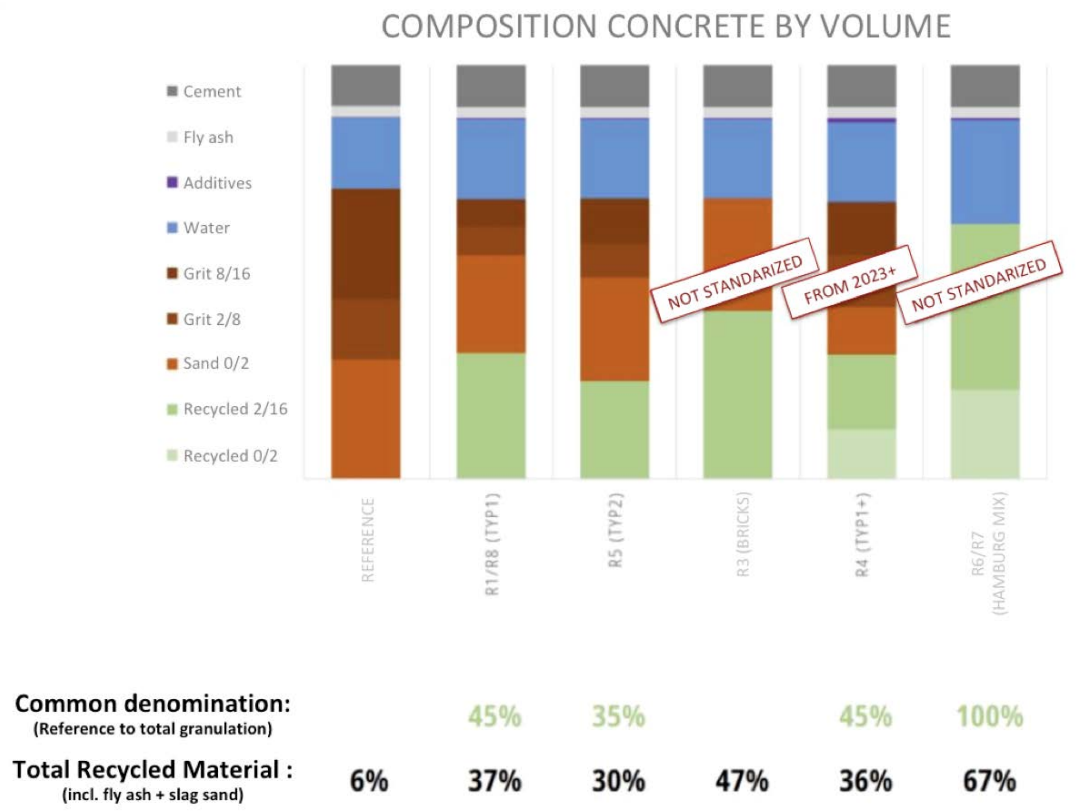


FIGURE 2: Composition of the tested concrete types by volume.

From Table 1, R6 corresponding to the "Hamburger Mishe" concrete has the lowest density and compressive strength values. This is due to the porous nature of the construction rubble used as the aggregate substitution in the mix. The high porosity in the R6 concrete mix increases the w/c ratio, which leads to an overall reduction in the concrete performance. Similarly, R4 shows a significant decrease in strength due to the replacement of sand. This increases the water content, thus, reducing the concrete performance.

5. DISCUSSION

Concrete mixes R1 and R8, both exhibited a notable increase of approximately 29.2% in total water content compared to the reference concrete mix. Moreover, there was a reduction in compressive strength, with the R1 mixture experiencing a decrease of 29.8% and the R8 mixture showing a decrease of 21.7% in compressive strength when compared to the reference concrete mix. In the case of R5, this specific mixture, which was applied to an exterior wall of the Musterbude, demonstrated a significant increase of 35% in total water content and a notable decrease of 32.7% in compressive strength when compared to the reference concrete. All of the previously mentioned concrete mix designs were according to the DIN 4226-100 (Deutsche Institut für Normung, 2002).

Regarding the non-standarized concrete mixes used in this project, the mix R4, applied in an exterior wall of the Musterbude, exhibited a 34.2% increase in total water content and a substantial 45.75% reduction in compressive strength when compared to the reference concrete. Moreover, the mix R3, using 60% of brick as the aggregate

TABLE 1: Hardened concrete tests at 28 days.

Concrete Mix	Density kg/m³	Compressive Strength kg/m²	Description
RB	2335	48,3	Reference Concrete
R1	2200	33,9	Typ1- 2/16 45%
R3	2130	35,6	Brick-2/16 60%
R4	2140	26,2	Type1- 0/2 18% 2/16 27%
R5	2220	32,5	Type2- 2/16 35%
R6	1980	20,8	HH Mische 100% Mix demolition waste
R8	2230	37,8	Type1- 2/16 45%

replacement had an outcome of a 37.9% increase in total water content and a 26.3% reduction in compressive strength when compared to the reference concrete. Despite the absence of current standards, this mix was successfully employed in an exterior wall, providing valuable insights for potential future guidelines regarding the use of high-brick-content mixes in construction practices. Finally, the Hambuger Mische, which consists of a 100% mix of construction and demolition waste as aggregate substitution, was applied in the construction of the floor, side panels, and part of the ceiling of the Musterbude, this mix displayed intriguing characteristics. It showed a significant 48.8% increase in total water content and a 56.9% reduction in compressive strength when compared to the reference concrete. Despite not adhering to recycled concrete standards, its compliance with DIN 4226-101 (Deutsche Institut für Normung, 2017) offers the assurance of safe usage with recycled materials, providing valuable insights for future sustainable construction practices.

It is important to emphasize for the purpose of this investigation that the aggregates used in this project were not prewashed or treated in any way before mixing to prevent excess water absorption, nor the use of chemical admixture to improve concrete performance. Because of this, the water absorption of recycled aggregates is significantly higher than using virgin aggregate due to the high porosity in the recycled concrete as aggregates.

Since the concrete mixes were created as a proof of concept for the use of different proportions of recycled aggregate in concrete, the concrete mixes can be replicated and improved outside the German context.

6. CONCLUSIONS

From the results obtained in this research, it can be concluded that a proportion of aggregates in concrete can be successfully replaced with recycled concrete. However, a series of steps have to take place before the addition of this recycled material in concrete. For example, elemental analysis of the recycled aggregate, especially for heavy metal content, and aggregate pre-washed are essential for good concrete performance.

The successful use of recycled concrete relies on defined and specific concrete property specifications, including exposure category, moisture class, and minimum compressive strength, among others. Additionally, ensuring a continuous flow of recycled concrete as aggregate in the market necessitates early planning for material reuse, involving all relevant stakeholders and concrete production facilities and building a strong standarized supply chain to drive the prices down and increase the demand of this materials.

To fully attain circularity in construction materials after demolition and to prevent the downcycling of concrete in civil engineering projects, further research and investigations are imperative, particularly focusing on increasing the proportion of recycled aggregate in concrete.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the financial support of the project “CIRCuIT- Circular Construction and Regenerative Cities” provided by the European Commission. This project has received funding from the European Union’s Horizon 2020 research and innovation program under grant agreement No 821201.

Additionally, special thanks to OTTO WULFF Bauunternehmung GmbH, EGGERS Tiefbau GmbH, and Otto Dörner Kies und Deponien GmbH & Co.KG for the creation of the Musterbude and for providing material and practical knowledge.

REFERENCE

Abdel-Shafy, H. I., & Mansour, M. S. (2016). A review on polycyclic aromatic hydrocarbons: Source, environmental impact, effect on human health and remediation. Egypt: Egyptian Journal of Petroleum. doi:https://doi.org/10.1016/j.ejpe.2015.03.011.

Deutsche Institut für Normung. (2002, 02). DIN 4226-100:2002-02 : Aggregates for concrete and mortar - Part 100: Recycled aggregates.

Deutsche Institut für Normung. (2008). DIN EN 12620:2008-07: Aggregates for concrete; German version EN 12620:2002+A1:2008. Germany: Deutsche Institut für Normung.

Deutsche Institut für Normung. (2017). DIN 4226-101:2017-08: Recycled aggregates for concrete in accordance with DIN EN 12620 - Part 101: Types and regulated dangerous substances. Germany: Deutsche Institut für Normung.

European Commission. (2018, September 18). Internal Market, Industry, Entrepreneurship and SMEs. Retrieved from https://single-market-economy.ec.europa.eu/news/eu-construction-and-demolition-waste-protocol-2018-09-18_en

Holcim. (2023, Januar). Preisliste 2023 Beton und Betonpumpen Gebiet Südbaden . Retrieved from https://www.holcim.de/sites/germany/files/2023-02/holcim-preisliste-beton-und-betonpumpen-2023-gebiet-sudbaden_01.pdf?v=3ec070fb

Jaawani, S., Franco, A., De Luca, G., Coppola, O., & Bonati, A. (2021). Limitations on the Use of Recycled Asphalt Pavement in Structural Concrete. Applied Sciences. doi: https://doi.org/10.3390/app112210901

Memminger-Rieve, D. B. (2021, 10). Build sustainably with recycled concrete. Retrieved from Enviro Sustain: https://www.envirosustain.com/build-sustainably-with-recycled-concrete

Purchase, C. K., Al Zulayq, D. M., O’Brien, B. T., Kowalewski, M. J., Berenjian, A., Tarighaleslami, A. H., & Seifan, M. (2021). Circular Economy of Construction and Demolition Waste: A Literature Review on Lessons, Challenges, and Benefits. New Zealand : Materials (Basel). doi:doi: 10.3390/ma15010076. PMID: 35009222; PMCID: PMC8745857.

Remexit. (2023). Remexit.de. Retrieved from https://remexit.de/en/mineral-recycling/construction-and-demolition-waste

Tao Ding, J. X. (2016). A closed-loop life cycle assessment of recycled aggregate concrete utilization in China. Waste Management ER, 367-375. doi:DOI: 10.1016/j.wasman.2016.05.031

detritus | Multidisciplinary Journal for Circular Economy and Sustainable Management of Residues

CISA

BIBLIOMETRIC ANALYSIS OF LANDFILL MINING: WORLDWIDE RESEARCH EVOLUTION

Anaxsandra da Costa Lima Duarte [1,2,*], Taise Bonfim Jesus [2] and Alessandra Cristina Silva Valentim [1]

[1] *UFRB, Center of Exact and Technological Sciences, Rua Rui Barbosa, Cruz das Almas, Bahia 44380-000, Brazil*
[2] *UEFS, Department of Exact Sciences, Avenida Transnordestina, Feira de Santana 44036-900, Brazil*

Article Info:
Received:
2 September 2023
Revised:
18 December 2023
Accepted:
8 January 2024
Available online:
9 February 2024

Keywords:
Enhanced Landfill Mining
Scopus
Fine Fraction
Circular Economy
Environmental Analysis
Ecotoxicological Assessment
Microplastics

ABSTRACT

Landfill Mining (LFM) aims to recover resources by partially or completely excavating waste stored in landfills. Research on Enhanced Landfill Mining (ELFM) has been advanced to include the combined valuation of waste as both materials and energy carriers. In this article we present an overview of the literature on the global development of landfill mining based on domestic waste. Here we analyze the existing information on the chronological and geographic distribution in countries that publish in the area, and to describe the dynamics of the conceptual and scientific knowledge. The analyzed articles were retrieved from Scopus, using the "Landfill* Mining" search term. The LFM research on co-occurrence network (1990-2022) found 29 terms in the first decade, increasing to 52 terms in the second decade and, finally, 234 terms in the third decade, indicating the importance of the LFM research field in present days. Four prominent aspects of LFM research can be observed: a. LFM provides an efficient contribution to waste management strategy, b. the objectives of LFM are similar to those of Circular Economy, c. LFM uses advanced techniques for identifying metals and chemical elements; and d. there is a need for ecological and ecotoxicological assessment, and determination of microorganisms and microplastics in the mined material.

1. INTRODUCTION

Landfill Mining (LFM) is a more sustainable waste management practice which aims to mitigate impacts related to landfills while recovering inactive resources (Laner et al., 2019). In the case of dumps, which cause greater concern due to environmental pollution, LFM practice is also relevant for revitalizing degraded areas (Sabour et al., 2020).

This practice was first carried out in Israel in 1953 as a way to obtain fertilizers for orchards (Krook et al., 2012). However, it was only revisited in the 1990s, with the aim of extracting methane and eliminating contaminants from the soil and water, without excavating the stored waste; only later landfill mining was developed to recover resources by partial or total excavation of waste (Jones et al., 2013).

LFM involves the excavation, processing, treatment and/or recycling of deposited materials, providing material and energy recovery, as well as land reclamation (Frändegård et al., 2013; Marella and Raga, 2014). However, mining can unearth fractions of hazardous waste and cause slope instability, due to excavation, and also generate large volumes of materials with low commercial value (partially and completely decomposed organic matter, corroded metals, contaminated soils) (Chandana et al., 2021).

In order to include operating landfills and emphasize the recovery of waste, a more advanced concept was proposed: the Enhanced Landfill Mining (ELFM), characterized by the combined valuation of different flows of waste, both as materials (waste-to material, WtM) and as carriers of energy (waste-to-energy, WtE), in addition to land reclamation (for residential and industrial uses) and extending landfill life (Einhäupl et al., 2019; Esguerra et al., 2021). The practice is carried out aiming at the maximum recovery, for example, the non-recyclable fraction needs to be stored again in such a way that future mining is possible (Bosmans et al., 2013).

ELFM has operational steps similar to LFM; enhancement consists of the use of innovative technologies (such as gasification, pyrolysis and plasma incineration) for energy recovery, aiming to reduce the final volume of waste to almost zero and including the recovery of historical and future waste, considering the ecological, social and economic criteria. It also involves actions regarding the mitigation of CO_2 emissions, health and safety of workers and

* Corresponding author:
Anaxsandra da Costa Lima Duarte
email: anaxsandra@ufrb.edu.br

https://doi.org/10.31025/2611-4135/2024.18351

neighbors, quality of separation fractions, location, cost of labor, equipment and market value (Burlakovs et al., 2017; Chandana et al., 2021; Danthurebandara et al., 2015; Van Passel et al., 2013).

The improvement proposed by ELFM is a consequence of the increasing environmental problems, and is not depending on the use of any specific technique or equipment. Thus in this paper both terms will be used interchangeable, and the acronym LFM will be used for both.

Calderón Márquez et al. (2019) cataloged, based on the relation between the proposed objectives and compliance with the Sustainable Development Goals, about one hundred projects carried out in North America, Europe, Asia and the Middle East; the authors concluded that LFM fits into the current transition that countries all over the globe are making towards the Circular Economy.

Despite being relatively recent, some literature review has already been published on the field of Landfill Mining. Krook et al. (2012) performed a meta-analysis with 39 papers published between 1988–2008, with the aim of identifying the main challenges for LFM implementation. The authors concluded that there are three main challenges in this field of research: a. technological innovation, b. addressing the underlying conditions for its achievement, and c. developing standardized frameworks for evaluating the performance of material recovery.

Additionally, Krook & Baas (2013) reviewed papers published in a special volume of the Journal of Cleaner Production, on urban mining and landfill mining, in order to explore the feasibility of such waste management approaches and also identify which social changes and which search fields are essential for its dissemination. The authors compared the environmental impact of two mining techniques, namely, biogas recovery (in-situ mining) and landfill waste recycling (ex-situ mining). They concluded that ex-situ mining are significantly more positive, as the recycling of mined materials avoids the extraction of raw materials and decreases primary emissions during the manufacture of products.

In a more recent review article, Vollprecht et al. (2021) analyzed the entire research output of NEW-MINE (European Union Training Network for Resource Recovery Through Enhanced Landfill Mining) with regard to its practical applicability in waste management systems. These authors found that the amount of resources recovered from landfills can be significant, if the use of the inert fraction and fuels become viable technological routes. They also point out that the quality and credibility of anthropogenic resources obtained from waste in landfills represent significant challenges for future ELFM projects.

Jain et al. (2023) published a review focused on the difficulties related to the extraction, analysis and use of excavated materials from 34 landfills (reported in 27 articles) and observed issues related to: a. convergence regarding the parameters that must be determined, which are defined according to the intended use of the material; and b. the application of the ore can be obstructed due to the high concentration of contaminants (fine solids, heavy metals and chlorine).Despite the relevance of the cited reviews, the LFM research field has advanced since the years 2012/2013 and is already present in several countries, in addition to those belonging to the European Union, which are in the article by Vollprecht et al. (2021). Thus, the aim of this work is to present an overview of the literature on the global development of domestic waste landfill mining. Here, we present information about the chronological and geographic distribution in countries that publish in the area and describe the conceptual structure underlying it. We also investigate the chronological development of publications and the main research institutions that take the lead in the research about LFM.

1.1 List of acronyms

DLM: Dynamic landfill management
DST: Decision Support Tool
ELFM: Enhanced Landfill Mining
FDEM: Frequency-domain electromagnetic
FTIR: Fourier Transform Infrared Spectroscopy
GCMS: Gas Chromatography Mass Spectrometry
IWWG: International Waste Working Group
KEG: Kalman Ensemble Generator
LBR: Aerobic Leach Bed Reactors
LCA : Life Cycle Analysis
LFM: Landfill Mining
MCA: Multi-criteria Analysis
NPV: Net Present Value
RDF: Refuse Derived Fuel
REE: Eletronic waste
SRF: Solid Recovered Fuel
WtE: waste-to-energy
WtL: waste-to-land
WtM: waste-to material
WtP: Waste-to-Product

2. METHODS

The analyzed articles here were retrieved on January 5, 2023 from the Scopus database, with the search equation “Landfill* Mining”; this term was required to appear in the abstract, title and/or keywords of the paper. An initial refinement was carried out, in which only article-type documents, published in Journal-type sources, published until 2022, remained in the database. In subsequent refinement, we removed articles which were: a. review or opinion articles; b. documents which do not present all the elements of a scientific article (authors, abstract, keywords); c. articles with content outside the specific theme; d. articles that deal with waste outside the scope of this research. With the resulting articles, using the function “Export”, the following information was collected: Citation information, Bibliographic information, Abstract and keywords, Financing details, Other information.

3. RESULTS AND DISCUSSION

The initial search on the Scopus database found 334 documents; after the first and second refinements, this number was reduced to 237 and 190 articles, respectively. A list of these articles can be found in the Supplementary material.

3.1 General status

The selected articles were published between 1990 and 2022, with an annual publication growth rate equal to 9.64% and an average of 5.97 articles per year. Figure 1 presents the world's annual scientific production in the Landfill Mining research field. It can be observed that in the first two decades (between 1990-1999 and 2000-2009) publication was incipient, with less than one article published per year. From 2013 on, a sharp growth line can be observed, with an annual growth rate of 27.8%, and an average of 13.8 articles published each year.

Dhar (2015) stated that the promulgation, in the USA, of stricter environmental legislation propelled the interest in LFM; in the early 1990s, landfills were closed and then post-closure costs increased. The author also reports that in Europe and Asia, legislation aimed at the remediation of old landfills and the removal of those that hinder urban development.

The year of 2013 marks a change in the curve slope in Figure 1 and coincides with the start of the operation of the first comprehensive Enhanced Landfill Mining (ELFM) project by the Machiels Group, Belgium (Danthurebandara et al., 2013).

The 190 articles in the field of LFM have been published in 63 different journals. By Bradfort's law, the essential sources (source core) for understanding the state-of-the-art of LFM are the first two journals with the highest publication, namely, Waste Management (total = 38 articles) and Detritus (total = 22 articles). The first journal, launched in 1989, renovated and managed by IWWG (International Waste Working Group) since 2002, is dedicated to the presentation and discussion of information on solid waste, in term of reserch, management, education, and economic and environmental assessment.

The second journal publishes work from scientific sources not limited to research laboratories but includes results from full-scale plants, best practices, operational activities, discussions in working groups and associations, unsuccessful experiences, case studies from developing countries, administration, etc. Probably for that reason, it has published on LFM a greater number of articles in the last five years than the journal Waste Management, which published only 12 articles in the same time frame.

The lack of a more flexible type of journal for LFM publication has been identified as an obstacle since 2012. Krook et al. (2012) suggested that, due to the immaturity of the research field, a significant amount of valuable practical knowledge would be available in the gray literature and in organizations that practice landfill mining, and that the creation of the journal Detritus would possibly allow the publication of this type of material.

Detritus and Waste Management are both official journals of IWWG and intend to promote integrated and sustainable waste management, practical scientific development in the field and effective communication within of the professional community (Cossu, 2018). Figure 2 presents the 20 institutions that most publish in the Landfill Mining area. It is important to note that from the 14 countries mentioned in Figure 2, only 6 of them (Brazil, China, India, Russia, Singapore and United Kingdom) are not part of the European Union, however, the United Kingdom was part of it until the beginning of 2020.

Among developing countries, the most expressive ones in the field of LFM are China and India. China began to publish in this field in 2006, but remained stagnant until 2013, when the "Thought of Ecological Civilization" (Xiang-Chao, 2018) gained force.

The Twelfth Chinese National Five-Year Plan for Municipal Solid Waste Treatment and Management suggested a budget of 21.1 billion Chinese Yuan ($ 3.5 billion) for the ecological remediation of 1,882 old landfills in China from 2011 to 2015 (Zhou et al., 2015). In turn, India only started publishing in 2018, but with a remarkable performance and

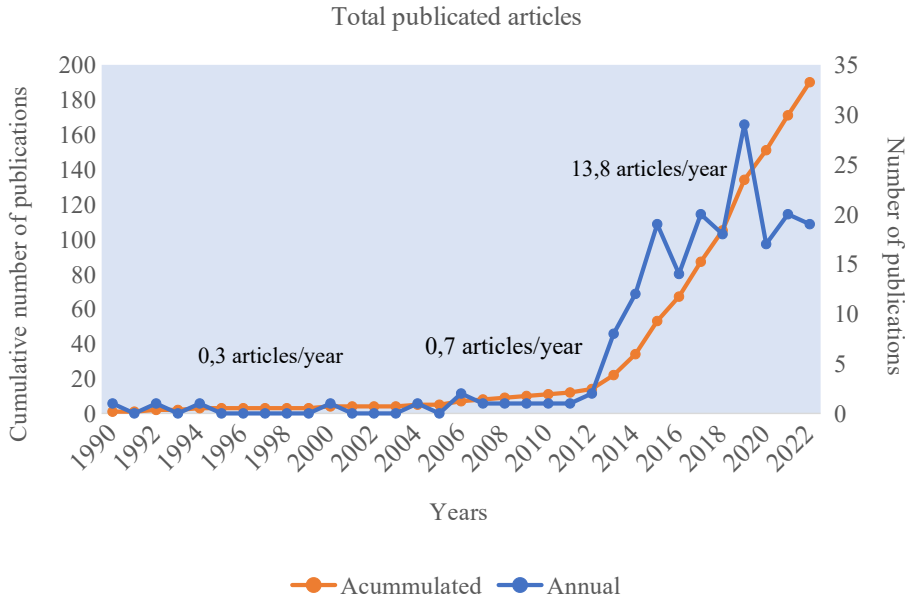


FIGURE 1: Worldwide Annual Scientific Production.

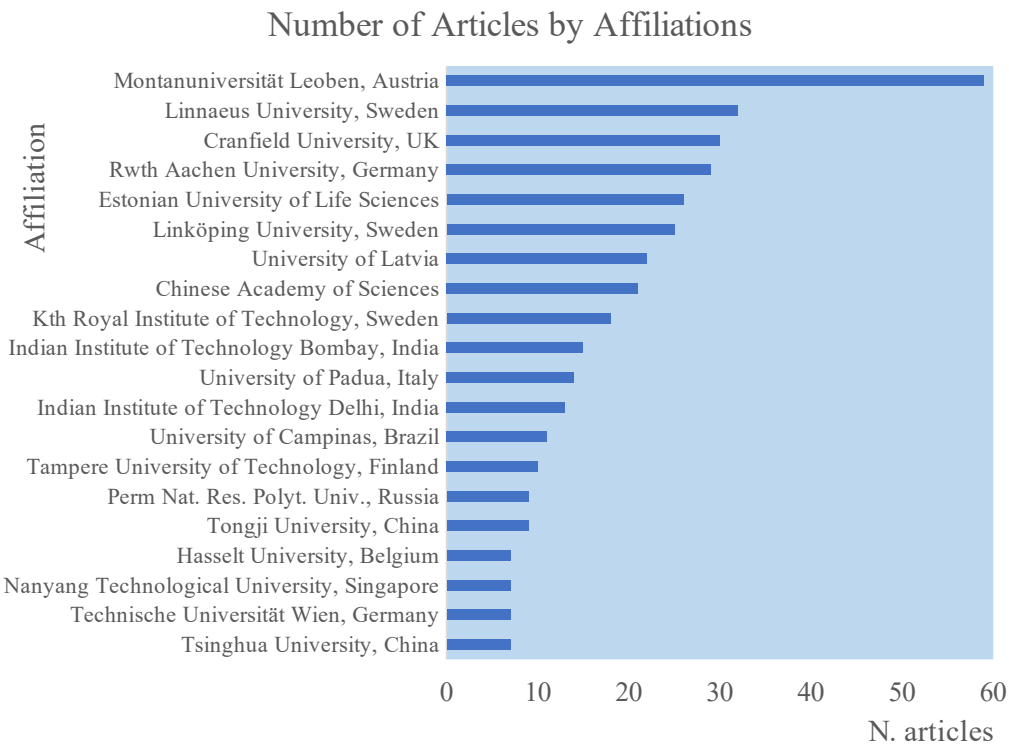


FIGURE 2: Number of articles published by the main research institutions.

is already on the top compared to other countries in number of articles.

3.2 Conceptual Framework

Figure 3 shows the distribution of co-occurrence terms over three decades of LFM research,between 1990 and 202. The terms were selected from theabstracts and titles of the papers. For each decades the terms were grouped according to clusters, reflecting the technical and scientific interests in the given period.

In the first decade (1990-1999)29 terms were grouped into three clusters. LFM Products, both beneficial ones (such as soil, aggregates, fine fraction) and others more linked to emissions and potencial contaminantions (such as leachate, gas production, methane, heavy metals, environmental analysis).

LFM space optimization, as a strategy for landfill operation, which includes varied terms (feasibility, landfill space, organic material, recycling, economic assessment, mining operation) reflectings the benefit deriving from LFM in terms of material and space recovery. Landfill mass conditioning, which includes terms related to improving and speeding waste stabilisation (aerobic landfill, airflow technology, composting, degradation, moisture).

In decade 2000-2009 the six following clusters (out of 52 terms) were determined: Mined waste components (black soil, fine fraction, glass, nitrogen and phosphorus). LFM management and strategies (reduction and recycling strategies, market, business studies and government regulation) suggesting the use of waste as material or energy. Characterization of mined waste, including dumps, probably with a focus on the application in fuel, humus and recovery of soil and metals. It is also noteworthy the high occurrence of the term Urban waste to reinforce the relevance of LFM for this type of waste. The other clusters are composed of terms with low occurrence, because they were, at the time, emerging techniques: Energy use of mined waste; Landfill geophysical characterization and Plastics recovery.

The extended decade 2010-2022 includes 234 terms grouped in eight clusters. It is noteworthy that the number of terms quadrupled in relation to the previous decade indicating the increased relevance of the LFM field.

Hull, Krogmann and Strom (2005) identified the reasons for the high prevalence of research on recovery of landfills through LFM in Central Europe, which coincides with the terms mentioned above: a. availability of special cleanup funds for contaminated sites; b. being a cheaper or more publicly accepted remediation option; c. clearing sites for housing establishment, especially in densely populated and gentrified areas; d. fuel supply for the cement industry; e. reusing available landfill infrastructure which simplifies the licensing process.Some terms that have recently emerged show the maturation of the technique, as several issues related to the technical feasibility are analyzed: e.g. ELFM, LCA, Landfill taxes, Stakeholders.

Cluster 1 (45 terms) refers to the Physicochemical characterization of mined residues (Arsenic, Cadmium, Carbon, Cobalt, Copper, Nitrogen, Organic material, Phosphorus) and the treatment given to these residues (Aerobic landfill, Aerobic leach bed reactors -LBR, Anaerobic Treatment, Biodegradation, Dry Mechanical process) in order to use this resource (Composting, Offsite application, Reuse, Soil).

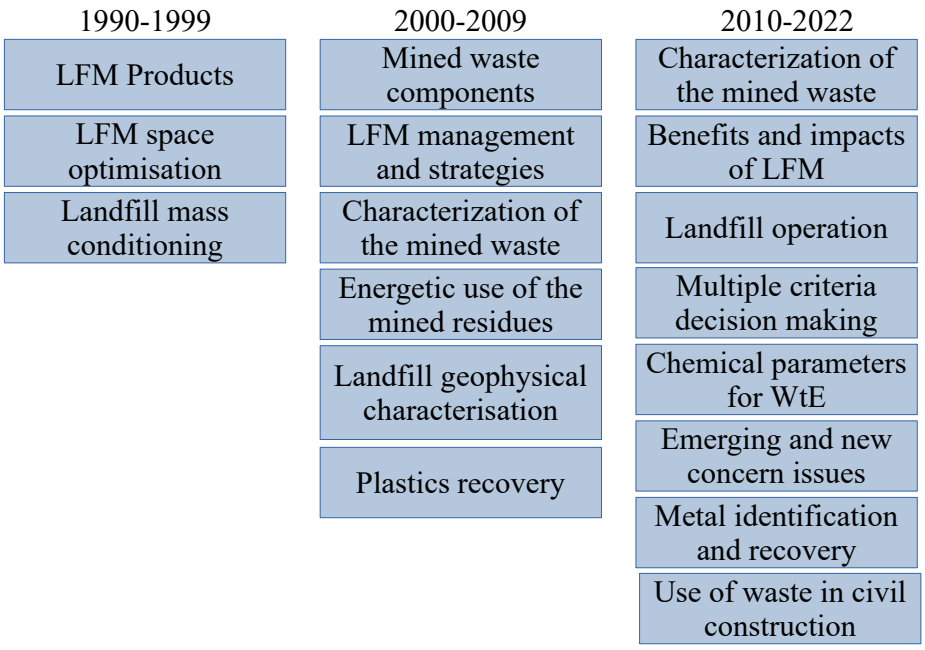


FIGURE 3: Clusters of significant terms which appeared in titles and abstracts of LFM papers published in course of three decades.

In this cluster appear the terms WtE (from waste to energy), WtL (waste-to-land, from waste to land space), and WtM (from waste to material) which consolidate the purpose of the LFM: to take advantage of the waste already landfilled in the energy, to production, to increase the useful time of the landfill or to make the area available for other purposes and material recovery to reinsert it directly into the production chain. There are also terms that deal with economic viability, such as the use of fine fractions from landfills, which would contribute to increased revenues and reduced expenses, given the ower need for backfilling (Parrodi et al., 2018).

Cluster 2 (44 terms) deals with the Benefits and impacts of LFM. There are terms that portray the various aspects that must be observed, such as a. economic (Economic Assessment, Market operational, Upcycling, Profitability, NPV - Net `Present Value); b. Environmental (Environmental analysis, Impact assessment, LCA, Global Warming, CH_4); c. social (Public acceptance); d. landfill costs (Aftercare control, Airspace use, Land reclamation, Land space, Material flow, Re-landfilling); e. possible uses (Aggregate, Cement industry, Coal, Fossil, Energy, Gas production, Plasma).

Gaitanarou, Tentes and Katselis (2014) argue that the market is not suitable for effective LFM for three reasons: a. there is no economically sustainable demand for recycled materials; b. there is a lack of technical advances for full exploration; c. There is evidence that landfilling waste can contribute to CO_2 sequestration. Therefore, Bhatnagar et al. (2017) state that LFM projects will become more profitable and necessary when the global demand for metals and the costs of their extraction grow, considering that primary sources of high-quality ores decrease.

NPV of a LFM project is inversely proportional to the waste treatment and disposal costs, re-landfilling taxes and gate fees for external WtE treatment; on other hand is directly proportional to the avoided costs for landfill management and aftercare (Laner et al., 2019).

Cluster 3 (36 items) refers to Landfill operation, its composition, management, location, collection rate and closure (Public park, Recreational area, Remediation) and how LFM can promote environmental benefits (Resource recovery, Renewable energy, Revenue) when considered a public policy (Government regulation) and a sustainable secondary source of raw material asmetals (Secondary copper, Zinc), trough techniques for extracting and processing excavated material (Stationary Separation Plant).. In this cluster, the term WtP summarizes the new perspective of LFM: excavated waste as raw material for industrialization in the form of new products. According to the WtP concept, waste treatment by-products are used to manufacture valuable co-products, that is, scalable (Bosmans et al., 2013).

It is important to note that, although the focus of this article is urban waste landfills, when it comes to metal recovery, the analyzed articles include in their studies two relevant terms: industrial landfill and REE (electronic waste) Despite the great theoretical benefit of LFM Burlakovs et al. (2018) found in the case of 2 REE landfills located in Sweden and Estonia that only a small fraction of elements can be exploited using existing technologies, therefore the potential can be referred to as a reserve for the future.

Cluster 4 (35 terms)deals with Decision-making with multiple criteria (Decision Maker,MCA - Multi-criteria analysis, DST - Decision support tool). These criteria are: a. environmental (Environmental footprint, Upcycling, Soil pollution), b. social (Stakeholders, Post consumer), c. operational (DLM- Dynamic landfill management, Mechanical sorting, Waste management) and d. economic (Circular economy, Secondary fuel). In this cluster, the term ELFM

appears for the first time, and already has a high occurrence. ELFM is an evolution of the term LFM whose objective is to fully determine the value of the various waste cases (Danthurebandara et al., 2015). Research with nanomaterials (Solgel) also becomes popular. The geophysical characterization, also present in the previous decade, continues to be relevant in this decade.

Cluster 5 (29 items) deals with and analyzes more deeply the Chemical characteristics (Chemical Composition, FTIR - Fourier Transform Infrared Spectroscopy, Thermogravimetry) aiming at the Energetic use of the mined residues (WtE) either in the form of thermal energy (Ash, Biochar, Lignina content), electricality (H_2, Syngas) or fuel (Biomass, Fuel RDF - Refuse Derived Fuel, Oil) through biological, thermal and thermochemical processes (airflow technology, gasification, thermal treatment, thermochemical process, torrefaction).

The most common challenges when using the fuel fraction as RDF are the high ash content, the presence of chlorine and low energy value. However, we can use this fraction by implementing pre-cleaning techniques like sorting, cleaning and drying (Jain, Kumar and Kumar, 2023).

The term Plastic is the one with the highest occurrence and the highest number of connections with other clusters; it is linked to the terms Fine Fraction, SRF-Solid Recovered Fuel, Gasification, Calorific Power, Power Generation, and Pyrolysis, which points out to the various technological routes for applying the material. Another point to be researched is the amount of lignin in landfills that function as bioreactors.

Cappucci et al. (2020) highlighted that the scenario of recovering mined plastic is environmentally preferable because it prevents the extraction of a non-renewable resource (crude oil) and emissions from its refining process.

Cluster 6 (19 terms), presents very recent issues (mainly published between 2021 and 2022), namely: determination of microorganisms and microplastics present in mined material, ecological and ecotoxicological evaluation, application of enzymes to stabilize the material and use of Gas Chromatography Mass Spectrometry (GCMS) for chemical characterization. These terms point to possible paths for Emerging and new concern issues.

Orupold et al. (2022) found a low toxicity of the fine fraction of the mined to bacteria, marine rotifer and microcrustaceans, and also a slight inhibitory effect on seed germination. On the other hand, Singh and Chandel (2022) concluded that the fine fraction cannot be used directly in agriculture, and that the most promising alternatives are soil enrichment for the growth of biomass or renewable energy crops.

Microplastics are a chemical contaminant that can be present in the fine fraction, and they can prevent, in the long term, water infiltration into the soil; therefore, further research is needed to develop adequate and economical treatments for the fine fraction (Singh and Chandel, 2021).

Cluster 7 (15 items) refers to an increasingly relevant theme: Metal identification and recovery. This is a very recent area of research, with studies published in 2022, which employ advanced techniques for identification (FDEM - Frequency-domain electromagnetic and KEG - Kalman Ensemble Generator) and separation of metallic materials (Magnetic sorting, Physical sorting).

Cluster 8 (11 terms) presents a new technological route for the Use of waste: in civil construction (Building material, Burnt clay brick, Green construction), which uses both more advanced techniques for the separation of fractions of the mined material (Ballistic separation, used to recover calorific and fuel fractions) and the most common ones (Manual screening, possibly targeting the coarsest fractions of demolition waste).

In relation to fine fractions, another factor must be considered in terms of economics: the costs of additional cleaning or treatment processes to recover critical metals and fuels; research on these techniques is in broad development (Esguerra et al., 2021). For the best use of this fraction, it is suggested to determine: chemical and mineralogical composition, location, size and volume of the landfill, type of landfilled waste, operational procedures, degree of degradation of landfilled waste, markets for recovered materials and environmental and health risks (Parrodi et al., 2018).

Figure 4 summarizes all the 238 key terms in LFM research. Thirteen terms were mostly cited in the three decades of LFM research,3 of which are very relevant. The production of stabilised organic matter (“Compost”) was the first case of LFM product that still today remains relevant, particulary in developing countries, where generally selective collection is not common and, consequently, a large amount of organic matter is sent to landfills.

The second important term is Environmental Analysis, since there is still no validated method for environmental assessment, although there is recent research employing the LCA. Additionally, there is a trend towards the increase of related terms, such as Biological Assessment, Ecological Assessment and Ecotoxicological Assessment. The third term is Fine Fraction, which corresponds to 40 to 80% by weight of the total waste excavated (Parrodi et al., 2018) and therefore can be decisive in determining the viability of Mining.

Some recent terms in the field of LFM, published around the 2020s, were: Torrefaction, Physical-chemical characteristics, Landfill age and Thermochemical processes. These terms may indicate the direction to which the research points: to know the mined material in greater detail, in order to identify its potential use and investigate the applicability of Technologies for energy production with the material.

In order to choose the best technological route, the age of the landfill, and consequently the degree of inertization of the excavated material, must be considered. Thus, the characterization of the deposited material (composition and/or physical-chemical characteristics) continues to be an important topic within landfill mining research (Krook et al., 2012).

Economic evaluation is also a very recurrent term. The literature points out that, in most cases, resource extraction through landfill mining cannot yet be carried out solely for commercial reasons, but it is only an economic option if there are subsidies or other types of support (Van Passel et al., 2013). On the other hand, standardization of eco-

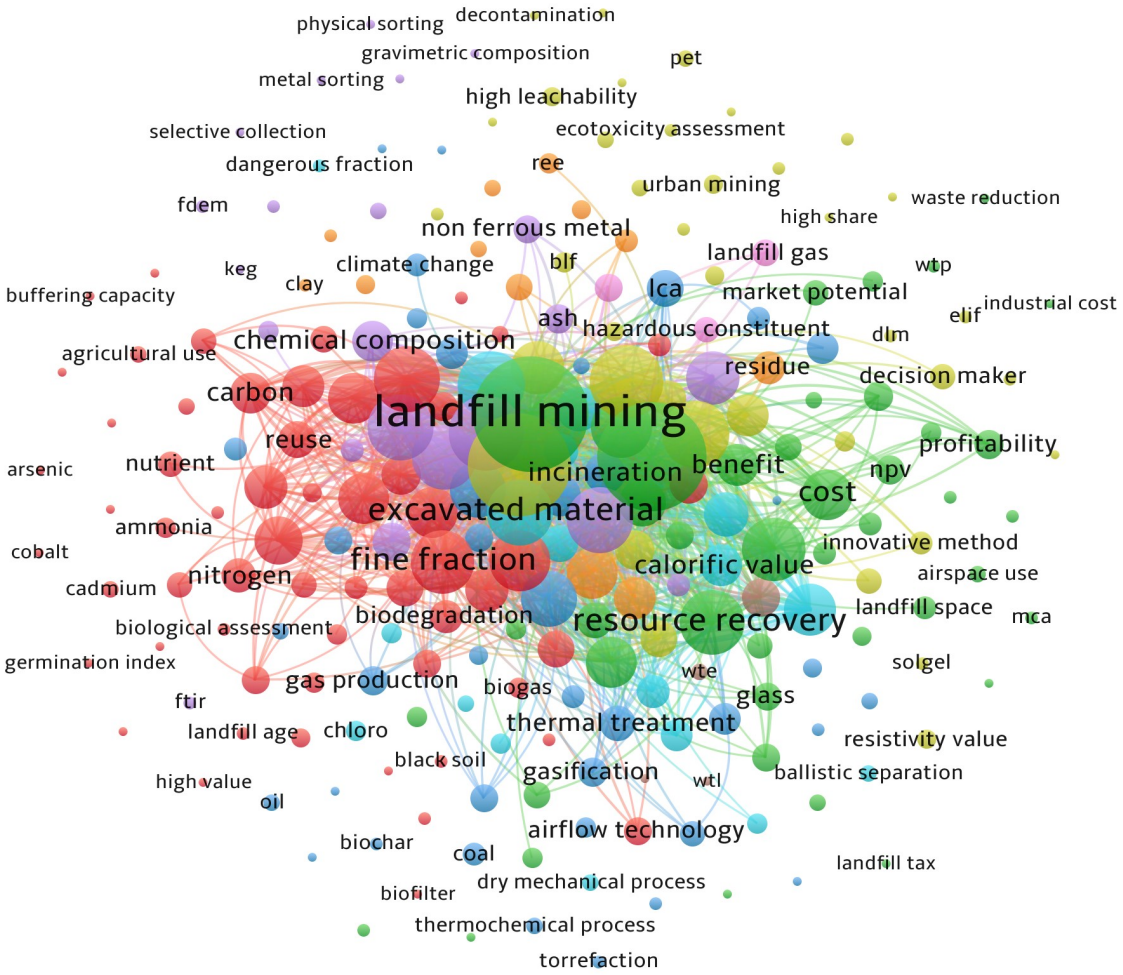


FIGURE 4: Complete network of co-occurrence of terms in the years 1990-2022.

nomic assessment is difficult, because the economic performance of landfill mining is restricted to highly specific projects carried out in different regions and under varying conditions and objectives (Laner et al., 2019).

The most recent terms, published in the years 2021 and 2022,that are noteworthy are: Standard limits and Regulatory body. Both keywords suggest the need for the public power to play a leading role in implementing the LFM. Esguerra et al. (2021) suggest two ways to improve the economic performance when using RDF and Fine Fraction: a. replacing taxes with tax incentives for the production of renewable energy and b. imposition of a quality standard dependent on the leachability of the pollutant and not the total concentration.

4. CONCLUSIONS

Based on information extracted from the Scopus database, we can observe the evolution of the research in Sanitary Landfill Mining. In the first decade of publication (1990-1999), the terms were centered on in-situ mining, whith the following technological aspects: a. with aerobic treatment aiming at obtaining compost; b. biogas capture (with or without reuse) and leachate treatment; and c. increased airspace. In the second decade (2000-2009) there was still a predominance of in-situ mining, as the most used terms in the articles related with energy use, compost production and remediation of dumps.

Over the years, four new aspects of research have been introduced and gained prominence in the last decade (2010-2022). The first aspect is the understanding that Mining is an efficient strategy for the complete management of waste, and that its implementation will positively influence the goals of reducing and recycling waste. In the second decade, LFM also started beeing seen as a business opportunity, subject to public regulation. In the third decade, LFM viability has been understood in the context of public policy.

The second aspect is the recognition that similarity between LFM's objectives with to those of the Circular Economysuch that, there is a prominence of terms related to ex-situ mining, in which the resource is mined in order to be used as energy, land, material or product. Thus LFM evolved into ELFM. In this context, the most promising techniques for operating a landfill (which will be mined in the future) and for treating the mined resources are BLF (Bioreactor Landfill) and Pyrolysis, respectively. Research on the application and cleaning/treatment techniques of the fine fraction is in full development.

The research of the Fine Fractions of the mined waste took place throughout the publication period and is still a field to be explored, since it is related to different routes of exploitation (plastic, fuel, RDF, energy). Therefore, its characterization is relevant even in cases of mining in landfills. Furthermore, the determination of heavy metals, mainly in fine fractions and in landfills, is also a relevant point of research, due to the risk of contamination and possible environmental restrictions.

The evolution of the LFM pratice can also be observed in relation to characterization techniques. In the first decade, characterization consisted of quantifying the common by-products of landfills; in the following decade there was a technological development, with the chemical and geophysical characterization. In the last decade, in order to recover metals or combustible materials, FPXRF analysis has also been used. This suggests a trend in this research field: the validation and standardization ofsampling and tests.

The third aspect is the use of advanced techniques for identifying metals (FDEM, KEG) and chemical elements (FTIR, GCMS, Thermogravimetry). The fourth aspect is in the field of ecological and ecotoxicological evaluation, with determination of microorganisms and microplastics present in the mined waste.

ACKNOWLEDGEMENTS

The researchers would like to thank the professors of the Modeling in Environmental Sciences course at PPGM/UEFS for the training in computational tools for bibliometric analysis and UFRB for granting the first author a doctoral license.

REFERENCES

Bhatnagar, A.; Kaczala, F.; Burlakovs, J.; Kriipsalu, M.; Hogland, M.; Hogland, W., 2017. Hunting for Valuables from Landfills and Assessing Their Market Opportunities A Case Study with Kudjape Landfill in Estonia. Waste Management & Research: The Journal for a Sustainable Circular Economy, v. 35, n. 6, p. 627–635. https://doi.org/10.1177/0734242X17697816

Bosmans, A.; Vanderreydt, I.; Geysen, D.; Helsen, L., 2013. The Crucial Role of Waste-to-Energy Technologies in Enhanced Landfill Mining: A Technology Review. Journal of Cleaner Production, v. 55, p. 10–23. https://doi.org/10.1016/j.jclepro.2012.05.032

Burlakovs, J.; Jani, Y.; Kriipsalu, M.; Vincevica-Gaile, Z.; Kaczala, F.; Celma, G.; Ozola, R.; Rozina, L.; Rudovica, V.; Hogland, M.; Viksna, A.; Pehme, K.-M.; Hogland, W.; Klavins, M., 2018. On the Way to 'Zero Waste' Management: Recovery Potential of Elements, Including Rare Earth Elements, from Fine Fraction of Waste. Journal of Cleaner Production, v. 186, p. 81–90. https://doi.org/10.1016/j.jclepro.2018.03.102

Burlakovs, J.; Kriipsalu, M.; Klavins, M.; Bhatnagar, A.; Vincevica-Gaile, Z.; Stenis, J.; Jani, Y.; Mykhaylenko, V.; Denafas, G.; Turkadze, T.; Hogland, M.; Rudovica, V.; Kaczala, F.; Rosendal, R. M.; Hogland, W., 2017. Paradigms on Landfill Mining: From Dump Site Scavenging to Ecosystem Services Revitalization. Resources, Conservation and Recycling, v. 123, p. 73–84. https://doi.org/10.1016/j.resconrec.2016.07.007

Calderón Márquez, A. J.; Cassettari Filho, P. C.; Rutkowski, E. W.; De Lima Isaac, R. 2019. Landfill Mining as a Strategic Tool towards Global Sustainable Development. Journal of Cleaner Production, v. 226, p. 1102–1115. https://doi.org/10.1016/j.jclepro.2019.04.057

Cappucci, G. M.; Avolio, R.; Carfagna, C.; Cocca, M.; Gentile, G.; Scarpellini, S.; Spina, F.; Tealdo, G.; Errico, M. E.; Ferrari, A. M., 2020. Environmental Life Cycle Assessment of the Recycling Processes of Waste Plastics Recovered by Landfill Mining. Waste Management, v. 118, p. 68–78. https://doi.org/10.1016/j.wasman.2020.07.048

Chandana, N.; Goli, V. S. N. S.; Mohammad, A.; Singh, D. N., 2021. Characterization and Utilization of Landfill-Mined-Soil-Like-Fractions (LFMSF) for Sustainable Development: A Critical Appraisal. Waste and Biomass Valorization, v. 12, n. 2, p. 641–662. https://doi.org/10.1007/s12649-020-01052-y

Cossu, R., 2018. Why This Journal? Why This Name? Detritus, v. 1, n. 0, p. 1–2. https://doi.org/10.26403/detritus/2018.1

Danthurebandara, M.; Passel, S. V.; Acker, K. V., 2013. Life Cycle Analysis of Enhanced Landfill Mining: Case Study for the Remo Landfill. In: 2nd International Enhanced Landfill Mining Symposium, 2013, Houthalen-Helchteren, Belgium. [...]. Houthalen-Helchteren, Belgium: Unpublished.

Danthurebandara, M.; Van Passel, S.; Vanderreydt, I.; Van Acker, K., 2015. Assessment of Environmental and Economic Feasibility of Enhanced Landfill Mining. Waste Management, v. 45, p. 434–447. https://doi.org/10.1016/j.wasman.2015.01.041

Dhar, A., 2015. Landfill Mining - A Comprehensive Literature Review. Disponível em: <http://rgdoi.net/10.13140/RG.2.2.31092.55687>. Acesso em: 29 nov. 2022.

Einhäupl, P.; Krook, J.; Svensson, N.; Van Acker, K.; Van Passel, S., 2019. Eliciting Stakeholder Needs – An Anticipatory Approach Assessing Enhanced Landfill Mining. Waste Management, v. 98, p. 113–125. https://doi.org/10.1016/j.wasman.2019.08.009

Esguerra, J. L.; Laner, D.; Svensson, N.; Krook, J., 2021. Landfill Mining in Europe: Assessing the Economic Potential of Value Creation from Generated Combustibles and Fines Residue. Waste Management, v. 126, p. 221–230. https://doi.org/10.1016/j.wasman.2021.03.013.

Frändegård, P.; Krook, J.; Svensson, N.; Eklund, M., 2013. A Novel Approach for Environmental Evaluation of Landfill Mining. Journal of Cleaner Production, v. 55, p. 24–34. https://doi.org/10.1016/j.jclepro.2012.05.045

Gaitanarou, Z., Tentes, G., & Katselis, Y., 2014. Landfill Mining: An empirical review on past and state-of-the-art applications. In: 2nd International Conference on Sustainable Solid Waste Management. Disponível em: <http://www.athens2014.biowaste.gr>. Acesso em: 11 dez. 2023.

Jain, M.; Kumar, A.; Kumar, A., 2023. Landfill Mining: A Review on Material Recovery and Its Utilization Challenges. Process Safety and Environmental Protection, v. 169, p. 948–958. https://doi.org/10.1016/j.psep.2022.11.049

Johansson, N., 2016. Linköping University, Department of Management and Engineering, Environmental Technology and Management. Linköping University, Faculty of Science & Engineering. https://doi.org/10.3384/diss.diva-132424

Jones, P. T.; Geysen, D.; Tielemans, Y.; Van Passel, S.; Pontikes, Y.; Blanpain, B.; Quaghebeur, M.; Hoekstra, N., 2013. Enhanced Landfill Mining in View of Multiple Resource Recovery: A Critical Review. Journal of Cleaner Production, v. 55, p. 45–55. https://doi.org/10.1016/j.jclepro.2012.05.021

Krook, J.; Baas, L., 2013. Getting Serious about Mining the Technosphere: A Review of Recent Landfill Mining and Urban Mining Research. Journal of Cleaner Production, v. 55, p. 1–9. https://doi.org/10.1016/j.jclepro.2013.04.043

Krook, J.; Svensson, N.; Eklund, M., 2012. Landfill Mining: A Critical Review of Two Decades of Research. Waste Management, v. 32, n. 3, p. 513–520. https://doi.org/10.1016/j.wasman.2011.10.015

Laner, D.; Esguerra, J. L.; Krook, J.; Horttanainen, M.; Kriipsalu, M.; Rosendal, R. M.; Stanisavljević, N., 2019. Systematic Assessment of Critical Factors for the Economic Performance of Landfill Mining in Europe: What Drives the Economy of Landfill Mining? Waste Management, v. 95, p. 674–686. https://doi.org/10.1016/j.wasman.2019.07.007

Marella, G.; Raga, R., 2014. Use of the Contingent Valuation Method in the Assessment of a Landfill Mining Project. Waste Management, v. 34, n. 7, p. 1199–1205. https://doi.org/10.1016/j.wasman.2014.03.018

Parrodi, J. C. H.; Höllen, D.; Pomberger, R., 2018. Characterization of Fine Fractions from Landfill Mining: a Review of Previous Investigations. Detritus, v. 2, n. 1, p. 46. https://doi.org/10.31025/2611-4135/2018.13663

Singh, A.; Chandel, M. K., 2021. Physicochemical and FTIR Spectroscopic Analysis of Fine Fraction from a Municipal Solid Waste Dumpsite for Potential Reclamation of Materials. Waste Management & Research: The Journal for a Sustainable Circular Economy, v. 39, n. 2, p. 374–385. https://doi.org/10.1177/0734242X20962844

Singh, A.; Chandel, M. K., 2022. Physicochemical and Biological Assessment of Legacy Waste for Application as Soil Conditioner. Environmental Science and Pollution Research, v. 30, n. 11, p. 29699–29710. https://doi.org/10.1007/s11356-022-24295-9

Sabour, M. R.; Alam, E.; Hatami, A. M., 2020. Global Trends and Status in Landfilling Research: A Systematic Analysis. Journal of Material Cycles and Waste Management, v. 22, n. 3, p. 711–723. https://doi.org/10.1007/s10163-019-00968-5

Van Passel, S.; Dubois, M.; Eyckmans, J.; De Gheldere, S.; Ang, F.; Tom Jones, P.; Van Acker, K., 2013. The Economics of Enhanced Landfill Mining: Private and Societal Performance Drivers. Journal of Cleaner Production, v. 55, p. 92–102. https://doi.org/10.1016/j.jclepro.2012.03.024

Vollprecht, D.; Machiels, L.; Jones, P. T., 2021. The EU Training Network for Resource Recovery through Enhanced Landfill Mining—A Review. Processes, v. 9, n. 2, p. 394, 22. https://doi.org/10.3390/pr9020394.

Wagner, T. P.; Raymond, T., 2015. Landfill Mining: Case Study of a Successful Metals Recovery Project. Waste Management, v. 45, p. 448–457. https://doi.org/10.1016/j.wasman.2015.06.034

Xiang-Chao, P., 2018. Research on Xi Jinping's Thought of Ecological Civilization and Environment Sustainable Development. IOP Conference Series: Earth and Environmental Science, v. 153, p. 062067. https://doi.org/10.1088/1755-1315/153/6/062067

Zhou, C.; Gong, Z.; Hu, J.; Cao, A.; Liang, H. A, 2015. Cost-Benefit Analysis of Landfill Mining and Material Recycling in China. Waste Management, v. 35, p. 191–198. https://doi.org/10.1016/j.wasman.2014.09.029

detritus | Multidisciplinary Journal for Circular Economy and Sustainable Management of Residues

CISA

CHEMICAL RECYCLING OF PVC-CONTAINING PLASTIC WASTE FOR RECYCLING OF CRITICAL METALS

Michael Peer [1,2,*], Burkhard Berninger [1], Thomas Fehn [2] and Alexander Hofmann [2]

[1] *Department of Mechanical Engineering and Environmental Engineering, Technical University of Applied Science, Kaiser-Wilhelm-Ring 23, 92224 Amberg, Germany*
[2] *Fraunhofer UMSICHT, Fraunhofer Institute for Environmental, Safety, and Energy Technology, An der Maxhütte 1, 92237 Sulzbach-Rosenberg, Germany*

Article Info:
Received:
12 September 2023
Revised:
16 March 2024
Accepted:
19 March 2024
Available online:
25 March 2024

Keywords:
Circular economy
Chemical recycling
Critical metals
PVC-waste
LED recycling
LCD panels recycling

ABSTRACT

Chemical recycling of polyvinyl chloride containing plastic waste to recover critical metals is a promising way to solve two important problems (polyvinyl chloride disposal and critical metal recovery) in waste management and is being transferred on a larger scale in the "CHM-Technology" project. Various polyvinyl chloride containing plastic wastes were pyrolyzed to generate a hydrogen chloride rich vapor. This hydrogen chloride rich vapor is used in a second step to chlorinate indium in liquid crystal displays. Indium chloride has a lower boiling point than indium-tin-oxide and evaporates. This is cooled down and generates a metal concentrate together with the decomposed volatile materials from liquid crystal displays. The chlorine content in the polyvinyl chloride containing plastic waste residues is reduced. The products solid, oil, hydrochloric acid and gas can be used for new products. For metal purification the metal concentrate is mixed with water, filtrated, distilled and an electrolysis is carried out to recover metallic indium. Nine waste containing PVC were used with significant differences: when more hydrochloric acid and less volatile organic fraction was produced, more indium was transferred to the metal concentrate. The best recovery of indium (78% purity after electrolysis) was 39 wt-% from LCD panels containing 83 mg In/kg.

1. INTRODUCTION

Plastics are one of the greatest inventions of the 20th century. Plastic products are used in many fields such as packaging, building and construction, agriculture, and many other applications, due to their light weight, mouldability, long life and low price (Geyer, Jambeck & Law, 2017). Plastic production has continuously increased in the last decade. The annual production exceeded 330 million metric tons (Mt) from 2016 to 2020. Polyvinyl chloride (PVC) accounted for 9.6% of all plastics in 2020, ranking in third place. There are different methods to dispose plastic waste (Geyer et al., 2017; Geyer, 2020). First, incineration decreases the volume of waste, and the resulting energy can be used for heating or generating electricity. However, incineration of plastic waste emits excessive CO_2 and may release some hazardous substances, such as polychlorinated biphenyls, dioxins, furans, and persistent organic pollutants (POPs) (Shibamoto et al., 2007). Further problems with the incineration of wastes with PVC are deposits on heat transfer tubes and the presents of Cl-species like potassium chloride, sodium chloride, hydrochloric acid and chlorine, which results in corrosion (Ma et al., 2020, Miliute-Plepiene et al., 2021, Lu et al., 2023). The cost for PVC-containing plastic waste is 275 €/t in Germany (Hofmann, 2021). Second, plastic waste can be dumped in sanitary landfills, which is a convenient and cost-effective, but landfill space is limited in many countries and an inadequate landfill can cause serious environmental pollution (Hopewell et al., 2009; Teuten et al., 2009; Wang, Ko, Liu & Xu, 2021). In some countries, such as Germany or Austria, the landfilling of Total Organic Carbon (TOC)-containing waste is prohibited (Bundesministerium der Justiz und für Verbraucherschutz, 2009). Third, mechanical recycling is suitable for various types of plastic waste (Braun, 2002). End-of-life PVC degradation causes release of chlorinated products into the surrounding environment (Maringer et al., 2017). Mechanisms of degradation during recycling include thermo-oxidation, crosslinking, functionalization of chains and hydrodechlorination (Awaja & Pavel, 2005; Sadat-Shojai & Bakhshandeh, 2011). PVC is unstable to both thermal and photoinduced stress. PVC waste streams must be pure and highly stabilized against unwanted degradation to enable useful mechanical recycling (Schyns &

* Corresponding author:
Michael Peer
email: m.peer@oth-aw.de

Detritus / Volume 26 - 2024 / pages 83-88
https://doi.org/10.31025/2611-4135/2024.18360

Shaver, 2021). A fourth method called "chemical recycling" summarized the development of alternative techniques for plastics recycling like pyrolysis, gasification and liquefaction (Quicker et al., 2022; Scheirs & Kaminsky, 2006). For PVC-containing plastic waste gasification and pyrolysis are mainly in the focus of research. For example, the company Ecoloop in Goslar (Germany) produces synthesis gas from PVC-containing plastic waste, but the chlorine (Cl) is absorbed with calcium oxide, where calcium chlorine is generated (VinylPlus, 2015). In this case the hydrogen chloride (HCl) or chlorine can`t be used for further processes. Therefore, pyrolysis of PVC can be used and the techniques like two-stage pyrolysis, co-pyrolysis or ad-/absorption of halogens in the vapor phase were tested for different purposes like removing chlorine in oil from mixed plastic waste (Bockhorn & Hornung, 1998; Liu et al., 2013; Muhammad et al., 2015; Shen et al., 2016).

Electronic products are another essential component of modern society, but their importance has perhaps never been more noticeable than when the COVID-19 pandemic forced almost every aspect of human interaction going online. However, the pandemic also demonstrated that the supply chains that provide crucial raw materials for manufacturing electronics are increasingly vulnerable to social, geopolitical, and technical disruptions. These vulnerabilities are likely to increase in the future, due to global health crises, natural disasters, and worldwide political instability, all of which will be magnified by looming climate change impacts almost 40 metals and minerals that provide critical functionality to electronic products (Althaf & Babbitt, 2021). A lot of these metals used in electronic products especially specialty metals like rare earth elements, gallium or indium (In) have End-of-Life-recycling rates (EoL-RR) of less than 1% (Graedel et al., 2011). In case of indium, EoL products are considered to be a promising secondary source (Lokanc et al., 2015). In the EU, total indium consumption is estimated at 64 tonnes per year from 2012 to 2016, with 60% of the total indium used in flat panel displays (FPDs), mainly in the form of indium tin oxide (ITO). In addition, 11% and 9% of the consumption is used in solders and photovoltaics, respectively, while the remaining 20% is used in thermal interface materials, batteries, alloys/compounds, and semiconductors & light emitting diodes (LED) (European Commission, 2020). This highlights the importance of considering EoL electronic products as a viable source of indium, particularly for FPDs. The liquid crystal displays (LCDs) have the highest market share among FPDs (Zheng et al., 2023) (Figure 1).

Pyrolysis of PVC was tested to use the generated hydrogen chloride for the recovery of indium from indium-tin-oxide powder and LCDs (Park et al., 2009). The utilization of hydrogen chloride from PVC for the recovery of metals like indium from other waste streams was inspiring to do further research with different PVC-containing material for the recovery of indium from LCDs and LEDs in the projects "chlorine platform" and "CHM-Technology" (Berninger & Peer, 2022).

2. MATERIALS AND METHODS

2.1 PVC-containing plastic waste and LCD-panels

PVC-containing materials were used for experiments further explained in chapter 2.3: automotive shredder residue (4,350 ± 57 mg/kg Cl), sorting residues from lightweight packaging (2,827 ± 196 mg/kg Cl), shredder residue from waste of electrical and electronic equipment (3,400 ± 328 mg/kg Cl), window frames (237,263 ± 6,233 mg/kg Cl), cable (129,442 ± 5,479 mg/kg Cl), shutter (192,827 ± 7,120 mg/kg Cl), PVC profiles (249,023 ± 6,043 mg/kg Cl), PVC-pipes (353,762 ± 10,138 mg/kg Cl) and wall paper (58,033 ± 3,496 mg/kg Cl), where the particle sizes are lower than 10mm. EoL–LCD-panels (83 ± 5 mg/kg In) were shredded to <40mm for the experiments.

2.2 Energy Dispersive X-Ray Fluorescence Spectroscopy

The elemental content in the input materials and products were analyzed by the X-ray spectrometer Epsilon 3XLE from PANalytical Kassel. The device was calibrated with the "omnian" standard from PANalytical Kassel, and the evaluation of the data was performed with the Epsilon Benchtop software of the same manufacturer. The elements from sodium to americium can be analyzed. The focus of this work is on the reduction of chlorine from PVC-containing materials and the volatilization of indium from LCDs, which

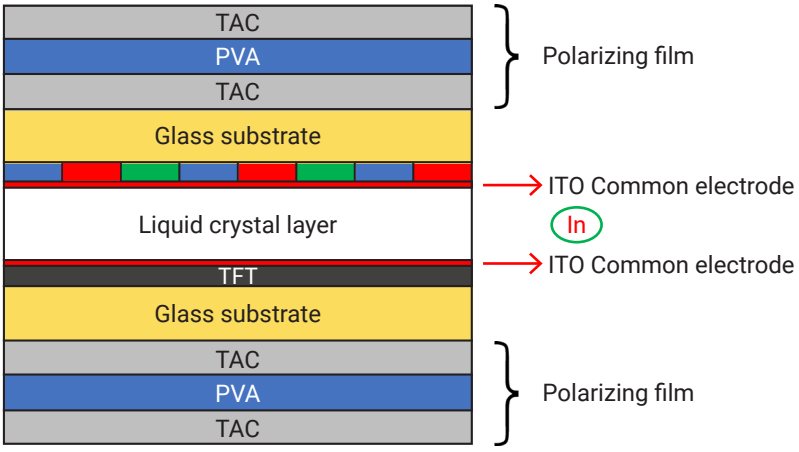


FIGURE 1: Lamination structure of the ITO layer from LCD panel (Zheng et al., 2023).

is why only the chlorine content is given for the PVC-containing materials and only the indium content for the LCDs. The solid samples were crushed to <1 mm with the cutting mill of the company Retsch at 600 rpm for analysis and the liquid samples were analyzed directly.

2.3 Experimental set-up

PVC-containing materials were treated in a semi-continous pyrolysis plant with a halogenation reactor (Figure 1). The Halogenation reactor was filled with 2,100 g LCDs before the plant was set-up, except for wallpaper, window frame and PVC-pipes. For these three materials, the Halogenation reactor was filled with 1050 g LCDs. The halogenation reactor is self-made with 1.4571 steel, inner diameter of 50 mm, a wall thickness of 3mm and electric heated with two heaters each with a power of 3 kW. The reactor of the pyrolysis plant is self-made. Prior to treatment, the plant was set-up andflushed with nitrogen to remove the oxygen at a gas flow of 0.5 liters per minute. The pyrolysis reactor was heated up to 650°C. The halogenation with LCDs was heated up to 650°C. The polarizing film decomposed to solid, gas and oil. The oil evaporates and condenses in cooling unit 3 as well as in cooling unit 4. 750 g PVC-containing material was filled into a cartridge in six batch with each batch 125 g. Only for wallpaper, window frame and PVC-pipes the masses were 375 g and each batch 62.5 g. The mass ratio between LCDs and PVC material was 1:2.8 in all experiments. The exact masses are listed in Table 1. After inertization with nitrogen, the PVC material from the cartridge was added to the reactor. The cartridge was flushed again with nitrogen to remove pyrolysis vapors. The thermochemical treatment and decomposition took place in the pyrolysis reactor at 650°C. Coke and pyrolysis vapor is generated. The coke remained in the pyrolysis reactor, was stirred and was transferred to the char container after 30 min dwell time. Then the next batch was filled in. The vapor flowed from the pyrolysis reactor through the cooling unit 1 and cooling unit 2, where it was cooled down and oil condensed. Then the HCl rich vapor reached the halogenation reactor. Here the HCl reacted with the indium in the LCDs to indium chloride. The indium chloride evaporated at 650°C and condensed at cooling unit 3 and cooling unit 4. The unreacted HCl was removed from the gas stream by scrubbing it at first in a washing bottle with water and then in two washing bottles with sodium hydroxide. In the bottle with cotton fine liquid particles were removed from the gas stream. The gas was analyzed with a gas analyzer from the company Pollutek. The measuring principles for the gases CO, CO_2, CH_4, and C_nH_m were a non-dispersive infrared sensor, O_2 was a electrochemical detector and for H_2 it was a thermal conductivity detector. The gas wascleaned with activated charcoal and released to the environment (Figure 2).

2.4 Recovery of the critical metal indium from metal concentrate

The indium was enriched in the liquid metal concentrate but mixed with organic material from the polarizing film decomposition from LCDs. The metal concentrate was mixed with water in a volume ratio of 1:1.75 and particles conglomerated. Then the particles were removed, by filtering two times with a 2µm filter. The metal concentrate and filtrate is shown in Figure 3. For electrolysis the indium concentration was enriched in the solution. Therefore the filtrate was distillated to remove the solvent. The indium concentrate for electrolysis was 15 gram per liter and a volume of 10 ml. The electrolysis was conducted at a current of 5.2 volts and 0.1 ampere with electrodes of platinated titanium with a diameter of 6mm for one hour.

3. RESULTS AND DISCUSSION

The pyrolysis of the PVC-containing materials generates the products solid residue, oil and gas. The mass of oil is containing the liquid in the bottles under cooling 1 and cooling 2 as well as the residue in the pipes from the cooling unit 1 and cooling unit 2. The masses are listed in Table 1.

The most amount of solid residue was produced from the automotive shredder fraction. Due to the low chlorine content of the input material, not much oil and gas was produced. The most gas produced in the from the input-material PVC profiles. Here the chlorine content was reduced by 60.5% (Table 2). The most oil was produced from the input-material shredder residue from waste of electrical and electronic equipment. This is caused due to the high polyolefin content. The chlorine content of the solid residues

TABLE 1: Input masses [g] and products solid residue [g], gas [g] and oil [g].

PVC-containing materials	Input material [g]	Solid residue [g]	Gas [g]	Oil [g]
automotive shredder fraction	752.55	572.45	115.20	64.90
sorting residues from lightweight packaging	751.3	206.05	262.25	283.00
shredder residue from waste of electrical and electronic equipment	751.00	201.30	199.65	350.05
window frames	375.15	98.05	232.00	45.10
cable	751.60	438.1	120.85	192.65
shutter	751.00	332.45	334.35	84.20
PVC profiles	751.35	233.45	414.00	103.90
PVC-pipes	375.7	151.25	164.60	59.85
wallpaper	374.95	145.15	126.55	103.25

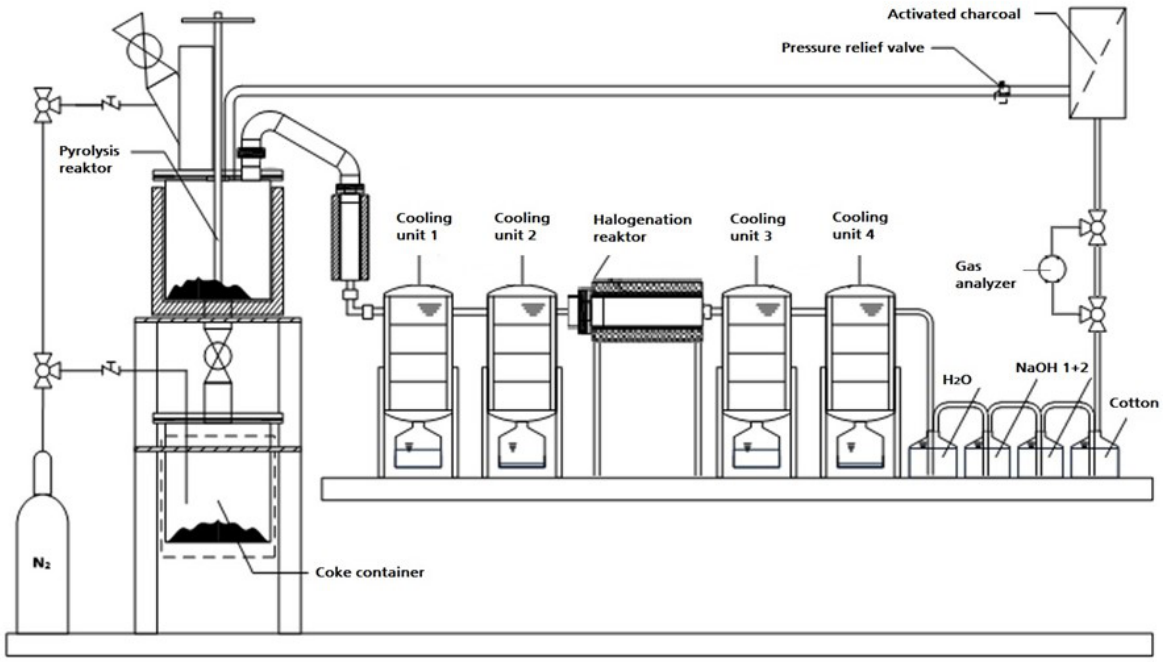


FIGURE 2: Schematic set-up of the plant for the experiments.

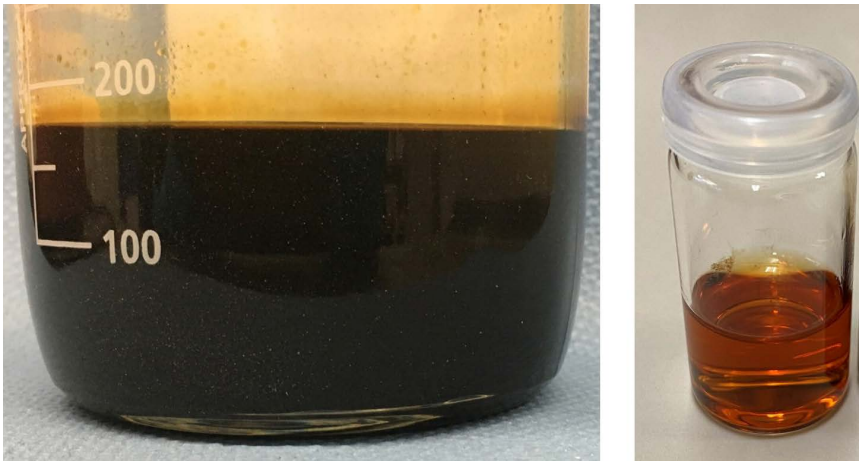


FIGURE 3: Metal concentrate (left) and filtrate (right).

TABLE 2: Chlorine removed from PVC-containing material [wt.-%], indium transferred to metal concentrate [wt.-%] and indium in metal concentrate [ppm].

PVC-containing materials	chlorine removed [wt.-%]	Indium transferred to metal concentrate [wt.-%]	Indium in metal concentrate [ppm]
automotive shredder fraction	8-10*	0.9	11
sorting residues from lightweight packaging	8-10*	6.2	61
shredder residue from waste of electrical and electronic equipment	8-10*	26.8	393
window frames	94.8	29.9	335
cable	57.3	13.3	126
shutter	37.9	38.9	392
PVC profiles	60.5	33.3	1057
PVC-pipes	86.3	29.5	267
wallpaper	99.0	67.7	1230

** chlorine reduction calculated by subtraction of the chlorine mass from the products except solid residue from the input mass of chlorine.*

were from automotive shredder fraction 9,167 ± 871 mg/kg, sorting residues from lightweight packaging 51,432±1,430 mg/kg, shredder residue from waste of electrical and electronic equipment 14,780±1,215 mg/kg, window frames 48,209 ± 926 mg/kg, cable 95,326 ± 17,114 mg/kg, shutter 279,746 ± 5,019 mg/kg, PVC profiles 322,837 ± 1,512 mg/kg, PVC-pipes 120,479 ± 1,778 mg/kg and wallpaper 1,466 ± 291 mg/kg. The highest chlorine content in the solid residue is in the PVC-profiles.

The calorific value of the solid residues were from automotive shredder fraction 2.60MJ/kg, sorting residues from lightweight packaging 19.96 MJ/kg, shredder residue from waste of electrical and electronic equipment 8.13 MJ/kg, window frames 22.74 MJ/kg, cable 13.75 MJ/kg, shutter 10.86 MJ/kg, PVC profiles 13.01 MJ/kg, PVC-pipes 17.39 MJ/kg and wallpaper 11.44 MJ/kg. The highest calorific value of the solid residue was from the window frames.

The chlorine mass in the PVC-containing materials could be reduced between 8% and 99% via pyrolysis. The results are shown in Table 2. Hereby the reduction is the difference between the chlorine mass of the input-material and in the solid residue after pyrolysis. The indium content could be enriched in the metal concentrate up to 15 times in comparison to LCDs. This reduces the mass in the following process steps to the metallic indium and decreases costs. Between 0.9 wt.-% and 67.7 wt.-% of the indium from the LCDs were transferred to the metal concentrate. This shows that some PVC-containing materials are better suited for this recovery of indium.

Normally by increasing the weight percent from indium transferred to metal concentrate, the indium in the metal concentrate should also increase, when the metal concentrate was only containing the indium and decomposed components from the LCDs. This is not the case. Therefore, this indicates that the gas stream was not completely purified from oil after cooling unit 1 and cooling unit 2. The cooling system has to be improved for further experiments to avoid dilution with oil from PVC-containing materials. When more chlorine is removed from the PVC-containing material, then more indium should be transferred to the metal concentrate. This tendency was the case, but this does not explain the difference between window frames and wallpaper. Here the difference was in the amount of gas, which was produced. The wallpaper produced 126.55 g gas and window frames 232.00 g gas. When more hydrochloric acid and less organic gaseous fraction was produced, then more indium was transferred to the metal concentrate.

The recovery of indium from the metal concentrate was achieved by mixing with water, filtration, evaporation and electrolysis. After filtration of the mixture of the metal concentrate with water 2/3 of the indium from the metal concentrate is in the filtrate and the rest in the filter residue. After the removal of solvents, the solution contains 15 g In/L. From electrolysis 20mg indium were recovered as metal and a yield of 57% from the indium in the metal concentrate was achieved by this process steps. The purity is 78% indium. This yield could be increased if the filterresidue is used as an additional input material for the halogenation reactor and if the electrolysis solution has a higher indium content, because then the current yield is higher. The best recovery of indium (78% purity after electrolysis) was 39wt-% from LCD panels containing 83 mg In/kg.

Here no dioxin or furan analysis was performed as the research focus was more on screening and product characterization. The de-/chlorination processes should be tested in continuous processes. Another promising waste stream with a lot of critical metals are LEDs. All these aspects will be examined in the project “CHM-Technology”.

4. CONCLUSIONS

Essential products from the pyrolysis process of PVC-containing plastic waste like solid residue, oil and gas can be used. In a pyrolysis reactor, which is used for industrial application, the generated products must be analyzed for dioxins/furans to be sure that no hazardous products are generated. There are PVC-containing plastic wastes like window frames, where a lot of chlorine remains in the solid residue. The pyrolysis process and combination with the total indium recovery yield of 30 wt-% with 78% purity are up to now only in small technical scale. This must be upscaled in a continuous process. The recovery of indium from LCDs is possible with the combination and further process steps. Here the limits are the heaters and material for the halogenation reactor to handle the heat together with the corrosive environment. For further byproducts from the process steps from the metal concentrate to the metal indium recycling opportunities should be found, to keep the cost for an industrial process low.

The chemical recycling of PVC-containing plastic waste for recycling of critical metals is a promising route to solve two important problems in waste management.

ACKNOWLEDGEMENTS

The project “CHM-Technology“ is part of the joint research project “ForCYCLE Technikum“ funded by the Bavarian State Ministry of the Environment and Consumer Protection (StMUV) and coordinated by the Centre for Basic Materials Efficiency (REZ).

REFERENCES

Althaf, S. & Babbitt, C. W. (2021). Disruption risks to material supply chains in the electronics sector. Resources, Conservation and Recycling, 167, 105248. https://doi.org/10.1016/j.resconrec.2020.105248

Berninger, B. & Peer, M. (2022). Plattformtechnologie zur Verwertung chlorhaltiger Abfälle und Rückgewinnung kritischer Metalle – Chlor-Plattform. Disponibile da https://www.stmuv.bayern.de/themen/ressourcenschutz/forcycle/forcycle2/doc/07_abschlussbericht.pdf

Bockhorn, H., Hornung, A. & Hornung, U. (1998). Stepwise pyrolysis for raw material recovery from plastic waste. Journal of Analytical and Applied Pyrolysis, 46(1), 1–13. https://doi.org/10.1016/S0165-2370(98)00066-7

Awaja, F. & Pavel, D. (2005). Recycling of PET. European Polymer Journal, 41(7), 1453–1477. https://doi.org/10.1016/j.eurpolymj.2005.02.005

Braun, D. (2002). Recycling of PVC. Progress in Polymer Science, 27(10), 2171–2195. https://doi.org/10.1016/S0079-6700(02)00036-9

Bundesministerium der Justiz und für Verbraucherschutz. (2009). Verordnung über Deponien und Langzeitlager (Deponieverordnung - DepV) Anhang 3 Zulässigkeits- und Zuordnungskriterien (zu § 2 Nummer 5 bis 9, 23 bis 26, 37, § 6 Absatz 2 bis 5, § 8 Absatz 1, 3, 5 und 8, § 14 Absatz 3, den §§ 15, 23, 25 Absatz 1). Disponibile da https://www.gesetze-im-internet.de/depv_2009/DepV.pdf

European Commission, Directorate-General for Internal Market, Industry, Entrepreneurship and SMEs, Blengini, G., El Latunussa, C., Eynard, U. (2020). Study on the EU's list of critical raw materials (2020) : critical raw materials factsheets, Publications Office. https://data.europa.eu/doi/10.2873/92480

Geyer, R. (2020). Production, use, and fate of synthetic polymers. In Plastic Waste and Recycling (pp. 13–32). Elsevier. https://doi.org/10.1016/B978-0-12-817880-5.00002-5

Geyer, R., Jambeck, J. R. & Law, K. L. (2017). Production, use, and fate of all plastics ever made. Science advances, 3(7), e1700782. https://doi.org/10.1126/sciadv.1700782

Graedel, T. E., Allwood, J., Birat, J.-P., Buchert, M., Hagelüken, C., Reck, B. K., Sonnemann, G. (2011). Recycling rates of metals: A status report. Nairobi, Kenya: United Nations Environment Programme.

Hofmann, R. (2021). Preisliste Abfälle. Disponibile da https://hofmann-entsorgung.de/wp-content/uploads/2020/01/HOFMANN_Preisliste.pdf

Hopewell, J., Dvorak, R. & Kosior, E. (2009). Plastics recycling: challenges and opportunities. Philosophical transactions of the Royal Society of London. Series B, Biological sciences, 364(1526), 2115–2126. https://doi.org/10.1098/rstb.2008.0311

Liu, W.-J., Tian, K., Jiang, H., Zhang, X.-S. & Yang, G.-X. (2013). Preparation of liquid chemical feedstocks by co-pyrolysis of electronic waste and biomass without formation of polybrominated dibenzo-p-dioxins. Bioresource technology, 128, 1–7. https://doi.org/10.1016/j.biortech.2012.10.160

Lokanc, Martin, Eggert, Roderick, & Redlinger, Michael. The Availability of Indium: The Present, Medium Term, and Long Term. United States. https://doi.org/10.2172/1327212Lu, L., Li, W., Cheng, Y. & Liu, M. (2023). Chemical recycling technologies for PVC waste and PVC-containing plastic waste: A review. Waste management (New York, N.Y.), 166, 245–258. https://doi.org/10.1016/j.wasman.2023.05.012

Ma, W., Wenga, T., Frandsen, F. J., Yan, B. & Chen, G. (2020). The fate of chlorine during MSW incineration: Vaporization, transformation, deposition, corrosion and remedies. Progress in Energy and Combustion Science, 76, 100789. https://doi.org/10.1016/j.pecs.2019.100789

Maringer, L., Grabmann, M., Muik, M., Nitsche, D., Romanin, C., Wallner, G. & Buchberger, W. (2017). Investigations on the distribution of polymer additives in polypropylene using confocal fluorescence microscopy. International Journal of Polymer Analysis and Characterization, 22(8), 692–698. https://doi.org/10.1080/1023666X.2017.1367120

Miliute-Plepiene, J., Fråne, A. & Almasi, A. M. (2021). Overview of polyvinyl chloride (PVC) waste management practices in the Nordic countries. Cleaner Engineering and Technology, 4, 100246. https://doi.org/10.1016/j.clet.2021.100246

Muhammad, C., Onwudili, J. A. & Williams, P. T. (2015). Catalytic pyrolysis of waste plastic from electrical and electronic equipment. Journal of Analytical and Applied Pyrolysis, 113, 332–339. https://doi.org/10.1016/j.jaap.2015.02.016

Park, K.-S., Sato, W., Grause, G., Kameda, T. & Yoshioka, T. (2009). Recovery of indium from In2O3 and liquid crystal display powder via a chloride volatilization process using polyvinyl chloride. Thermochimica Acta, 493(1-2), 105–108. https://doi.org/10.1016/j.tca.2009.03.003

Quicker, P., Seitz, M. & Vogel, J. (2022). Chemical recycling: A critical assessment of potential process approaches. Waste management & research : the journal of the International Solid Wastes and Public Cleansing Association, ISWA, 40(10), 1494–1504. https://doi.org/10.1177/0734242X221084044

Sadat-Shojai, M. & Bakhshandeh, G.-R. (2011). Recycling of PVC wastes. Polymer Degradation and Stability, 96(4), 404–415. https://doi.org/10.1016/j.polymdegradstab.2010.12.001

Scheirs, J. & Kaminsky, W. (Edd.). (2006). Wiley series in polymer science. Feedstock recycling and pyrolysis of waste plastics: Converting waste plastics into diesel and other fuels. Chichester, UK, Hoboken, NJ: J. Wiley & Sons. Disponibile da http://onlinelibrary.wiley.com/book/10.1002/0470021543

Schyns, Z. O. G. & Shaver, M. P. (2021). Mechanical Recycling of Packaging Plastics: A Review. Macromolecular rapid communications, 42(3), e2000415. https://doi.org/10.1002/marc.202000415

Shen, Y., Zhao, R., Wang, J., Chen, X., Ge, X. & Chen, M. (2016). Waste-to-energy: Dehalogenation of plastic-containing wastes. Waste management (New York, N.Y.), 49, 287–303. https://doi.org/10.1016/j.wasman.2015.12.024

Shibamoto, T., Yasuhara, A. & Katami, T. (2007). Dioxin formation from waste incineration. Reviews of environmental contamination and toxicology, 190, 1–41. https://doi.org/10.1007/978-0-387-36903-7_1

Teuten, E. L., Saquing, J. M., Knappe, D. R. U., Barlaz, M. A., Jonsson, S., Björn, A.,. . . Takada, H. (2009). Transport and release of chemicals from plastics to the environment and to wildlife. Philosophical transactions of the Royal Society of London. Series B, Biological sciences, 364(1526), 2027–2045. https://doi.org/10.1098/rstb.2008.0284

VinylPlus. (2015). PVC-Recycling-Technologien. Disponibile da https://vinylplus.eu/wp-content/uploads/2017/02/2015-12-08_Recycling-Technologies-German.pdf

Wang, Q., Ko, J. H., Liu, F. & Xu, Q. (2021). Leaching characteristics of heavy metals in MSW and bottom ash co-disposal landfills. Journal of hazardous materials, 416, 126042. https://doi.org/10.1016/j.jhazmat.2021.126042

Zheng, K., Benedetti, M. F. & van Hullebusch, E. D. (2023). Recovery technologies for indium, gallium, and germanium from end-of-life products (electronic waste) - A review. Journal of environmental management, 347, 119043. https://doi.org/10.1016/j.jenvman.2023.119043

detritus | Multidisciplinary Journal for Circular Economy and Sustainable Management of Residues

CISA

THE PRESENCE OF PFAS IN WASTES AND RELATED IMPLICATIONS ON THE CURRENT AND PROPOSED EUROPEAN REGULATORY FRAMEWORK: A SYSTEMATIC CRITICAL REVIEW

Alberto Pivato [1], Giovanni Beggio [1,*], Stefano Maggi [2], Francesco Marrone [2], Tiziano Bonato [3], Federico Peres [4], Wei Peng [5,6,7] and Maria Cristina Lavagnolo [1]

[1] *Department of Civil, Environmental and Architectural Engineering, University of Padova, via Marzolo 9, 35131 Padova, Italy*
[2] *LabAnalysis Srl, via Europa 5, 27041 Casanova Lonati (PV), Italy*
[3] *Department of Environmental Sciences, Informatics and Statistics, Ca' Foscari University of Venice, Venice, Italy*
[4] *Butti and Partners, Palazzo Pindemonte, via Leoni 4, 37121 Verona, Italy*
[5] *Institute of Waste Treatment and Reclamation, Tongji University, Shanghai, 200092, PR China*
[6] *Shanghai Institute of Pollution Control and Ecological Security, Shanghai, 200092, PR China*
[7] *Shanghai Engineering Research Center of Multi-source Solid Wastes Co-processing and Energy Utilization, Shanghai, 200092, China*

Article Info:
Received:
21 September 2023
Revised:
19 December 2023
Accepted:
9 January 2024
Available online:
28 February 2024

Keywords:
Perfluoroalkyl
Polyfluoroalkyl
PFAS
Recycling
Disposal
End of Waste
Circular Economy

ABSTRACT

Nowadays the use of PFAS is widespread in products in modern society and their exposure can occur directly through emissions such as dietary intake, water intake, air inhalation, and skin contact. Additionally, exposure can happen indirectly through the environmental release and degradation of their precursors. To fully understand the potential for life cycle emissions, it is necessary to consider the waste stage, as it is an integral part of a substance life cycle, whether PFAS exists in its pure form as part of a mixture or within an article. Overall, knowledge about the impact of PFAS on current and future waste management remains limited. Therefore, this study conducted a critical analysis of the presence of PFAS in relevant waste streams (plastic; metals; textile and leather; paper and cardboards). It also discussed how this presence could influence waste management, taking into account ongoing updates of the legal framework, with particular attention to proposed new provisions regarding their restriction in the REACH regulation. Within the discussed limits of the critical review, only a very small number of outliers were found to exceed the considered limit of 25 ppb for each material category. The percentage of exceedances ranged from nearly 1% (PFOS measurements in paper and cardboard waste) to 8% ("Other PFAS" in textiles and leather waste). Regarding the analytical methods and current limits identified, a pragmatic solution is suggested. This solution combines "not targeted" and "targeted" methodologies in a stepwise procedure, building upon the OECD definition of PFAS.

1. INTRODUCTION

The term "Per- and polyfluoroalkyl substances" (PFAS) identifies a class of synthetic compounds that have attracted much public attention since the late 1990s and early 2000s, when the hazards, the ubiquitous occurrence, and the persistence of two PFAS, perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS), started to be reported and recognized.

Nowadays the use of PFAS is widespread in products for the modern society. This includes for example applications in personal care products and cosmetics, ski waxes, firefighting foams, durable water and stain repellence in textiles, food contact materials, medical devices, pharmaceuticals, laboratory supplies, equipment, and instrumentation, perfluorosulfonic membranes, used in a wide range of chemical synthesis and separation operations and in analytical instrumentation (Cousin et al., 2019). Exposure to these substances may arise directly from emissions, such as dietary intake, water intake, air inhalation, and skin contact, or indirectly via the environmental release and degradation of their precursors.

As PFAS are chemicals with diverse molecular structures and physical, chemical and biological properties, the regulatory framework highly recommends that such diversity should be properly recognized.

The basic structure of a PFAS consists of a carbon chain with substituted fluorine atoms replacing hydro-

* Corresponding author:
Giovanni Beggio
email: giovanni.beggio@unipd.it

Detritus / Volume 26 - 2024 / pages 89-105
https://doi.org/10.31025/2611-4135/2024.18352

gen atoms on the chain, and with different categories of PFAS chemicals possessing different substituents and functional groups within (e.g., ethers) or terminal to the chain (Williams et al., 2022). From this rough structural explanation different definitions have been made to encompass broad working scopes or satisfy narrower regulatory guidelines.

In one of the earliest attempts, Buck et al. (Buck et al., 2011) defined PFAS as aliphatic substances that "contain one or more carbon atoms on which all of the hydrogen substituents (present in the nonfluorinated analogues from which they are notionally derived) have been replaced by fluorine atoms, in such a manner that they contain the perfluoroalkyl moiety (– C_nF_{2n+1} –)".

According to the revised PFAS definition by OECD (2021), "PFAS are defined as fluorinated substances that contain at least one fully fluorinated methyl or methylene carbon atom (without any H/Cl/Br/I atom attached to it), i.e., with a few noted exceptions, any chemical with at least a perfluorinated methyl group (–CF_3) or a perfluorinated methylene group (–CF_2–) is a PFAS". The "noted exceptions" refer to a carbon atom with a H/Cl/Br/I atom attached to it (Wang et al., 2021). Hereafter, it is referred to as the OECD 2021 definition.

Finally, a new definition by Gaines et al. (Gaines et al., 2023) combined a chemical structure with the percentage of fluorine. Here PFAS are defined as substances based on four substructures (Figure 1) along with any structures where the molecular formula is at least 30% fluorine by atom count.

A 2015 study reported that more than 3,000 PFAS were on the global market for commercial use (Swedish Chemicals Agency, 2015). In 2018, the OECD found 4730 different CAS numbers for PFAS (OECD, 2018). The United States Environmental Protection Agency's (USEPA) toxicity database, DSSTox, lists 14735 unique PFAS chemical compounds (USEPA, 2022; Gaines et al., 2023).

The abovementioned synthetic and representative statistics demonstrate the large variation in the numbers of chemicals that could be considered as a PFAS, based on the different definitions, including the variations in chemical fluorination (Gaines et al., 2023; Williams et al., 2022).

Figure 2 shows the total number of substances of PFAS according to different definitions compared with the number of substances for which regulation limits are existing (see next paragraph).

The waste stage is part of the life cycle of a substance in a mixture or in an article. Therefore, its distribution via the supply chain including service-life of articles and waste stage as an emission source with its associated risks should be taken into account.

The understanding of waste management (recycling, landfill, incineration, or composting) and the fate of PFAS

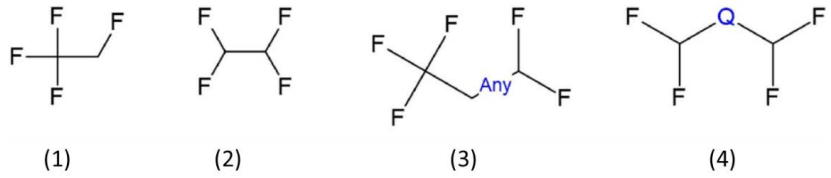


FIGURE 1: Substructures used in combination with percentage of fluorine. In Substructure 3 "any" indicate the type of bond between the two carbons. For Substructure (4) the heteroatom Q can be B, O, N, P, S, or Si.

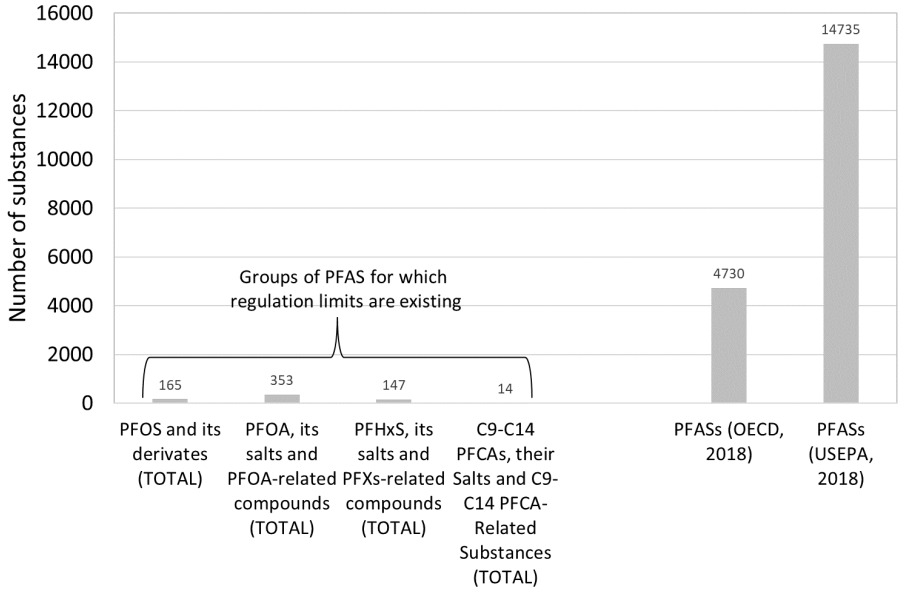


FIGURE 2: Number of substances for: PFOS and its derivates (Department for Environment, Food and Rural Affairs, 2015); PFOA, its salts and PFOA-related compounds (UNEP, 2022); PFHxS, its salts and PFHxS -related compounds (UNEP, 2019); C9-C14 PFCAs, their Salts and C9-C14 PFCA-Related Substances (ECHA, 2017); PFAS according to OECD classification (2018) and EPA classification (EPA, 2018).

in the waste stage is important if the aim is to understand the potential of complete life cycle emissions.

The EU waste classification system is primarily governed by the Waste Framework Directive (2008/98/EC), which sets out the general principles for managing waste in the EU. It establishes a harmonized waste classification system known as the European Waste Catalogue (EWC). The EWC provides codes and descriptions for different types of waste, allowing for standardized identification and classification of waste materials. PFAS, which are a group of man-made chemicals used in various industrial and consumer products, do not have specific codes or classifications within the EWC. However, depending on the specific characteristics and properties of the waste containing PFAS, it may fall under existing waste codes that pertain to related substances or materials. For example: if the waste containing PFAS exhibits hazardous properties according to the EU's Hazardous Waste Directive (Commission regulation (EU) No 1357/2014; 2017/997/EU), it would be classified as hazardous waste. Hazardous waste is further categorized based on specific hazardous properties, such as being toxic, flammable, or corrosive. PFAS-containing waste that displays any of these properties would be today classified accordingly.

Consequently, when it comes to the disposal or recovery of waste containing PFAS, several considerations come into play. These may include Hazardous Waste Classification that generally requires special handling, treatment, and disposal procedures.

Currently, the recycling of waste containing PFAS can be problematic due to the persistent characteristics and high bioaccumulation potential of these compounds. PFAS can be difficult to remove completely from materials and can persist into the recycling cycle, contaminating other materials or recycling processes.

Incineration is one method used for the treatment of certain wastes, including hazardous waste. Waste containing PFAS may require specific considerations when incinerated, as some PFAS compounds may release harmful by-products if inadequately burned. Proper incineration facilities equipped to handle PFAS-containing waste and prevent or minimise the release of PFAS into the environment are necessary.

Certain waste containing PFAS may be disposed of in regulated landfills designed to handle hazardous waste. Additionally, the long-term management and monitoring of landfill sites may be required due to the persistence and potential environmental risks associated with PFAS. Dedicated acceptance criteria for PFAS should be defined accordingly.

Research and development are ongoing to identify effective treatment technologies for PFAS-containing waste. Advanced treatment methods such as thermal desorption, chemical degradation, or adsorption techniques may be used to remove or reduce PFAS concentrations in the waste stream. In some cases, additional and final treatments can be required specifically for the residues generated where PFAS may be concentrated.

The End of Waste (EoW) procedure, is a regulatory process that establishes when certain waste materials cease to be classified as waste and can be considered as products or secondary raw materials. The EoW procedure aims to promote recycling and resource recovery by providing clarity on when waste materials have undergone sufficient treatment or processing to meet specific quality standards and no longer pose significant risks to human health and the environment. The specific criteria and procedures for determining the EoW status can vary between countries or regions. However, there are typically common elements involved, such as:

- quality standards: EoW criteria define the specific quality parameters that waste materials must meet to be considered as products or secondary raw materials. These parameters may include chemical composition, physical properties, contaminants levels, or other relevant characteristics;
- verification process: the verification process involves assessing and documenting that the waste material meets the established quality standards. This is typically done through testing, analysis, and documentation, either by the waste generator or a third-party certification body;
- regulatory approval: once the waste material has undergone the necessary treatment and meets the EoW criteria, it may require regulatory approval or acknowledgment to be officially recognized as a non-waste product or secondary raw material. This approval process may involve submitting applications, providing evidence of compliance with the criteria, and obtaining permits or certifications;
- market acceptance: Even if a waste material meets the EoW criteria, its acceptance in the market as a product or secondary raw material depends on factors such as demand, market conditions, and specific industry requirements.

The EoW procedure is important as it incentivizes the recycling and recovery of waste materials, reduces reliance on virgin resources and promotes a circular economy. Indeed, a new regulation on PFAS contents in substances, matrixes and articles could limit the circularity of materials.

There is another relevant aspect to consider: the presence of PFAS in the waste streams will remain for a long while; this is due to:

- nowadays it is neither practical nor reasonable to ban all uses of PFAS in one step, because some specific applications may serve a critical role for which alternatives currently do not exist (Cousin et al., 2019). This is the case for example of the use of PFAS for occupational protective clothing. In other words, the use of some PFAS is still considered "essential", meaning that they are "necessary for health, safety or is critical for the functioning of society" and that "there are no available technically and economically feasible alternatives" (United Nations, 1987);
- the long-life cycle of some products, such as laboratory supplies, equipment, and instrumentation, will determine the presence of PFAS in waste long after the time of

placing on the market of those products;

- in some cases, such as landfill mining, wastes potentially contaminated by PFAS, originally disposed of in a landfill as their final destination, can be newly considered for recovery;
- leachates from landfills can be contaminated by PFAS for a long period (Zhang et al., 2023; Lu et al., 2023).

The general objective of this study is to deepen the knowledge of the presence of PFAS in relevant waste streams for recycling issue, and to understand how this could influence current and future waste management and recycling practises, considering continuous updates of the relative legal framework, paying particular attention to the proposed new provisions on their restriction in the REACH regulation (BAuA et al, 2023a).

To do so, a systematic critical review of the scientific literature was performed to collect PFAS concentration ranges in waste items categorized within relevant four waste material categories (i.e., plastic; paper and cardboard; textile and leather; metals), as presented and discussed in both peer-reviewed articles already published and other significant documents. The collected results were compared with regulation limits to ease the understanding of their impacts on waste management practices.

2. THE EU REGULATORY FRAMEWORK

Here, the regulation analysis is concerned with the presence of PFAS in solid wastes and as a substance, whether on their own or in mixtures, or in articles. In fact, there is a strong connection between waste and manufacturing sectors because they both place those substances on the market on their own, in mixtures or in articles. At the end-of-life stage, products become waste and this can return on the market after a recycling process as EoW. Therefore, specific limits, provisions, restrictions, etc. on PFAS in one sector will have consequences in the other sector. Figure 3 graphically depicts the established concentration limits which have or may have impacts on waste management, while Table S1 in the Supplementary Material provides a comprehensive list of regulation limits or proposed limits on PFAS that currently impact or may potentially affect waste management.

In the section below, the state of art, derived from (I) the Stockholm Convention on Persistent Organic Pollutants (POPs), (II) the EU POPs Regulation, (III) Regulation on classification, labelling and packaging of substances and mixtures (CLP), (IV) REACH Regulation, (V) classification of waste, (VI) specific provisions for disposal or recovery

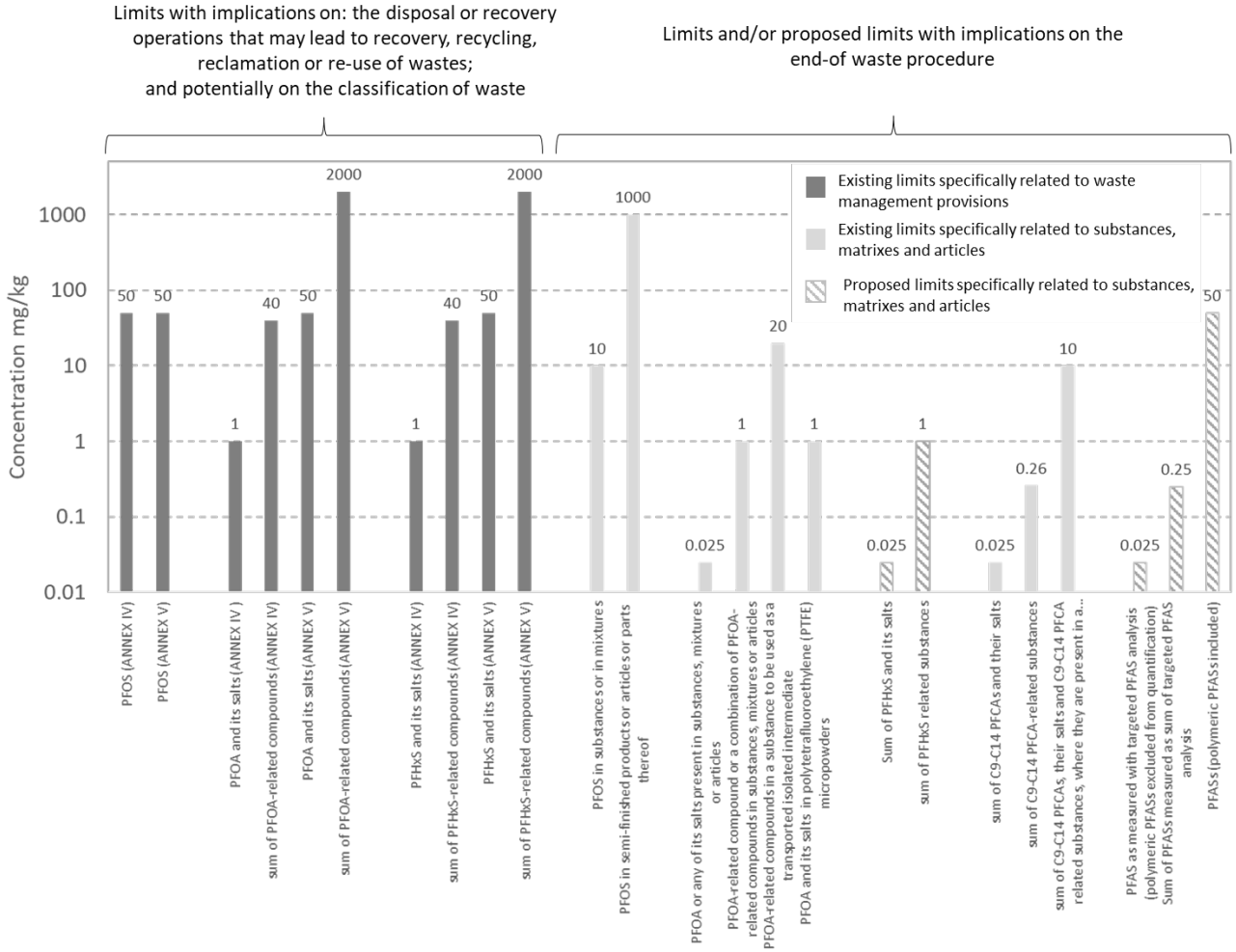


FIGURE 3: Graphical representation of limits on PFAS with implications on waste management.

operations of waste and (VII) the EoW procedure, is introduced and analysed.

Then, specific considerations regarding the application of the circular economy policy are introduced with respect to the recent restriction proposal under REACH from the national authorities of Denmark, Germany, the Netherlands, Norway, and Sweden (BAuA et al, 2023a). This is because this last proposal is the most conservative with consideration to all the PFAS.

2.1 The state of the art

Only few PFAS, PFOA, and PFOS, and PFHxS have been listed under the Stockholm Convention on Persistent Organic Pollutants (POPs) in Annex "A" or "B" (UN Environment Programme and Stockholm Convention, 2023). For chemicals listed in Annex "A" (PFOA and PFHxS), parties must take measures to eliminate their production and use, even if specific exemptions can be available. For chemicals listed in Annex "B" (PFOS), parties must take measures to restrict their production and use considering any applicable acceptable purposes and/or specific exemptions listed in the Annex.

Consequently, these chemicals are now restricted under the EU POPs Regulation (Regulation (EU) 2019/1021, as amended by Regulation (EU) 2022/2400).

Some other long-chain PFAS have a harmonised hazard classification under the Regulation on classification, labelling and packaging (CLP) of substances and mixtures.

Actually, REACH Regulation has included a PFAS group for restriction only for one case: C9-C14 PFCAs, their salts and C9-C14 PFCA- related substances. However, there are some proposals for other groups (see Table 1) for being assessed for a restriction under REACH.

For the purpose of this study, the recent restriction proposal under REACH from the national authorities of Denmark, Germany, the Netherlands, Norway and Sweden is relevant (BAuA et al, 2023a). Since the proposal considers all the PFAS according to OECD 2021 definition; it suggests a solution on a fundamental problem of the approach followed until now for PFAS in REACH: that the restriction or elimination is limited to individual substances or groups of closely related substances. Likewise, this proposal is in line with the recast of the Drinking Water Directive (Directive EU 2020/2184) which includes a grouping approach for all PFAS i.e., a limit of 0.5 µg/l for all PFAS.

The proposal further includes a combination of limits which can be detected in a solid matrix using different analytical approaches: targeted analysis regarding the limit of 25 ppb (0.025 mg/kg) for any potential PFAS (polymeric PFAS excluded from quantification); total oxidizable precursors (TOPs) regarding the limit of 250 ppb (0.25 mg/kg) for the sum of PFAS (polymeric PFAS excluded from quantification); non targeted method (total organic fluorine) regarding the limit of 50 ppm (50 mg/kg) for PFAS (polymeric PFAS included).

Concerning waste management only PFOA, and PFOS, and PFHxS have been identified in Annex IV and V of Regulation (EU) 2019/1021. The limits in Annex IV represent specific provisions in waste management such as the prohibitions of disposal or recovery operations that may lead to recovery, recycling, reclamation, or re-use of wastes with concentrations above these limits. The limits in Annex V represent the maximum concentration limits of substances listed in Annex IV allowed in specific waste streams to be otherwise dealt with in accordance with a method listed in Part 2 of Annex V (permanent storage in hazardous waste landfills or underground permanent storage (incl. salt mines) providing that competent authorities agreed).

For the classification of waste as hazardous, the EU Commission Decision 955 of 18 December 2014, amending Decision 2000/532/EC, states that wastes containing the first POPs indicated in the former POPs regulation (Regulation (EC) No 850/2004) exceeding the reported concentration limits listed in Annex IV shall be classified as hazardous. It is worth mentioning that in this list PFAS are not mentioned but amendments of the Directive 2008/98/EC or Decision 955 of 18 December 2014, modifying Decision 2000/532/EC, could introduce new concentration limits for PFAS affecting the classification of waste.

For the EoW procedure, a waste containing PFAS that achieves EoW status, the associated producer of this material, i.e., the person who places the material on the market for the first time after it ceases being waste, must ensure that the material meets any relevant requirements under REACH Regulation (EC) 1907/2006 and CLP Regulation (EC) 1272/2008. Therefore, provisions for restriction or elimination of PFAS in substances, mixtures, or articles must be applied also to materials from EoW procedure. This concept is clearly mentioned in the proposal from the national authorities of Denmark, Germany, the Netherlands, Norway, and Sweden is relevant (BAuA et al, 2023a). In their "Questions and Answers" the agencies affirmed that the "proposed restriction apply to articles regardless of whether they are made from virgin or recycled materials" (BAuA et al, 2023b).

Figure 4 shows a comprehensive overview of the most relevant regulations in the waste field where existing and proposed limits for PFAS could influence current and future waste management practises.

2.2 Implications on circular economy from the recent restriction proposal under REACH

This new proposal (BAuA et al, 2023a) could impact the circular economy. In fact, it must be considered that among the requirements to obtain the EoW status, the legislation in force provides that "the substance or object fulfils the technical requirements for the specific purposes and meets the existing legislation and standards applicable to products".

Therefore, if the proposal - as previously mentioned - will also apply to materials from a waste recycling process, since treatments for removing PFAS from waste are not currently available, they will not be destined for material recovery, but for disposal and, if possible, energy recovery.

This would create a conflict between two objectives; from one side the policies of the European Union require Member States to encourage the circular economy favouring as much as possible the recovery of waste (in particu-

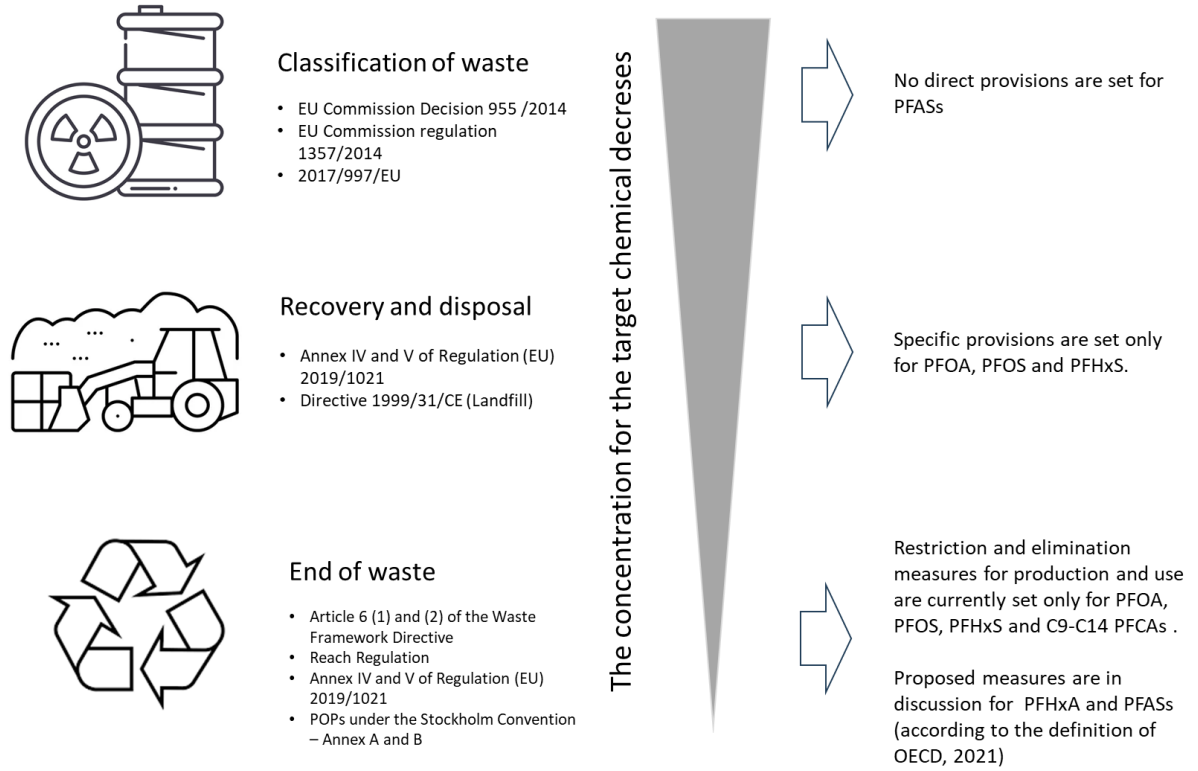


FIGURE 4: Graphical representation of the most relevant regulation applications in the waste field where PFAS can be interested.

lar of the textile and plastic sector), while on the other side they introduce new conservative limits of PFAS to prevent harm to human health and to the ecosystem which could limit the recovery of waste.

The legislator has the aim to resolve these conflicts considering also the conclusions of the EU Court of Justice (decision of 19 January 2023, case C-147/21) where two relevant principles are explicated: (I) the obligation of Member States to respect the principle of proportionality and (II) the burden of proving the existence of proportionality falls on those who invoke it, not on those who deny it. The aforementioned conclusions can be read as follows:

- *"53. it is for the national authorities, in each individual case, to demonstrate that the national legislation at issue satisfies the principle of proportionality, that is to say, that it is necessary to achieve the declared objective and that it could not be achieved by prohibitions or restrictions that are less extensive or have less effect on trade within the European Union. To that end, it is for those authorities to provide the necessary evidence to that effect. The reasons which may be invoked by a Member State by way of justification must thus be accompanied by an analysis of the appropriateness and proportionality of the restrictive measure adopted by that State, and by specific evidence substantiating its arguments (judgment of 23 December 2015, Scotch Whisky Association and Others, C-333/14, EU:C:2015:845, paragraphs 53 and 54).*
- *54. It follows that, where a national court examines national legislation in the light of the justification relating to the protection of the health and life of humans, under Article 36 TFEU, it is bound to examine objectively whether it may reasonably be concluded from the evidence submitted by the Member State concerned that the means chosen are appropriate for the attainment of the objectives pursued and whether it is possible to attain those objectives by measures that are less restrictive of the free movement of goods (see, to that effect, judgment of 23 December 2015, Scotch Whisky Association and Others, C-333/14, EU:C:2015:845, paragraph 59)."*

3. MATERIALS AND METHODS

The stepwise procedure for literature sources selection (Figure 5), was based on the so-called "Preferred Reporting Items for SRs and Meta-Analyses "(PRISMA) guidelines (Gurevitch et al., 2018; PRISMA, 2023). Documents identification was carried out in the electronic repositories of i) Elsevier Bibliographic Database (Scopus) and ii) Web of Science (WOS), by searching, in the Titles, Abstracts or Articles Keywords, the following keywords chains, one for each specific investigated waste stream:

- "PERFLUOROALKYL*" OR "POLYFLUOROALKYL*" OR "PFAS" AND "PLASTIC*" AND "WASTE*" AND NOT "WASTEWATER";
- "PERFLUOROALKYL*" OR "POLYFLUOROALKYL*" OR "PFAS" AND "PAPER* WASTE*" OR "CARDBOARD" OR "CELLULOSIC WASTE" AND "WASTE*" AND NOT "WASTEWATER";
- "PERFLUOROALKYL*" OR "POLYFLUOROALKYL*" OR "PFAS" AND "METAL* WASTE*" OR "FERROUS WASTE*" AND "WASTE* AND NOT WASTEWATER" OR "SCRAP*";

- "PERFLUOROALKYL*" OR "POLYFLUOROALKYL*" OR "PFAS" AND "TEXTILE*" OR "LEATHER" AND "WASTE*" AND NOT "WASTEWATER".

Documents were retrieved from the online databases according to the following criteria: electronic version of the articles is available; the language of the articles is English; and documents type was Article. Documents were excluded if consisting of Review Article, Proceeding Paper, Book Chapters, Letters etc. Furthermore, the documents cited in the literature reviews (identified but excluded from the scope of the current analysis according to the PRISMA guidelines) were further included as external sources.

Identified documents underwent a screening and those with abstracts not providing a description or a discussion of quantitative data about PFAS concentrations were filtered out.

A futher full-text reading of the screened documents was conducted toto include the papers considered eligible according to the scope of the analysis. In this phase, papers not showing quantitative data derived from analytical measurements, or those presenting PFAS concentration on substrates not relevant for this study (e.g., landfill leachates) were considered not eligible. Also, those items reporting data as mass per unit area (e.g, μg m^{-2}) were considered not eligible to ease direct comparison of PFAS concentrations and regulation limits.

Eligibility was extended to those documents, mostly derived from three identified but excluded review articles (Barhoumi et al., 2022; Bulson et al., 2023; Coffin et al., 2023), even if showing analytical data measured in products (i.e., still not yet "waste"), since they were considered as significant for the assessment of the presence of PFAS in the studied waste streams, as suggested by the review articles themselves. In other words, the so-included documents were assumed characterizing products representative of "waste-to-be", thus ultimately influencing their management practices (i.e., characterization and classification, treatment, disposal or potential recycling to achieve EoW status).

The final list of the documents considered eligible is reported in the Supplementary Materials.

Two reviewers (BG & GG) independently extracted data from each original publication. Data extraction performed on the eligible documents allowed the retrival of information regarding: the material streams of the analysed sample; the specific waste or product item of the analysed sample; the geographical origin of the sample; the year of sampling; the concentration values of the quantified parameters (i.e., single substance concentrations or sums of them); the analytical methods used for the analytical quantification; where available, the value of the Limit of Detection/Limit of Quantification (LOD/LOQ); information on possible specific treatments or analytical procedures performed on the sample that can be useful to include/exclude the single entries from the statistical analysis.

When concentration data were reported lower than the LOD or LOQ, they were extracted as equal to the reported LOD or LOQ value divided by two (EFSA, 2012; SNPA, 2021). Values of LOD or LOQ reported higher than 25 ppb (0.025 mg/kg) were excluded from the data extraction since they could not be compared with all the regulation limits (both established or proposed). Where LOQ or LOD values were not reported, an average value of LOD or LOQ values available in other documents were extracted, preferentially for each single parameter, or groups of parameters (e.g., FTOHs) where this latter approach could not be applied.

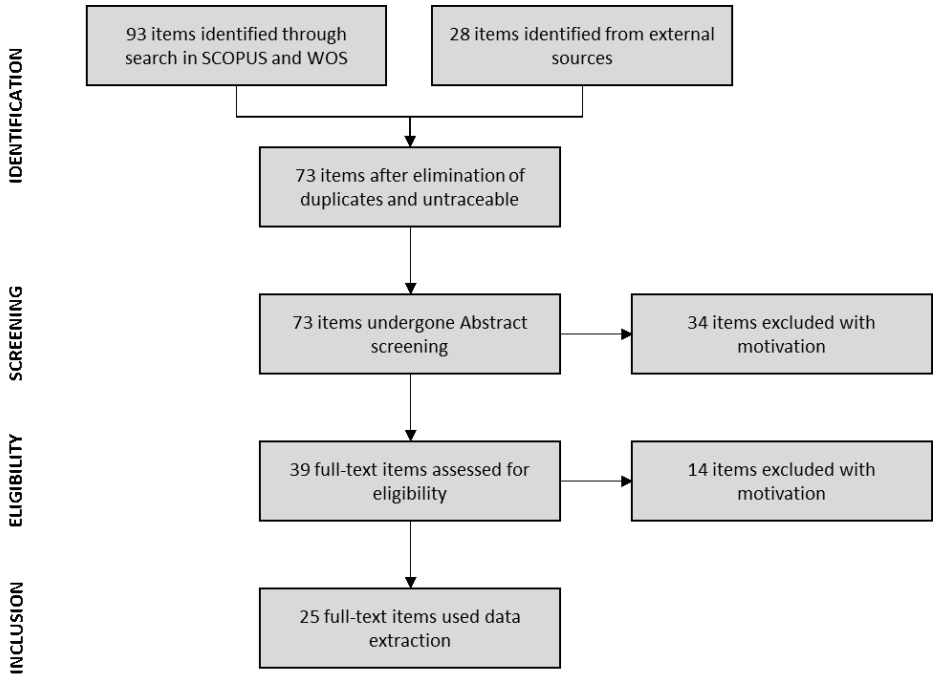


FIGURE 5: Flow diagram resuming the stepwise procedure followed for the performance of the systematic critical review.

Overall, a total of 5795 single concentration values from 25 papers were extracted. Among them, 4836 were used for descriptive statistical analysis and comparison with regulation limits; the exclusions included data which could not be organized consistently to the aim of the statistics such as sums of concentrations of different parameters (e.g., ∑PFAS, ∑PFCAs, ∑FTOHs, etc.).

Likewise, a specific comparison was performed considering material-specific PFAAs concentration data between two relevant analytical approaches. In this way it was possible to assess the influence of a specific sample preparation method (i.e., TOP assay) on the results of the quantification step.

These concentration values were organised in categories according to the detected substances and the waste stream of origin (i.e., paper and cardboard waste, textile and leather waste, plastic waste and metal waste) and to the measured parameters.

The analysis performed on categorized data included descriptive statistics (i.e., median, min-max range, Q1 and Q3 values, and 5%-95% percentiles) and graphical representation of data through box plots. The results of this latter allowed to compare the collected concentration data with the regulation limits and thus calculate the percentage of limit exceedances for each considered category.

For the purpose of this study, the comparison relied on the lowest limit value which could be applied to all single targeted PFAS i.e., 25 ppb (Figure 3).

3.1 Waste streams

Only the following waste categories were considered in the scope of this study because of the known potential presence of PFAS in these streams: plastic; metals; textile and leather; paper and cardboards.

The Table 1 shows the percentages of the above-mentioned waste streams on the total amount of waste excluding major mineral waste generated in EU for 2020.

Furthermore, the specific items (plastic straws, carpets, automotive shredder residues, plastic scraps from end-life vehicles, etc.), on which the targeted substances were measured, were recorded.

TABLE 1: Waste generation (Hazardous and non-hazardous) in 2020 for European Union - 27 countries. (reference: https://ec.europa.eu/eurostat/databrowser/view/env_wasgen/default/table?lang=en).

Waste stream	tonne	%
Textile [(1)]	1,950,000	0.25%
Plastic	19,030,000	2.45%
Paper and cardboard	43,490,000	5.60%
Metal [(2)]	82,180,000	10.59%
Other wastes [(3)]	629,640,000	81.11%
Total waste excluding major mineral wastes	776,290,000	100.00%

[(1)] including leather
[(2)] sum of metal wastes, ferrous, metal wastes, non-ferrous and metal wastes, mixed ferrous and non-ferrous
[(3)] sum of sludges and liquid waste from waste treatment, sorting residues, chemical and medical wastes, glass wastes, rubber wastes, wood wastes, equipment, animal and vegetal wastes, household and similar wastes excluding major mineral wastes

3.2 Detected substances

The PFAS measured in the selected papers have been organized according to the definition laid down by the OECD, (2021), as graphically represented in Figure 6. Different subgroups of PFAS have been associated with the class of chemicals as explicitly mentioned in existing or proposed regulations.

Finally, considering all the available data, concentration values were grouped into the following 5 categories for each considered material:

1. PFOS, i.e., values relative to single sample concentrations of PFOS;
2. PFOA, i.e., values relative to single sample concentrations of PFOA;
3. PFHxS, i.e., values relative to single sample concentrations of PFHxS;
4. C9-C14 PFCAs, i.e., values relative to single sample concentrations of PFNA, PFDA, PFUnDA, PFDoDA, PFTrDA and PFTeDA;
5. other, i.e., values corresponding to single sample concentrations of PFAS molecules not listed in the previous categories, but considered in the updated OECD definition, i.e., including non-regulated PFAAs together with the so-called "PFAAs precursors".

3.3 Analytical methods

From a testing point of view, PFAS analysis is carried out primarily through extraction and purification followed by liquid chromatography coupled with tandem mass spectrometry. As a "targeted" analytical procedure, its application is limited to the quantification of the concentration for a fixed set of parameters. Thus, it doesn't provide a measure of either the magnitude of the "pool" of PFAS that may exist, nor the potential for targeted PFAS formation due to natural transformation of precursor compounds. In this class, the following standard methods are identified:

- ASTM D 7968-17A: 2017 "Determination of Polyfluorinated Compounds in Soil by Liquid Chromatography Tandem Mass Spectrometry (LC/ MS/MS)";
- EPA 3550 C: 2007 "Ultrasonic Extraction" + EPA 8327: 2021 "per- and polyfluoroalkyl substances (PFAS) by liquid chromatography/tandem mass spectrometry (LC/MS/MS)".

In these methods, targeted analytes include a range of PFCAs and PFSAs as well as a smaller number of PFAS precursors and intermediate transformation products (e.g., partially oxidized PFAS precursors). Methods can be modified to broaden the set of quantified analytes to a limit defined by i) the commercial availability of appropriately certified reference materials and ii) the compatibility with existing types of analytical equipment. Currently, standards are available for almost 40 substances, as reported in Figure 7 (Ateia et al., 2023). However, the number of PFAS potentially analysed via targeted analysis will likely increase over time.

In this context, the Total Oxidizable Precursors (TOP) assay was developed to quantify the presence of targeta-

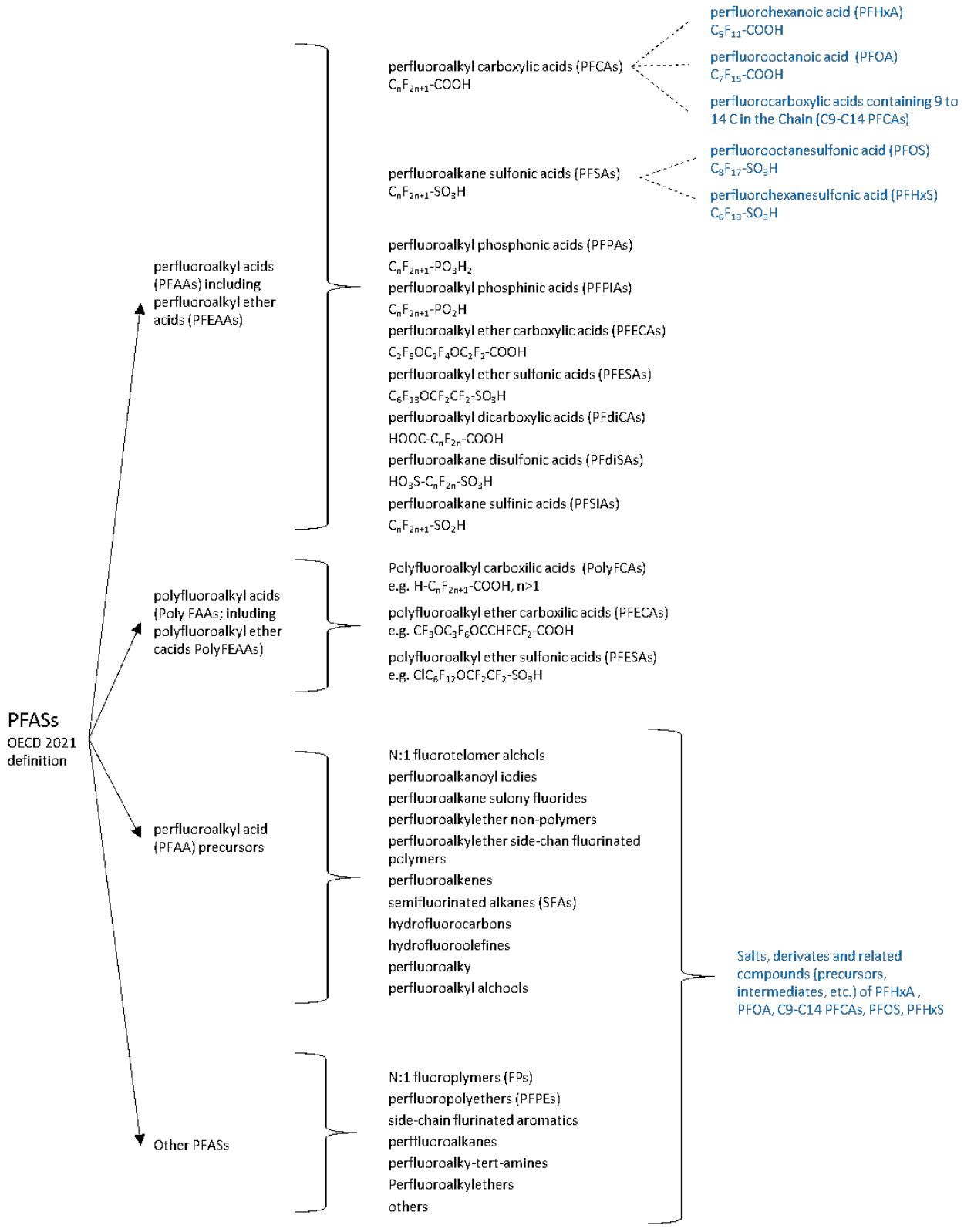


FIGURE 6: A comprehensive overview of PFAS groups associated with regulated classes of PFAS (based on OECD, 2021).

ble PFAS precursors. Here, the term "PFAS precursor" refers to PFAS with the potential for oxidative transformation resulting in terminal products such as PFAAs (Figure 6). The TOP assay allows the conversion of oxidizable PFAS precursors into PFAAs, which are then measured using a targeted PFAS analytical method. One of the most relevant benefits of this method is its compatibility with the same analytical instrumentation utilized in targeted analysis.

More recently, there has been a focus in the industry to develop and validate lower cost alternatives that also

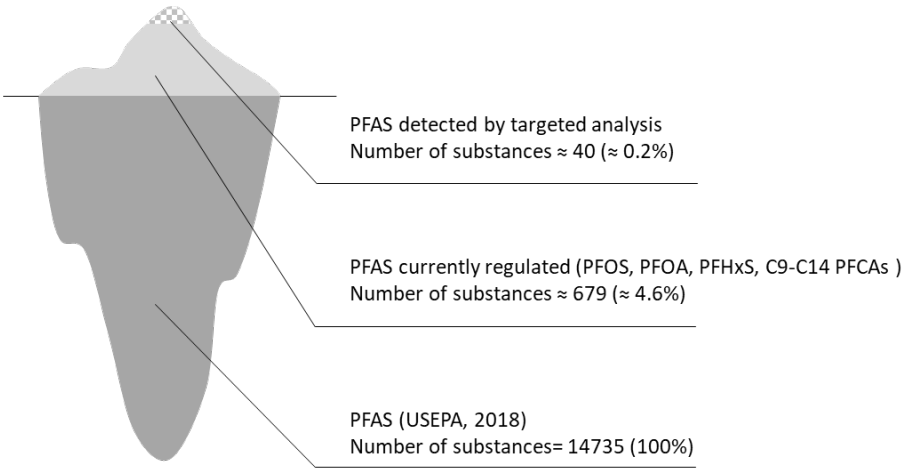


FIGURE 7: The "iceberg" knowledge of PFAS from a regulation perspective. Modified from Ateia et al., (2023).

provide a more comprehensive measure of total PFAS presence. This has resulted in several "non-targeted" methods able to quantify fluorine concentration, in terms of Total Fluorine (TF), Adsorbable Organic Fluorine (AOF), Extractable Organic Fluorine (EOF) and total organic fluorine (TOF). These methods are often used to screen out samples showing very low fluorine content from further targeted analysis. However, these methods do not identify the molecular configuration and may therefore deliver non-realistic estimations of PFAS concentration (Schwartz-Narbonne et al., 2023).

4. RESULTS AND DISCUSSION

The resulting box plots showing the distribution of concentration data extracted from the eligible papers are depicted in Figures 8, 9, 10 and 11. Further, the entire dataset is available in Supplementary Materials together with detailed descriptive statistics for each waste flow and parameter category.

4.1 Considerations on the waste streams investigated

Considering sample sizes of each considered material category, most eligible documents focused on the paper and cardboard waste (17 papers) and textile and leather waste (seven papers), with a total of 2680 and 1488 observations, respectively. The plastic waste category was investigated by a lower number of documents (six papers) resulting in 613 observations. Instead, metal waste was the category less investigated by the documents considered for the data extraction, with only two papers covering the category and a significantly smaller amount of extracted data (55). Looking at the analyzed waste items, measurements for paper and cardboard waste were mainly done on disposable food contact materials (e.g., bowls, paper table wares, beverage cups, paper bags, etc.), several dedicated to substitute single use plastics, and disposable fast food packaging materials (e.g., fast food wraps, pop-corn bags, boxes for French fries, etc.). Textile and leather waste data refers mostly to treated upholstery (both from hous-

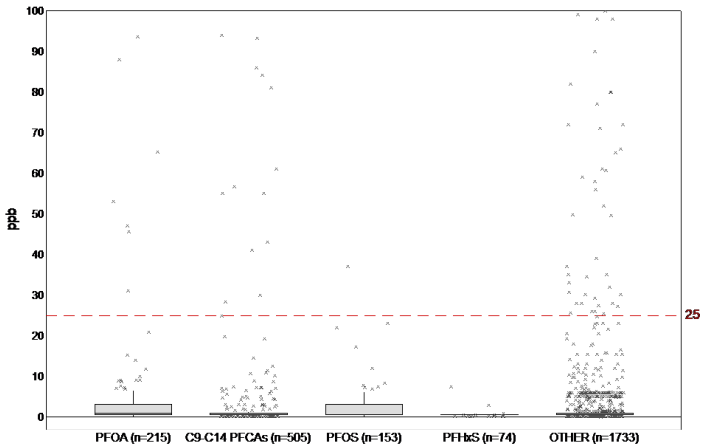


FIGURE 8: Box Plot resuming the concentration data gathered for the category "Paper and Cardboard waste". The line within the boxes shows the median value, the box denotes the range of 50% of data, whiskers range from the lower to the higher value within 1.5 interquartile ranges and asterisks stand for outliers. The y axis was trunked at 100 ppb to ease the comparison between the collected data and the proposed limit value of 25 ppb (red dashed line). The range of values for each investigated parameter is indicated in Supplementary Materials.

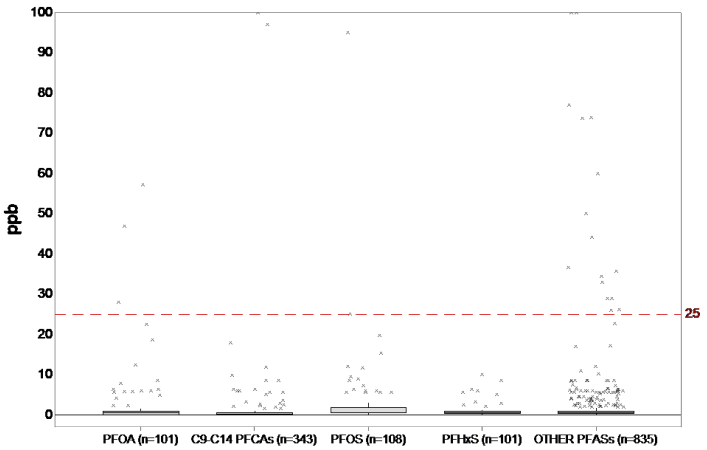


FIGURE 9: Box Plot resuming the concentration data gathered for the category "Textile and leather waste". The line within the boxes shows the median value, the box denotes the range of 50% of data, whiskers range from the lower to the higher value within 1.5 interquartile ranges and asterisks stand for outliers. The y axis was trunked at 100 ppb to ease the comparison between the collected data and the proposed limit value of 25 ppb (red dashed line). The range of values for each investigated parameter is indicated in Supplementary Materials.

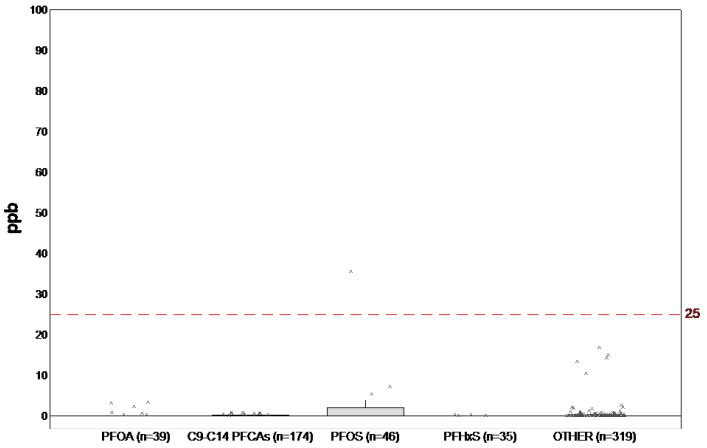


FIGURE 10: Box Plot resuming the concentration data gathered for the category "Plastic waste". The line within the boxes shows the median value, the box denotes the range of 50% of data, whiskers range from the lower to the higher value within 1.5 interquartile ranges and asterisks stand for outliers. The y axis was trunked at 100 ppb to ease the comparison between the collected data and the proposed limit value of 25 ppb (red dashed line). The range of values for each investigated parameter is indicated in Supplementary Materials.

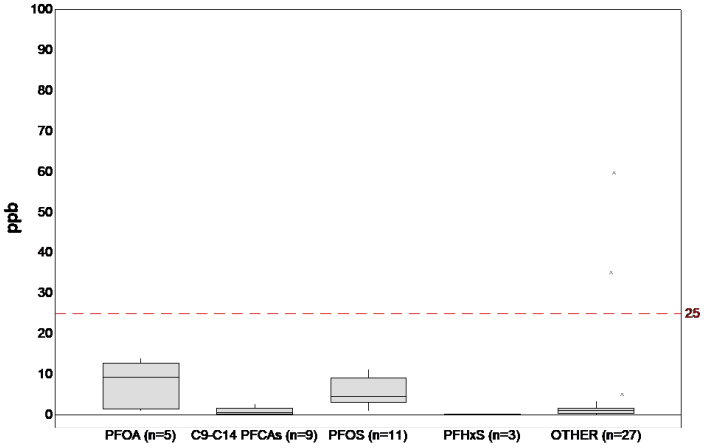


FIGURE 11: Box Plot resuming the concentration data gathered for the category "Metal waste and metal scraps". The line within the boxes shows the median value, the box denotes the range of 50% of data, whiskers range from the lower to the higher value within 1.5 interquartile ranges and asterisks stand for outliers. The y axis was trunked at 100 ppb to ease the comparison between the collected data and the proposed limit value of 25 ppb (red dashed line). The range of values for each investigated parameter is indicated in Supplementary Materials.

es -e.g., carpets- and End-Life-Vehicles (ELV)) and treated apparels. Plastic waste data were mainly collected from measurements done on single-use plastic packaging, ELV plastic components and parts of household appliances. Finally, metal waste dataset was mainly composed of concentration data derived from the analysis of Automotive Shredder Residues (ASR) derived from treatment of ELV. The detailed information about the specific waste types are included, for each entry, in the dataset available in the Supplementary Materials.

4.2 Comparison between PFAS concentrations and proposed limits

Looking at the box-plots, for each material, all the investigated parameters (or groups of them) show similar rightly skewed distributions, with the large majority of data characterized by very small concentration values and only few rare high to very high observations, with median values squeezed near the Q1 and lower whiskers approaching zero ppb, with the only exception of PFOA category for metal waste, which is however characterized by very small sample size.

Except for metal waste for which little data is available, high percentages of data for each group parameter were interestingly recorded below the LOQ or LOD, as quantified in Table 2. Within each material category, the lower fractions of concentration values recorded lower than LOQ or LOD were those related with PFOS and PFOA content, with an average of about 40%, 60% and 50% values < LOQ/LOD for paper waste, textile waste and plastic waste, respectively.Conversely, higher percentages of unquantified concentration values were recorded for the parameter PFHxS, ranging from 68% in textiles and leather waste to more than 90% of data in the paper and cardboard waste. Further, C9-C14 PFAS and the remaining parameters grouped under “Other PFAS”, were also characterized by similar trends, showing a peak of 90% of C9-C14 PFAS data under the limit of detection in textile and leather waste and 76% of Other PFAS concentrations not detected for paper and cardboard waste.

As it is visible from the box-plots, just relatively few outliers resulted higher than the considered limit of 25 ppb, for each material category. The percentages of exceedances for each material and groups of parameters are resumed in Table 3. Overall, percentage of exceedances ranged from almost 1% (PFOS measurements in Paper and cardboard waste) to 8% (“Other PFAS” in Textiles and leather waste). With the only exception of plastic waste (characterized by exceedances occurring only for PFOS content), the higher number of exceedances was observed for the other waste categories for the “Other PFAS” groups, with no further clear trends among the other parameters investigated.

Indeed, the higher amount of data per category led to higher number of exceedances. In particular, the material category with the highest average percentage of data above the limit resulted the textile and leather waste, with an average 4,3% of non-compliances, followed paper and cardboard waste with an average total of 3,9% of exceedances. Whether these latter material categories were characterized by at least one exceedance for each parameter or groups of them (with the exception of PFHxS), plastic and metal waste were characterized by values measured above the limits for just one parameters category, namely PFOS for plastic waste (3,23% of exceedances) and “Other PFAS” (11,11%) for metal waste.

4.3 Consideration on the analytical methods

Among the identified papers, a wide range of performed methods could be noted for PFAS analysis in the chosen solid matrixes. Thus, no unique approaches could be observed for the extraction, purification and quantification phases and, unfortunately, not all studies indulged in a thorough description of the performed methods. The role of extraction and purification is crucial in assessing the varying degrees of accuracy of measured PFAS concentrations. Different analytical settings could determine under-estimated concentrations or false positives in the extracts subjected to further quantification step. Also, different waste types could necessitate different approaches for the best performance of PFAS quantification.

TABLE 2: Percentage of data recorded under the LOD/LOQ for each considered material category and investigated parameters.

Parameter	Paper And Cardboards	Textile And Leather	Plastic	Metals
PFOA	40.93%	63.37%	79.49%	0.00%
C9-C14 PFASs	71.68%	90.38%	88.51%	0.00%
PFOS	41.83%	60.19%	41.30%	0.00%
PFHxS	90.54%	68.32%	85.71%	0.00%
Other PFASs	76.28%	62.04%	78.06%	22.22%

TABLE 3: Percentage of data recorded over the concentration limits of 25 ppb.

Parameter	Paper And Cardboards	Textile And Leather	Plastic	Metals
PFOA	6.51%	2.97%	0.00%	0.00%
C9-C14 PFASs	5.35%	0.87%	0.00%	0.00%
PFOS	0.65%	7.41%	2.17%	0.00%
PFHxS	5.35%	0.87%	0.00%	0.00%
Other PFASs	6.98%	8.14%	0.00%	11.11%

Within the manuscripts investigated in this study, diverse methodological approaches concerning extraction media are presented. While methanol stands as the most frequently used, several other media such as ammonium, ethyl acetate, acetonitrile, tetrabutyl ammonium hydrogen sulfate along with methyl tert-butyl ether, acetone, and ethanol, among others, have been utilized. Various extraction times have been employed, ranging from under 60 seconds to overnight periods, achieved through methods like hand or orbital shaking, or vortex mixing. Additionally, a broad spectrum of extraction treatments has been applied, including sonication (focused ultrasound liquid extraction, executed at varying contact times and irradiation power), along with specific pressure (i.e., pressurized liquid extraction) and temperature regimes, ranging from 0°C to 80°C.

Furthermore, the effectiveness of the purification step plays a crucial role, as it eliminates compounds that could potentially interfere with accurate quantification, thereby avoiding false positives. Notably, the inclusion of the solid-phase extraction step is not consistent across all studies. When included, there are disparities in the materials constituting the cartridges, such as weak anion exchange resins, silica, fluorisil, alumina, and variations in the solvent mixtures used for their functioning.

Centrifugation of extracts is a standard practice, with variations in applied rpm values and process durations. Similarly, filtration methods encompass diverse filtering materials (e.g., pp, polyamide, regenerated cellulose) and mesh sizes, spanning from 0.2 µm to 0.45 µm.

While out of the scope of its scopes,this heterogeneity could, indeed, represent a limit of the present study, due to the possible inconsistencies in the comparison and/or underestimation of analytes concentration due to non-efficient extraction methods (e.g., considering quantification on test portions undergone or not to TOP assay in the extraction step). However, the considered papers were assumed as already validated works, where validation is ensured by their peer-reviewed nature and publication in indexed scientific journals. However, an additional comparison was performed to further investigate this issue, between those measurements performed on test portions undergone or not to TOP assays, for those waste categories showing suitable data.

The results of the comparisons between the extracted PFAAs concentrations data quantified on material-specific test samples undergone and not to TOP assay are summarized in Table 4 and depicted in Figure 12, 13 and 14 for textile and leather waste, plastic waste and metal waste, respectively. No data on post TOP targeted concentrations was available for the paper and cardboard waste category.

As the Figures 12,13 and 14 show, there is a significant trend characterizing overall higher concentration of the quantified analytes in samples undergone TOP assay. This pattern implies a notable increase in the quantified concentration values obtained through targeted analysis, as a result of TOP assays. This arises from the fact that targeted analysis can effectively measure the additional quantity of precursors as targeted PFAS, once they undergo oxidation during TOP, resulting in the formation of the analyzed PFAS terminal products. In the case of the metal waste, this could contribute to also a significant increase in the number of exceedances when concentration data are compared with the proposed Regulation limit (Figure 14).

4.4 Proposing a pragmatic solution for PFAS analysis in solid samples for regulatory purposes

Overall, the relevant knowledge on the impact of PFAS in solid waste management is still scarce. According to European regulations, waste is defined as hazardous if it satisfies at least one of the 15 hazard properties (HP) or contains concentrations of certain (POPs) over specific legal thresholds (European Commission, 2014; European Parliament and European Council, 2019). In this list of chemicals, PFAS are not included therefore the hazardous classification of waste is currently not directly impacted by the concentration of PFAS in the waste. However, the presence of PFASs could influence other hazardous properties, such as ecotoxicity (HP 14), when assessed by direct testing.

The current regulations governing the disposal and recovery of waste containing PFAS are limited to a few groups (less than 5% of the total of PFAS) and their implementation and impact in the waste sector are known, with one relevant exception. This is due to the “ambiguous” definitions of the correlated chemicals to the perfluoroalkyl acids (PFAAs) that should be covered by the regulations. In fact, the following general terms are reported: derivates of perfluorooctane sulfonic acid (PFOS); salts and related compounds of perfluorooctanoic acid (PFOA); salts and related compounds of perfluohexane sulfonic acids (PFHxS). These definitions involve hundreds of compounds for which no regulatory lists exist. Furthermore, only a few substances can currently be detected analytically inducing – de facto – a regulatory void.

TABLE 4: Descriptive statistics of PFAAs concentration data measured on test samples undergone TOP Assay (AFTER TOP ASSAY) and not (BEFORE TOP ASSAY) of textile and leather waste, plastic waste and metal waste.

Waste Type	Type Of Analysis	n	Median	75%	90%	95%
		-	ppb			
Textile	PRE TOP	1418	0.61	0.87	4.29	8.65
	POST TOP	424	1.95	8.25	10.78	37.91
Plastic	PRE TOP	591	0.08	0.11	0.34	0.83
	POST TOP	112	1.52	5.47	11.78	23.09
Metal	PRE TOP	55	1.21	4.23	10.53	20.34
	POST TOP	51	7.71	28.76	59.18	107.66

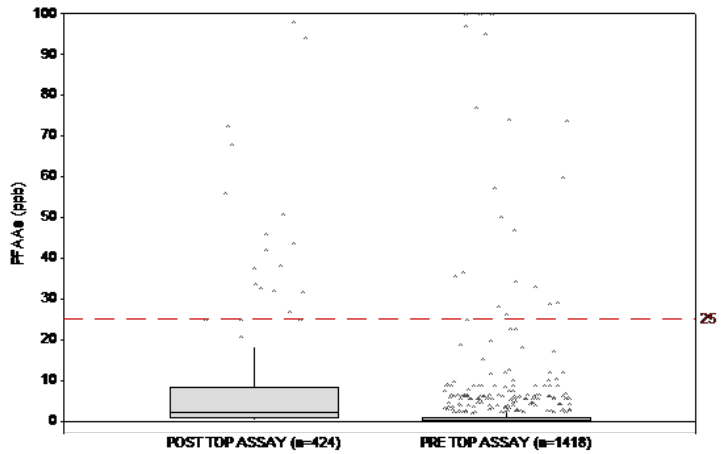


FIGURE 12: Box Plot resuming the differences between the PFAAs concentration data before and after TOP assay performance on textile and leather waste test samples. The y axis was trunked at 100 ppb to ease the comparison between the collected data and the proposed limit value of 25 ppb (red dashed line). The range of values for each investigated parameter is indicated in Supplementary Materials.

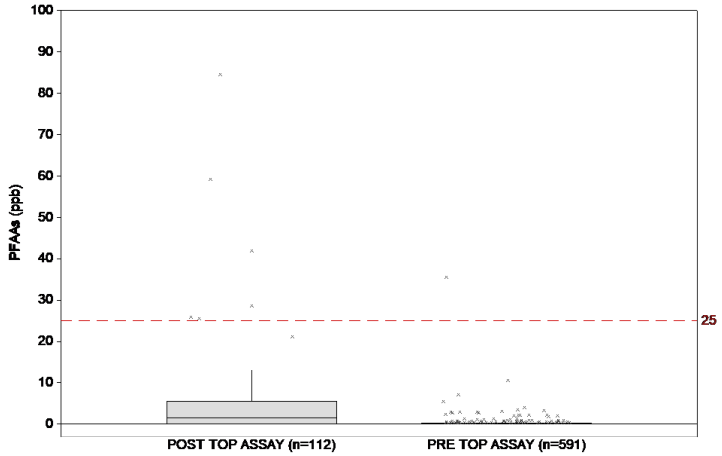


FIGURE 13: Box Plot resuming the concentration data gathered for the category "Plastic waste". The line within the boxes shows the median value, the box denotes the range of 50% of data, whiskers range from the lower to the higher value within 1.5 interquartile ranges and asterisks stand for outliers. The y axisBox Plot resuming the differences between the PFAAs concentration data before and after TOP assay performance on plastic waste test samples. The y axis was trunked at 100 ppb to ease the comparison between the collected data and the proposed limit value of 25 ppb (red dashed line). The range of values for each investigated parameter is indicated in Supplementary Materials.

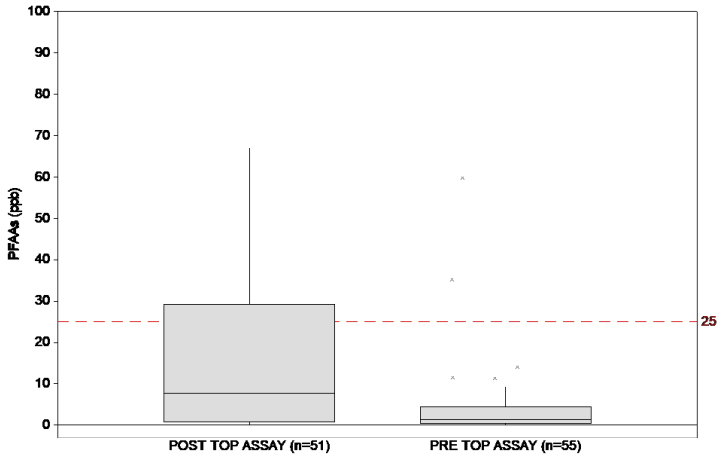


FIGURE 14: Box Plot resuming the differences between the PFAAs concentration data before and after TOP assay performance on metal waste test samples. The y axis was trunked at 100 ppb to ease the comparison between the collected data and the proposed limit value of 25 ppb (red dashed line). The range of values for each investigated parameter is indicated in Supplementary Materials.

Much more complex is the implication of the current, and more importantly, ongoing proposed regulations (see BAuA et al, 2023a) concerning limits specifically related to substances, matrixes, and article. The complexity is due to the connection between the characteristics of the new materials which should be guaranteed before being placed on the market and the criteria upon which the waste should respect to be gain the status of EoW. This issue can be analysed by considering three main points: (I) the time interval between the moment of implementation of new provisions on substances and the moment in which these limits are also required for the EoW procedure; (II) the analytical method to measure the PFAS; (III) the specific values of new regulatory limits.

The limits on the use of PFAS will determine a reduction of PFAS concentration in new articles and products only from the moment new regulations will enter into force. However, in the waste cycle older products containing higher concentrations of PFAS could end their life cycle and become waste. Besides, the use of PFAS in some products is still considered "essential" and if there isn't a good pre-selection before any recovery process, the presence of PFAS in waste cycles could endure for a long time. In this context, "tagging" products (chemically or optically through a label or code) to identify those with PFAS concentration higher than a limit (e.g., 25 mg kg^{-1}) could improve sorting before recovery.

These aspects must be carefully evaluated by eventually introducing express derogations for the EoW or at least defer the date for when these limits come into force. This would continue to allow the recovery of the waste already generated before the new limits become mandatory. Another solution to guarantee human safety could be the introduction of limits without any exemption for the waste sector (derogations, deferred time, etc.). This could have an impact on the recycling market.

Concerning the methodology to measure PFAS in solid samples, it should be considered that "PFAS" is a broad, general, non-specific term, which does not inform whether a compound is harmful or not, but only communicates that the compounds under this term share the same chemical structure. To this regard, whereas PFOA and PFOS have been well characterized in terms of their hazard, little to no toxicity information exists for the vast majority of PFAS. Evaluating thousands of PFAS using traditional toxicity approaches, in turn, would be impractical, costly and time-prohibitive, as well as requiring extensive use of animal testing. Therefore political decision makers must assess whether a transitional period is necessary to establish a comprehensive set of technical guidelines regarding the appropriate methodologies to analyse the parameters for the 'PFAS Total' and the 'Sum of PFAS'. Different aspects should be part of the analysis: such as human protection, the necessity of avoiding environmental disputes, and the aims of the circular economy.

A pragmatic solution could start from the proposal of the national authorities of Denmark, Germany, the Netherlands, Norway, and Sweden (BAuA et al, 2023), but considering the acknowledged limitations of the analytical procedures, the solution could include the following steps:

- since the definitions of PFAS will likely continue to be modified by developing regulations and enhanced research, it is necessary/important to identify an updated, and operative definition for PFAS that is accepted by the scientific community, as the proposal put forward by the OECD in 2021;
- define a first limit of concentration (screening level) for all the PFAS as a definite total to overcome the approach followed up until now in REACH, where the provisions of restriction and eliminations were limited to individual substances or groups of closely related substances. Unlike the mentioned proposal (BAuA et al, 2023), the analytical technique should be "non-targeted" as the total organic fluorine (TOF) analysis, since it represents a more accurate method compared to the total fluorine analysis (TF) suggested in BAuA et al. (2023a);
- if the screening level is not respected, a further analysis should be implemented considering "targeted techniques" on the base of a "positive" official list of specific chemicals for which the toxicity of the compounds is known or assessed by chemical similarity and/or toxicity modelling with state-of-the art tools. This list should name harmful substances and could be continually updated alongside the progress made from new scientific analysis. Furthermore, this list could represent a solution for the interpretation of general terms such as "salts", "related compounds" and "derivates" of perfluoroalkyl acids. It is worth mentioning that when a TOP assay is applied, a higher concentration of targeted PFAS should be expected as suggested by the systematic critical review.

5. CONCLUSIONS

Currently, the relevant knowledge on the impact of PFAS in solid waste management, from disposal to recycling, is still scarce. In this context, regulation updates on PFAS contents in substances, matrixes and articles could influence these latter, e.g. by limiting the circularity of recycled materials and affecting EoW procedures. In this context, this review tries to answer to the stringent need to discuss the possible consequences of proposed new limits for PFAS in products on relevant waste recycling sectors.

In order to achieve this, a systematic analysis of scientific literature was conducted to gather concentration ranges of PFAS in waste items across four key material categories (plastic, paper and cardboard, textile and leather, metals). This review encompassed peer-reviewed articles and other pertinent documents, aiming to compare the obtained results against the lowest proposed regulatory limit for any PFAS in products (i.e., 25 ppb). For each material category, very few outliers resulted higher than the considered limit of 25 ppb. The percentage of exceedances ranged from almost 1% (PFOS measurements in paper and cardboard waste) to 8% ("Other PFAS" in Textiles and leather waste). The analysis of various papers revealed diverse methods for PFAS analysis in solid matrices. Discrepancies in extraction, purification, and quantification methods could have impacted accuracy and hindered comparison.

Notably, results showed higher analyte concentrations in samples where TOP assay was performed prior to the quantification step.

Based on a thorough discussion on the specific nature of the term "PFAS" as defined in the current regulation and the current need for an harmonized analytical strategy to quantify the parameter 'PFAS Total' and the 'Sum of PFAS', a pragmatic solution for the waste sector was finally proposed. A stepwise procedure is suggested. First, there is the necessity to establish an updated and universally accepted definition for PFAS, reflecting changes in regulations and scientific advancements. Secondly, it supports setting an initial concentration limit (as a screening level) for "Total PFAS". This can involve a more accurate non-targeted analytical technique, such as total organic fluorine (TOF) analysis, rather than total fluorine analysis (TF). Finally, if the screening level isn't met, the proposal advocates employing "targeted techniques" based on a verified list of known harmful chemicals, derived from toxicity assessments.

6. FURTHER DEVELOPMENT

To better foresee the implication on management practices of PFAS containing waste, it is suggested to design a systematic experimental activity in which representative samples of wastes are collected and analysed by means of the same standardized methodologies under a uniquely defined scope. This could overcome the limits of the data made available by the systematic critical review which were obtained from the application of a set of different methodologies and often with different aims.

ACKNOWLEDGEMENTS

This study was carried out within the MICS (Made in Italy – Circular and Sustainable) Extended Partnership and received funding from Next-GenerationEU (Italian PNRR – M4 C2, Invest 1.3 – D.D. 1551.11-10-2022, PE00000004).

Further, the study was supported by the FEAD – European Waste Management Association (https://fead.be/).

REFERENCES

Ateia, M., Chiang, D., Cashman, M., Acheson, C., 2023. Total Oxidizable Precursor (TOP) Assay Best Practices, Capabilities and Limitations for PFAS Site Investigation and Remediation. Environ. Sci. Technol. Lett. https://doi:10.1021/acs.estlett.3c00061

BAuA (Federal Institute for Occupational Safety and Health), 2019. Annex XV Restriction Report. Proposal for a restriction. Available at: https://echa.europa.eu/it/registry-of-restriction-intentions/-/dislist/details/0b0236e18323a25d (accessed 6.10.23).

BAuA (Federal Institute for Occupational Safety and Health), Bureau REACH (National Institute for Public Health and the Environment -RIVM), Swedish Chemicals Agency (KEMI), Norwegian Environment Agency, The Danish Environmental Protection Agency. 2023a. Annex XV Restriction Report. Proposal for a restriction. Available at: https://echa.europa.eu/it/registry-of-restriction-intentions/-/dislist/details/0b0236e18663449b (accessed 6.10.23).

BAuA (Federal Institute for Occupational Safety and Health), Bureau REACH (National Institute for Public Health and the Environment -RIVM), Swedish Chemicals Agency (KEMI), Norwegian Environment Agency, The Danish Environmental Protection Agency. 2023b. Webinar: Restriction of per- and polyfluoroalkyl substances (PFAS) under REACH Questions and answers – Answers by the five national authorities to questions on the content of the proposed restriction.

Buck, R.C., Franklin, J., Berger, U., Conder, J.M., Cousins, I.T., Voogt, P. De, Jensen, A.A., Kannan, K., Mabury, S.A., van Leeuwen, S.P.J., 2011. Perfluoroalkyl and polyfluoroalkyl substances in the environment: Terminology, classification, and origins. Integr. Environ. Assess. Manag. 7, 513–541. https://doi:10.1002/ieam.258

Cousins, I. T., Goldenman, G., Herzke, D., Lohmann, R., Miller, M., Ng, C. A., Patton, S., Scheringer, M., Trier, X., Vierke, L., Wang, Z., & Dewitt, J. C. (2019). The concept of essential use for determining when uses of PFAS can be phased out. Environmental Science: Processes and Impacts, 21(11), 1803–1815. https://doi.org/10.1039/c9em00163h

Department for Environment, Food and Rural Affairs, UK, 2015. Persistent organic pollutants (POPs) List of perfluorooctane sulfonates and related compounds.

Directive (EU) 2020/2184 of the European Parliament and of the Council of 16 December 2020 on the quality of water intended for human consumption (recast)

ECHA, 2017. Annex XV Restriction Report Proposal for a restriction substance name(s): C9-C14 PFCAs -including their salts and precursors-

ECHA, 2023a. Registry of restriction intentions until outcome [WWW Document]. URL https://echa.europa.eu/registry-of-restriction-intentions/-/dislist/details/0b0236e1827f87da (accessed 6.9.23).

ECHA, 2023b. Registry of restriction intentions until outcome [WWW Document] https://echa.europa.eu/it/registry-of-restriction-intentions/-/dislist/details/0b0236e18323a25d (accessed 6.9.23).

ECHA, 2023c. Registry of restriction intentions until outcome [WWW Document] https://echa.europa.eu/it/registry-of-restriction-intentions/-/dislist/details/0b0236e18663449b (accessed 6.9.23).

EFSA, 2012. Scientific Opinion on the presence of dioxins (PCDD/Fs) and dioxin-like PCBs (DL-PCBs) in commercially available foods for infants and young children. EFSA Journal, 10(12), 1–29. https://doi.org/10.2903/j.efsa.2012.2983

European Commission, 2014. Commission Regulation No 1357/2014 of 18 December 2014 replacing Annex III to Directive 2008/98/EC of the European Parliament and of the Council on waste and repealing certain Directives

European Parliament and European Council, 2019. Regulation (EU) 2019/1021 of the European Parliament and of the Council of 20 June 2019 on persistent organic pollutants. URL https://eur-lex.europa.eu/legal-content/en/TXT/?uri=CELEX:32019R1021

Gaines, L.G.T., Sinclair, G., Williams, A.J., 2023. A proposed approach to defining per- and polyfluoroalkyl substances (PFAS) based on molecular structure and formula. Integr. Environ. Assess. Manag. 00, 1–15. https://doi:10.1002/ieam.4735

Gurevitch, J., Koricheva, J., Nakagawa, S., Stewart, G., 2018. Meta-analysis and the science of research synthesis. Nature 555, 175–182. https://doi:10.1038/nature25753

Lu J, Lu H, Liang D, Feng S, Li Y, Li J, 2023. A review of the occurrence, monitoring, and removal technologies for the remediation of per- and polyfluoroalkyl substances (PFAS) from landfill leachate. doi: 10.1016/j.chemosphere.2023.138824. Epub 2023 May 8. PMID: 37164196.

Norwegian Environment Agency, 2019. Annex XV Restriction Report. Proposal for a restriction. Available at: https://echa.europa.eu/it/registry-of-restriction-intentions/-/dislist/details/0b0236e1827f87da (accessed 6.10.23).

OECD, 2007. Toward a new comprehensive global database of per and polyfluoroalkyl substances (PFAS): summary report on updating the OECD 2007 list of per and polyfluoroalkyl substances (PFAS).

OECD. 2018. Toward a New Comprehensive Global Database of Per- and Polyfluoroalkyl Substances (PFAS). [WWW Document] https://www.oecd.org/chemicalsafety/risk-management/global-database-of-per-and-polyfluoroalkyl-substances.xlsx (accessed 30.06.23).

Organisation for Economic Co-operation and Development (OECD). 2021. Reconciling Terminology of the Universe of Per- and Polyfluoroalkyl Substances: Recommendations and Practical Guidance. Series on Risk Management No. 61.

PRISMA, 2023 [WWW Document], URL http://prisma-statement.org/PRISMAStatement/ (accessed 7.6.23).

Schwartz-Narbonne, H., Xia, C., Shalin, A., Whitehead, H.D., Yang, D., Peaslee, G.F., Wang, Z., Wu, Y., Peng, H., Blum, A., Venier, M., Diamond, M.L., 2023. Per- and Polyfluoroalkyl Substances in Canadian Fast Food Packaging. Environ. Sci. Technol. Lett. 10, 343–349. https://doi.org/10.1021/acs.estlett.2c00926

SNPA, 2021. Criteri condivisi del sistema per la stima e l'interpretazione dell'incertezza di misura e l'espressione del risultato. (in Italian) ISBN 978-88-448-1077-1

Stockholm Convention, 2023. Persistent Organic Pollutants Review Committee (POPRC) [WWW Document]. URL https://chm.pops.int/Convention/POPsReviewCommittee/Chemicals/tabid/243/Default.aspx (accessed 6.9.23).

Swedish Chemicals Agency, 2015. Occurrence and use of highly fluorinated substances and alternatives: Report from a government assignment

UN Environment Programme and Stockholm Convention, 2023. The new POPs under the Stockholm Convention. [WWW Document] https://www.pops.int/TheConvention/ThePOPs/TheNewPOPs/tabid/2511/Default.aspx (accessed 12.6.23).

UNEP, 2019. Initial indicative list of perfluorohexane sulfonic acid (PFHxS), its salts and PFHxS-related compounds (UNEP/POPS/POPRC.15/INF/9).

UNEP, 2022. Updated indicative list of substances covered by the listing of perfluorooctanoic acid (PFOA), its salts and PFOA-related compounds (UNEP/POPS/POPRC.17/INF/14/Rev.1).

United Nations, 1987. Montreal Protocol on Substances that Deplete the Ozone Layer, Montreal, Canada, 1987. Decision IV/25.

USEPA 2022. PFAS structures in DSSTox (update August 2022). [WWW Document]. URL https://comptox.epa.gov/dashboard/chemical-lists/PFASTRUCT (accessed 01.07.23).

Wang, Z., Buser, A.M., Cousins, I.T., Demattio, S., Drost, W., Johansson, O., Ohno, K., Patlewicz, G., Richard, A.M., Walker, G.W., White, G.S., Leinala, E., 2021. A New OECD Definition for Per- And Polyfluoroalkyl Substances. Environ. Sci. Technol. 55, 15575–15578. https://doi:10.1021/acs.est.1c06896

Williams, A.J., Gaines, L.G.T., Grulke, C.M., Lowe, C.N., Sinclair, G.F.B., Samano, V., Thillainadarajah, I., Meyer, B., Patlewicz, G., Richard, A.M., 2022. Assembly and Curation of Lists of Per- and Polyfluoroalkyl Substances (PFAS) to Support Environmental Science Research. Front. Environ. Sci. 10, 1–13. https://doi:10.3389/fenvs.2022.850019

Zhang M, Zhao X, Zhao D, Soong TY, Tian S, 2023. Poly- and Perfluoroalkyl Substances (PFAS) in Landfills: Occurrence, Transformation and Treatment. Waste Manag. https://doi: 10.1016/j.wasman.2022.10.028. Epub 2022 Nov 12. PMID: 36379166.

detritus | Multidisciplinary Journal for Circular Economy and Sustainable Management of Residues

CISA

TOWARDS REAL-TIME MONITORING OF ODOUR EMISSIONS FROM WASTE TREATMENT PLANTS: A CASE STUDY

Christian Ratti, Beatrice Julia Lotesoriere, Carmen Bax * and Laura Capelli

Politecnico di Milano, Department of Chemistry, Materials and Chemical Engineering "Giulio Natta", Piazza Leonardo da Vinci 32, 20133 Milan, Italy

Article Info:
Received:
15 September 2023
Revised:
29 January 2024
Accepted:
19 February 2024
Available online:
31 March 2024

Keywords:
Odour concentration
Ambient air quality
Quantification
Electronic nose
IOMS

ABSTRACT

The most recent Best Available Techniques (BAT) for waste treatment plants indicate odour as environmental pollutants to be monitored and controlled. In Italy, the prescription of permanent installations of electronic noses (or Industrial Odour Monitoring Systems - IOMS) in the environmental permit of waste treatment plants (WTPs) is becoming more and more frequent. IOMS are intended to provide a real-time estimation of the odour concentration at the fenceline of the plant. Although this type of IOMS application is becoming very common, it is far from being state-of-the-art. In this context, this paper describes a research project aimed at the implementation at the fenceline of a WTP of an IOMS network, comprising two IOMS and a meteorological station. The paper focuses on presenting the experimental procedure involved for training IOMS and verifying their performance in the field. 5 olfactometric campaigns were carried out at the plant to build IOMS calibration models aimed at WTP odours detection, classification, and quantification. Results of field performance testing proved, with classification accuracies above 95% achieved by both IOMS, a very good capability of properly trained IOMS to recognize WTP odours. Moreover, they pointed out a great agreement between the estimations of the odour concentration provided by the IOMS and the odour concentration assessed by dynamic olfactometry, thereby boosting the research in this field. Finally, the paper reports the results of 1-year monitoring at the WTP with the purpose of evaluating the possibility to define an alarm threshold for the odour concentration.

1. INTRODUCTION

Odours currently are one of the major causes of citizens' complaints to local authorities and, in the case of activities related to the treatment and disposal of wastes, often represent a limiting factor to the operation of plants (Capelli et al., 2020). The most recent Best Available Techniques (BAT) conclusions for waste treatment include odours among the environmental parameters to be monitored (Pinasseau et al., n.d.). For these reasons, odours are subjected to regulations and rules at national and European level have been published to regulate the odour impact from industrial facilities (Brancher et al., 2017).

Different approaches have been developed to characterize environmental odours (Bax et al., 2020b). Dynamic olfactometry is the reference method for odour quantification at emission sources (standardized by the EN 13725:2003) and can provide information to be used as input for dispersion modelling to evaluate citizens' exposure to odours. The major limitations related with this approach are that this technique is discontinuous, and its inapplicability to ambient air, making it unsuitable for a real-time monitoring of odour exposure. An alternative sensorial technique that can be used to measure odors in the field is represented by field inspection. It allows estimating the degree of annoyance in term of "odour hours" in a determined area. However, as dynamic olfactometry, this technique is discontinuous and considerably time- and cost-intensive. Thus, it is not suitable for the continuous monitoring of odours (Bax et al., 2020b). The use of electronic noses (or Industrial Odour Monitoring Systems - IOMS), able to perform a continuous real-time monitoring of odour emissions, allows overcoming these limitations. Indeed, despite the costs and time required for a proper instrument training, they have proved to be effective for the real-time of odour emissions directly at the emission sources or either at the nearest sensible receptors (De Vito et al., n.d.; John et al., 2021; Oliva et al., 2021; Panzitta et al., 2022; Prudenza et al., 2023).

Currently, in Italy, the permanent installation of IOMS is sometimes prescribed within the environmental permit of waste treatment plants (Cangialosi et al., 2018). Such

* Corresponding author:
Carmen Bax
email: carmen.bax@polimi.it

https://doi.org/10.31025/2611-4135/2024.18361

systems are usually prescribed with the purpose of continuously monitoring the ambient air at plant fencelines to detect, classify and quantify odour emissions from the plant. The final goal is, in general, the real-time identification of anomalous odour emissions, thus enabling prompt interventions aimed at reducing odour events on the neighborhoods. Despite the increasing number of such prescriptions, the use of IOMS for the continuous monitoring of odour emissions and the real-time measurement of odour concentrations is still far from being state-of-the-art. In this context, this paper describes a research project aimed at the implementation of an IOMS network at the fenceline of waste treatment plant (WTP), producing biomethane and high-quality compost, intended to provide a real-time estimation of the odour concentration. The IOMS network comprises two electronic noses produced and commercialized by Ellona (i.e., WT1 1179 and WT1 1180) and a meteorological station.

The paper focuses on the description of the experimental procedure involved for the IOMS training and data processing. Furthermore, it presents the results of one-year monitoring at the WTP fenceline with the purpose of evaluating the applicability of IOMS for a real-time estimation of the odour concentration at the fenceline of a WTP plant and the possibility to set an alarm threshold for the odour concentration.

2. MATERIALS AND METHODS

2.1 Waste treatment plant

The WTP under investigation converts the organic fraction of municipal solid waste (OFMSW, 80'000 ton/y) into biomethane (550 Sm^3/h) and high-quality compost (36'000 ton/y). After plastic and sand separation, the OFMSW is mixed with water and enters the anaerobic digestion tanks. Anaerobic digestion leads to the formation of biogas and digestate, which are further sent to upgrading and composting sections to obtain biomethane and high-quality compost, respectively. To prevent odour emissions into the atmosphere, OFMSW storage and treatments are carried out in closed sheds operated under slight vacuum and equipped with ventilators collecting exhaust air to a biofilter unit. Thus, the biofilter unit represents the only odour emission source of the plant. However, fugitive emissions from storage and treatments sheds cannot be completely neglected.

2.2 Monitoring systems

2.2.1 Description

The monitoring system comprises two IOMS (i.e., Ellona WT1 1179 and 1180) and a weather station (i.e., Davis Instruments, Vantage Pro2) (Figure 1). The two IOMS are equipped with 7-sensors each, comprising 4 metal oxide sensors (MOS), 2 electrochemical sensors specific for the detection of hydrogen sulphide (H_2S) and ammonia (NH_3) and one photoionization detector (PID) calibrated in isobutylene. The instruments also include sensors for monitoring temperature and relative humidity levels. The weather station Vantage Pro2 is equipped with Anemometer, Rain Collector, Temperature and Humidity Sensors. IOMS and meteorological data can be visualized in real-time and downloaded through the Ellona web interface.

2.2.2 Monitoring sites

The monitoring sites at the WTP fenceline were defined based on the results of a parametric dispersion modelling of the odour emissions from the WTP, which allowed correlating the odour condition at the fenceline with the impact at closest receptors. The two IOMS were installed at the western and eastern corner of the plant along the prevailing wind direction, as illustrated in Figure 2. More in detail,

a)

b)

FIGURE 1: Monitoring system: a. Ellona outdoor electronic nose and b. Davis Instruments, Vantage Pro2 meteorological station.

FIGURE 2: Illustration of monitoring sites at the WTP fenceline.

the WT1 1179 was installed in the proximity of WTP anaerobic digester and emergency flare, while the WT1 1180 is expected to be mainly exposed to diffuse emissions from OFMSW storage and treatments sheds.

2.3 Experimental protocol

2.3.1 General outline

The research was structured in six phases: 1) Analysis of the process and definition of the monitoring sites at the plant fenceline; 2) IOMS training for the implementation of specific quantification and classification models to be further used for the real-time analysis of the ambient air; 3) IOMS performance verification in the field; 4) Monitoring phase, during which the IOMS provided real-time estimations of the odour concentration at the monitoring sites; 5) Analysis of IOMS outputs relevant to the monitoring phase in combination with meteorological conditions; 6) Comparison of IOMS monitoring outcomes with odour observations made by human "sentinels" during the monitoring phase, with the purpose of defining suitable alarm thresholds for the real-time detection of odorous conditions potentially responsible for odour events in the vicinity of the plant.

Five olfactometric campaigns, distributed among different seasons, were conducted at the plant from February 2022 to October 2022 to train and test the IOMS. They involved the collection of odour samples at WTP emission sources (i.e., buildings dedicated to OFWMS storage, pre-treatments, and de-sandblasting, bio-pulpers, digesters, and biofilter), their olfactometric characterization according to EN 13725:2022, and their analysis by IOMS. A total of 230 samples, whose concentration ranged from 20 to 800 ou_E/m^3, were used. These data were split in a Training Set (TS) and in an independent external test set, for the field performance verification, following this criteria: 170 samples collected in the first four olfactometric campaigns were used to build the TS (Table 1), instead, the samples analysed in the last campaign conducted on October 2022 were incorporated in the external validation set (Table 2).

2.3.2 IOMS training phase

During training, odourless ambient air, collected at the fenceline when no odour could be perceived, were analysed to define the IOMS baseline. The training set (TS) was built combining IOMS sensors signals (i.e., MOS electrical resistances and concentrations provided by H_2S, NH_3 and PID sensors) with samples' class and concentration. Three classes were considered: air indicative of the absence of odour condition, biogas representative of fugitive leaks from digesters, and organic odour relevant to emissions from buildings dedicated to OFWMS storage and processing and biofilter. The TS was processed according to the procedure illustrated in Figure 3. After an initial pre-treatment aimed at normalizing the data and compensating potential interferences, different features (comprising electrical resistance ratio, area under the curve, etc…) from the sensors' signal curves were extracted and ranked by means of Boruta algorithm (Kursa & Rudnicki, 2010). Selected features were processed by Principal Component Analysis (PCA), and PCA scores on the first 3 principal components were used as input of a two-step classification model. The classification model, based on Support Vector Machine (SVM) (Cortes et al., 1995), was trained to detect WTP odours and identify their type (i.e., landfill gas or organic odour). Finally, a class-specific regression model, based on Support Vector Regression (SVR) (Smola et al., 2004), was used to estimate the odour concentration.

2.3.3 Field performance verification

According to the recently published Italian Standard on Instrumental Odour Monitoring with IOMS (UNI 11761:2023), field performance tests were carried out after the IOMS training and installation on site. They involved the sampling at emission sources of new samples and their analysis by dynamic olfactometry and IOMS. A total of 60 samples, defined as in Table 2, with odour concentration ranging from ca. 20 to ca. 700 ou_E/m^3, were analysed.

Such tests aimed at assessing the capability of the trained IOMS to estimate the odour class and concentration on external validation. IOMS classification performance was expressed in terms of classification accuracy and recalls for each class (Bax et al., 2020a). In addition, the IOMS odour quantification performance was evaluated by comparing the IOMS prediction with the odour

TABLE 1: Number of samples analysed for training each IOMS for each class with the respective range of odour concentration.

Class	N° of samples analysed	Range Cod [ou_E/m^3]
Air	26	20 - 50
Biogas	44	25 - 810
Organic odour	100	28 - 690

TABLE 2: Number of samples analysed for the field verification by each IOMS for each class with the respective range of odour concentration.

Class	N° of samples analysed	Range Cod [ou_E/m^3]
Air	20	20 - 50
Biogas	17	26 - 720
Organic odour	23	35 - 590

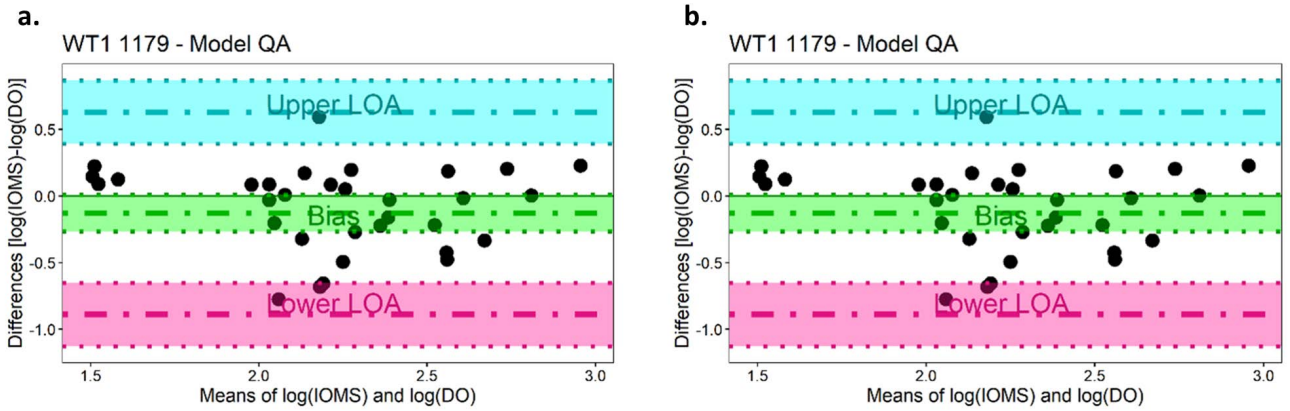


FIGURE 3: Data processing procedure adopted.

concentration assessed by dynamic olfactometry by means of a Bland-Altman model (Bland & Altman, 1999). For applying Bland-Altman test (Bland & Altman, 1999), which quantifies the agreement of two measurements in terms of mean difference (Bias) and Limits of Agreement (LoA), the logarithm of the odour concentration was considered.

2.3.4 Monitoring phase

The monitoring phase, during which the IOMS performed a continuous characterization of the ambient air, lasted about 1 year. IOMS monitoring data (i.e. continuous time series) were divided into 5 min timespans to be processed according to the procedure illustrated in Figure 3 to obtain an estimation of the odour class and concentration every 5 min.

IOMS qualitative predictions were then expressed in terms of frequency of detection of odours attributable to the different classes, with the aim of determining the odour impact, defined by the following equation, and the odour type most frequently detected at WTP fenceline.

$$\%\ odour\ impact = \frac{\sum IOMS\ detections\ of\ WTP\ odours}{\sum IOMS\ detections}$$

The odour concentration estimates, on the other hand, were used to evaluate the temporal trend of the concentration at the plant fenceline and evaluate the possibility to define an alarm threshold. The concentration values at the 95th and 98th percentiles were also calculated to determine the concentration values exceeded for 5% and 2% of the monitoring time, respectively.

Finally, a comparative evaluation between IOMS detections and odour reports by citizens living nearby the plant was carried out. Citizens' odour reports were collected by local municipality distributing questionaries to the population. For each odour event, the citizens were required to indicate the date and time of detection, the intensity (i.e., + perceptible odour, ++ strong odour, +++ very strong odour) and eventually notes regarding the odour type in the notes.

Given the significant influence of atmospheric conditions on the dispersion of odorous emissions, the wind speed and direction in force at the time of odour detection at the receptors were considered, as well.

3. RESULTS AND DISCUSSION

3.1 Field performance verification

IOMS predictions relevant to field testing were organized in confusion matrixes, reported in Table 3. The classification performance was assessed in terms of recalls and accuracy, whose value for both IOMS are summarized in Figure 4. Results achieved by both IOMS proved, with classification accuracies above 95%, their very good capability to accurately detect the odour presence and recognize the odour class. Based on these results, it is possible to state that real-time odour monitoring by adequately trained IOMS enables effective identification of the odour sources that may generate odour events outside the WTP, and thus helps undertaking rapid counteracting interventions.

The quantification performance was assessed by comparing the WT1 estimations of the odour concentrations performed on field test samples with the results of dynamic olfactometry according to EN 13725:2022, which is the reference method for odour quantification. Figure 5 illustrates Bland-Altman plots obtained for both IOMS: the x-axis reports the arithmetic mean of the logarithm of the two measurements, while the y-axis reports their difference.

TABLE 3: Confusion matrix for assessing the IOMS classification performance: a. WT1 1179, b. WT1 1180.

a.WT1 1179		Reference			b.WT1 1180		Reference		
		Air	Biogas	Organic odour			Air	Biogas	Organic odour
Prediction	Air	20	0	0	Prediction	Air	20	0	0
	Biogas	0	10	1		Biogas	0	9	0
	Organic odour	0	0	19		Organic odour	0	1	15

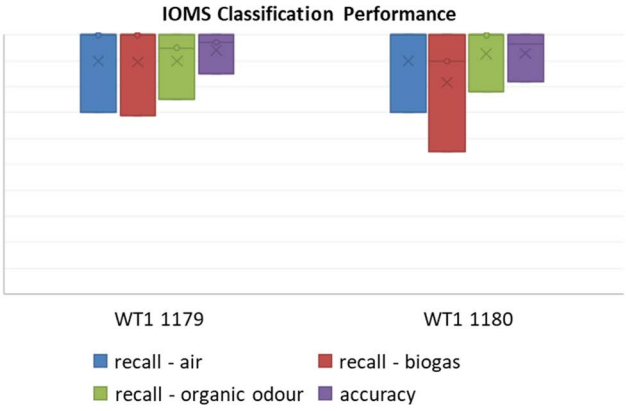


FIGURE 4: Summary of recalls and accuracy achieved by WT1 1179 and WT1 1180 on field testing.

The B&A plots illustrates the field measurements (black points), the bias (green dash-dot line), the Upper Limit of Agreement (LoA, blue dash-dot line), the Lower LoA (pink dash-dot line) and their relative 95% confidence intervals (delimited by the corresponding colour dot lines).

The visual inspection of the B&A plots proves a good agreement between IOMS and dynamic olfactometry: measurements are all comprised between the upper and lower LoA for both IOMS tested.

With the purpose of evaluating the IOMS quantification performance, the intermediate precision criterion reported in EN 13725:2022 for two consecutive measurements performed by olfactometry was used as reference, even if this is not directly defined for IOMS estimations. According to the intermediate precision criterion, the factor expressing the difference between two consecutive odour concentration measurements in 95% of cases (i.e., 1.96 * standard deviation) should not be larger than 3. In this case, factors slight above 3 were obtained for both IOMS (i.e., 3.56 for WT1 1179 and 3.74 for WT1 1180), thus proving the capability of properly trained IOMS to provide accurate estimations of the odour concentration at the WTP fenceline. Such results pointed out the potential of IOMS as tools for the real-time monitoring of the odour concentration and boost further developments in this field.

3.2 Monitoring phase

3.2.1 Processing and interpretation of IOMS outcomes

During the monitoring phase, the WT1 1179 and WT1 1180 detected the presence of WTP odours for about 7% and 11% of the monitoring period, respectively. Both instruments mostly detected odours attributed to the organic odour class. For a deeper analysis of the monitoring data, the frequency of odour detection was also calculated for each monitoring month. Figure 6 summarizes the odour impacts assessed by WT1 1179 and 1180 over the monitoring period, respectively.

Over the monitoring period, a decreasing trend of the odour impact assessed by the WT1 1179 was recorded. The reduction of odour detections from about 11% down to 4% can be explained considering that after the start-up of a new plant, it progressively reaches a regime condition.

A similar trend was also registered for the other IOMS, i.e., WT1 1180, from February to October 2022. Conversely, in the last two months of the monitoring period, an increase of the odour detection frequency up to about 21% was recorded. The increase in the frequency of odour events at fenceline in November and December combined with the analysis of the IOMS qualitative predictions allowed identifying a malfunction in the ventilation system of the OFWMS storage buildings, which resulted in increased fugitive odorous emissions impacting on the monitoring site at the eastern corner of the plant.

The odour concentrations measured at the WTP fenceline over the monitoring period were also analysed. Odour concentrations ranging from ca. 60 eq_ou_E/m^3 up to 350 eq_ou_E/m^3 were mostly measured by WT1 1179 and up to 280 eq_ou_E/m^3 by WT1 1180. Some spikes up to 1000 eq_ou_E/m^3 were recorded by the WT1 1179, installed in the proximity of the emergency flare in March and October. These anomalous concentrations were associated to the stop of the upgrading section of the plant devoted to the reefing of the biogas produced by anaerobic digestion.

The analysis of odour concentration trends at the WTP fenceline aimed at evaluating the possibility to define an alarm threshold for the odour concentration. Such alarm threshold should enable the prompt identification of plant malfunctions that could result in odour events in the proximity of the WTP. As first approximation, this threshold can

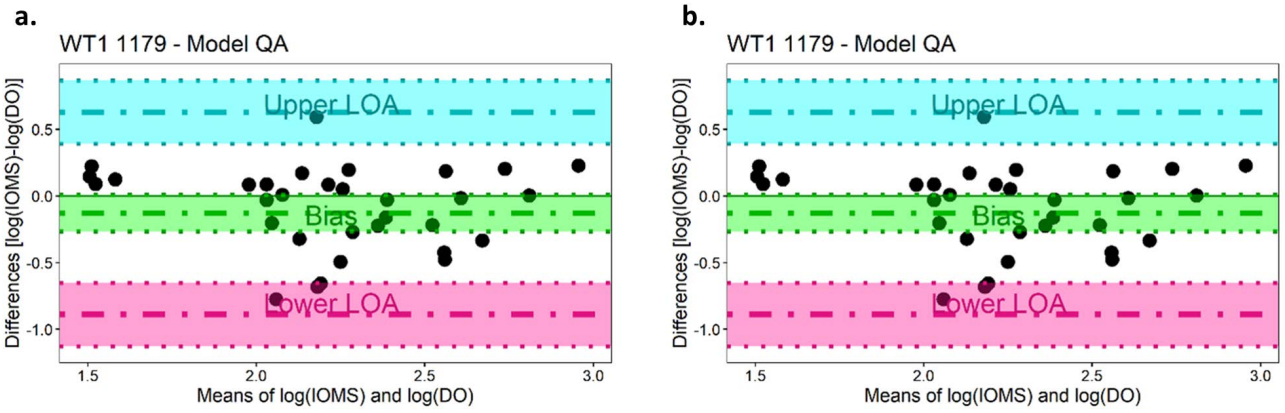


FIGURE 5: Bland-Altman plots obtained for WT1 1179 (a.) and (b.) WT1 1180 field testing results.

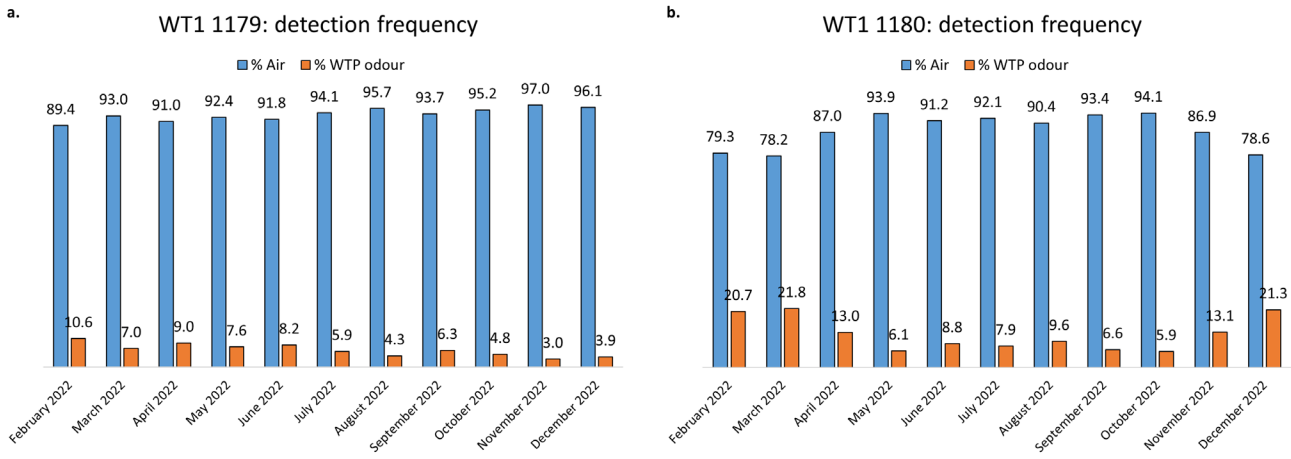


FIGURE 6: Odour impact assessed over the monitoring period: a. WT1 1179 and b. WT1 1180.

be defined in terms of a given percentiles of the odour concentration values assessed by the IOMS. Table 4 summarizes the 95th and 98th percentiles obtained on monitoring data. It is worthy to highlight that results here presented should be considered as preliminary, since the definition of a solid threshold for the odour concentration requires the analysis of IOMS predictions in combination with the meteorological conditions occurring during the monitoring phase. Moreover, the reports made by citizens should be considered to verify the existence of a correspondence between the odour nuisance perceived outside the WTP with the odour events detected at the plant fenceline.

3.2.2 Comparison of IOMS outcomes with citizens' odour reports

With the purpose of further validate IOMS predictions relevant to the monitoring period, the IOMS monitoring outcomes at the fenceline were compared with odour events reported by citizens living nearby the plant.

During the monitoring period, 37 odour events were reported by the citizens involved. In general, the reports of odours at the receptors located near the biodigester were recorded in the morning between 7 a.m. and 10 a.m. in conditions of calm winds or weak winds, which are like to worse the odour dispersion into the atmosphere.

Before performing the comparative analysis, citizens' odour reports were purged of odour events occurred under incompatible meteorological conditions (wind speed and direction not likely to favour the detection of odours from the plant at the reporting sites). Thus, 30 out of 37 odour events, listed in Table 5, were analysed. For each odour event, Table 5 reports the duration of the event indicated by citizens, the IOMS outcomes in terms of odour class detected and odour concentration, and a consideration about the agreement between IOMS and citizens' reports.

TABLE 4: 95th and 98th percentiles obtained on monitoring data recorded by WT1 1179 and WT1 1180 from February to December 2022.

IOMS	98° percentile [eq_ou$_E$/m^3]	95° percentile [eq_ou$_E$/m^3]
WT1 1179	201	174
WT1 1180	182	132

In general, the analysis pointed out a good correlation between the IOMS predictions at the plant fenceline and the odour events reported by citizens outside the plant. Indeed, only in 3 cases out of 30 odour events, both IOMS did not detect any odour in correspondence of odour events signalled by citizens. Thus, the odour events could be likely associated to external odour sources. Conversely, in most of the cases, at least one of the two instruments detected at the fenceline the presence of odours attributed to the WTP under exam, thereby confirming citizens' complaints. It is worthy to highlight that most of the times the IOMS provided information about the cause of the odour presence, thereby allowing a prompt intervention. As an example, in correspondence of odour events numbered from 8 to 12 in Table 5, both IOMS reported the highest odour concentrations at the fenceline (i.e., close to 300 eq_ou$_E$/m^3), which turned out to be a consequence of the malfunction of the ventilation system in the building devoted to the storage and pre-treatment of wastes. Therefore, properly trained IOMS can serve not only as system for controlling odorous emissions from WTP plant, but also as useful tools for the plant management.

4. CONCLUSIONS

The paper describes the realization of an IOMS network at the fenceline of a WTP plant for the real-time monitoring of its odorous emissions. Results obtained by means of validation tests in the field proved the reliability of the IOMS outputs, thus pointing out the potential of IOMS as tools for the real-time measurement of the odour concentration at plant fencelines. Indeed, IOMS predictions turned out to be in line with the odour concentration assessed by the reference technique for odour quantification, i.e., dynamic olfactometry (EN 13725:2022).

The analysis of the odour concentration trends measured at the WTP fenceline and the comparison of IOMS outcomes with meteorological conditions preliminarily proved the possibility to define an alarm threshold for the odour concentration at the fenceline, whose exceedance could

TABLE 5: Summary of odour events reported by citizens during the monitoring phase.

Citizens' odour report	Odour event duration [min]	WT1 1179 outcomes (type, concentration)	WT1 1180 outcomes (type, concentration)	Agreement
1	60	Organic, 160 eq_ou_E/m^3	Organic, 120 eq_ou_E/m^3	Yes
2	40	Organic, 150 eq_ou_E/m^3	Organic, 190 eq_ou_E/m^3	Yes
3	180	Organic, 200 eq_ou_E/m^3	Organic, 110 eq_ou_E/m^3	Yes
4	60	Air, 30 eq_ou_E/m^3	Biogas, 60 eq_ou_E/m^3	Yes
5	120	Air, 30 eq_ou_E/m^3	Biogas, 80 eq_ou_E/m^3	Yes
6	70	Organic, 120 eq_ou_E/m^3	Organic, 120 eq_ou_E/m^3	Yes
7	120	Organic, 120 eq_ou_E/m^3	Organic, 120 eq_ou_E/m^3	Yes
8	90	Organic, 280 eq_ou_E/m^3	Organic, 280 eq_ou_E/m^3	Yes
9	50	Organic, 170 eq_ou_E/m^3	Organic, 230 eq_ou_E/m^3	Yes
10	30	Organic, 170 eq_ou_E/m^3	Organic, 230 eq_ou_E/m^3	Yes
11	15	Organic, 180 eq_ou_E/m^3	Organic, 220 eq_ou_E/m^3	Yes
12	240	Organic, 180 eq_ou_E/m^3	Organic, 220 eq_ou_E/m^3	Yes
13	45	Air, 50 eq_ou_E/m^3	Organic, 110 eq_ou_E/m^3	Yes
14	30	Organic, 180 eq_ou_E/m^3	Organic, 100 eq_ou_E/m^3	Yes
15	20	Air, 30 eq_ou_E/m^3	Air, 20 eq_ou_E/m^3	No
16	140	Air, 30 eq_ou_E/m^3	Air, 20 eq_ou_E/m^3	No
17	90	Organic, 190 eq_ou_E/m^3	Organic, 110 eq_ou_E/m^3	Yes
18	15	Organic, 190 eq_ou_E/m^3	Organic, 110 eq_ou_E/m^3	Yes
19	20	Organic, 200 eq_ou_E/m^3	Organic, 120 eq_ou_E/m^3	Yes
20	120	Organic, 150 eq_ou_E/m^3	Organic, 90 eq_ou_E/m^3	Yes
21	60	Organic, 150 eq_ou_E/m^3	Organic, 90 eq_ou_E/m^3	Yes
22	120	Organic, 200 eq_ou_E/m^3	Biogas, 100 eq_ou_E/m^3	Yes
23	90	Organic, 210 eq_ou_E/m^3	Biogas, 30 eq_ou_E/m^3	Yes
24	120	Organic, 180 eq_ou_E/m^3	Air, 20 eq_ou_E/m^3	Yes
25	100	Organic, 150 eq_ou_E/m^3	Air, 20 eq_ou_E/m^3	Yes
26	80	Organic, 150 eq_ou_E/m^3	Air, 20 eq_ou_E/m^3	Yes
27	30	Organic, 150 eq_ou_E/m^3	Air, 20 eq_ou_E/m^3	Yes
28	150	Organic, 200 eq_ou_E/m^3	Air, 30 eq_ou_E/m^3	Yes
29	15	Air, 30 eq_ou_E/m^3	Air, 20 eq_ou_E/m^3	No
30	90	Organic, 200 eq_ou_E/m^3	Air, 30 eq_ou_E/m^3	Yes

be related to the occurrence of odour events outside the plant that may generate an odour nuisance problem. However, the definition of a robust and representative threshold (which may not necessarily be a fixed value but may vary with meteorological conditions to account for atmospheric dispersion) requires deeper investigations. Future developments of the project should also evaluate the stability over time of the monitoring network and consider the implementation of specific drift compensation models.

ACKNOWLEDGEMENTS

This research has carried out within the MUSA – Multilayered Urban Sustainability Action – project, funded by the European Union – NextGenerationEU, under the National Recovery and Resilience Plan (NRRP) Mission 4 Component 2 Investment Line 1.5: Strenghtening of research structures and creation of R&D "innovation ecosystems", set up of "territorial leaders in R&D.

REFERENCES

Bax, C., Sironi, S., & Capelli, L. (2020a). Definition and application of a protocol for electronic nose field performance testing: Example of odor monitoring from a tire storage area. Atmosphere, 11(4). https://doi.org/10.3390/ATMOS11040426

Bax, C., Sironi, S., & Capelli, L. (2020b). How can odors be measured? An overview of methods and their applications. In Atmosphere (Vol. 11, Issue 1). MDPI AG. https://doi.org/10.3390/atmos11010092

Bland, J. M., & Altman, D. G. (1999). Measuring agreement in method comparison studies.

Brancher, M., Griffiths, K. D., Franco, D., & de Melo Lisboa, H. (2017). A review of odour impact criteria in selected countries around the world. In Chemosphere (Vol. 168, pp. 1531–1570). Elsevier Ltd. https://doi.org/10.1016/j.chemosphere.2016.11.160

Cortes, C., Vapnik, V., & Saitta, L. (1995). Support-Vector Networks Editor. In Machine Leaming (Vol. 20). Kluwer Academic Publishers.

De Vito, S., Karatzas, K., Bartonova, A., & Fattoruso, G. (n.d.). Environmental Informatics and Modeling Environmental Informatics and Modeling Air Quality Networks Data Analysis, Calibration & Data Fusion.

John, A. T., Murugappan, K., Nisbet, D. R., & Tricoli, A. (2021). An outlook of recent advances in chemiresistive sensor-based electronic nose systems for food quality and environmental monitoring. In Sensors (Vol. 21, Issue 7). MDPI AG. https://doi.org/10.3390/s21072271

Kursa, M. B., & Rudnicki, W. R. (2010). Feature Selection with the Boruta Package. In JSS Journal of Statistical Software (Vol. 36). http://www.jstatsoft.org/

Oliva, G., Zarra, T., Pittoni, G., Senatore, V., Galang, M. G., Castellani, M., Belgiorno, V., & Naddeo, V. (2021). Next-generation of instrumental odour monitoring system (IOMS) for the gaseous emissions control in complex industrial plants. Chemosphere, 271. https://doi.org/10.1016/j.chemosphere.2021.129768

Panzitta, A., Bax, C., Lotesoriere, B. J., Ratti, C., & Capelli, L. (2022). Realisation of a Multi-Sensor System for Real-Time Monitoring of Odour Emissions at a Waste Treatment Plant. Chemical Engineering Transactions, 95, 139–144. https://doi.org/10.3303/CET2295024

Prudenza, S., Bax, C., & Capelli, L. (2023). Implementation of an electronic nose for real -time identification of odour emission peaks at a wastewater treatment plant. Heliyon, 9(10). https://doi.org/10.1016/j.heliyon.2023.e20437

Smola, A. J., Sch¨olkopf, B., & Sch¨olkopf, S. (2004). A tutorial on support vector regression *. In Statistics and Computing (Vol. 14). Kluwer Academic Publishers.

detritus | Multidisciplinary Journal for Circular Economy and Sustainable Management of Residues

CISA

WASTE PICKER RIGHTS AND SOCIAL INCLUSION: THE CREATION OF A UNIVERSITY WITH KNOWLEDGE DEMOCRACY

Jutta Gutberlet [1,*] and Isabella de Carvalho Vallin [2]

[1] *Department of Geography, University of Victoria, 3800 Finnerty Road, Victoria, BC, V8P 5C2, Canada*
[2] *Postgraduate Programme in Environmental Science, Institute of Energy and Environment, University of São Paulo, São Paulo, Brazil*

Article Info:
Received:
27 November 2023
Revised:
2 February 2024
Accepted:
11 March 2024
Available online:
20 March 2024

Keywords:
Waste pickers
Education
Recycling
University
Knowledge democracy

ABSTRACT

UNICATA is a university for and with waste pickers based on Paulo Freire's popular education pedagogy, knowledge democracy and the practice of peer learning. The aim is to create a learning space of excellence where one can dream, dare, innovate, and be inspired by transformative ideas and achievements. This university will increase access to knowledge and expand the possibilities for reflection, for a population that suffers from social exclusion and high vulnerability. Worldwide waste pickers are major protagonists in collecting, separating, and redirecting recyclable materials into the circular economy. Research demonstrates that waste pickers are central figures in educating households on waste separation practices, adding value to recovered materials, building community by integrating socially excluded individuals into their collective workspaces, indirectly also mitigating environmental and climate impacts. While these positive effects of inclusive recycling are increasingly recognized in the academic literature, unfair remuneration, stigmatization, and risk-prone or unhealthy working conditions are still the prevailing realities. This paper discusses reflections on recent experiences of implementing UNICATA in the metropolitan region of São Paulo, Brazil, in 2023, with a pilot project developing and delivering the introductory module which was successfully completed by 22 students. The research takes a social constructivist lens to uncover the colonial social and political injustices through experiential and student-centered education. Our results reveal some noticeable assets and barriers in creating inclusive education for a large population that is widely neglected, in many different geographic contexts, thus also filling a gap towards achieving the Sustainable Development Goals (SDGs).

1. INTRODUCTION

Waste pickers are independent or organized workers who reclaim and divert recyclable materials for a circular economy (Gutberlet and Carenzo, 2020; Carenzo, 2020; Dias, 2016). Worldwide waste pickers comprise about 2 percent of the urban population (Gutberlet, Carenzo, Kain and Mantovani Martiniano de Azevedo, 2017). While they fulfill a needed service and play an important role in the recovery of materials that are considered waste, they persistently are stigmatized and marginalized (Bulla, Rendon and Trenc, 2021; Rutkowski and Rutkowski, 2015). Moreover, there exists a large diversity in working conditions among waste picker organizations (WPOs). High member turnover rates coupled with lacking skills and technical capacity and many other bottlenecks and difficulties often create unproductive workspaces. Additionally, the majority of the WPO members lack knowledge around solid waste legislation and public policy; consequently, they are excluded from municipal debates and policy discussions regarding solid waste management.

To overcome the predicament of social and economic exclusion, to improve environmental quality and to progress the Sustainable Development Goals (SDGs), appropriate education for this disadvantaged population is strategic and essential (Kopnina, 2020).

Despite the prevailing precarious working conditions referred to above, many WPOs have been successful in managing their operations, creating a better work environment and in establishing contracts with governments and the industry. While being central figures in educating households on waste separation practices, they also add value to recovered materials, build community by integrating socially excluded individuals into their collective workspaces, and indirectly they also mitigate environmental and climate impacts. Such achievements and knowledge will be harnessed, mobilised, shared and expanded with the university for and with waste pickers (UNICATA).

* Corresponding author:
Jutta Gutberlet
email: gutber@uvic.ca

https://doi.org/10.31025/2611-4135/2024.18358

The proposed creation of UNICATA aims at expanding the access to knowledge and generating possibilities for engagement, goals that have the potential to make significant transformative impacts in society. Lavagnolo and Grossule (2018), underline the benefit of actively involving waste pickers for outreach to increase awareness among the population and public administrators to promote the implementation of a sus¬tainable waste management system.

UNICATA, as a collaborative project, represents a partnership between academics and practitioners, which constitute autonomous waste pickers, waste picker collectives and the national waste pickers movement in Brazil. These key partners will collaboratively implement a customised educational program catered to serve waste pickers and their needs. For transformative change to take place, UNICATA applies a bottom-up approach grounded in theories as articulated by Paulo Freire (2018), Michel Thiollent (2011), Orlando Fals-Borda (1987), among others. From the student perspective, the concept of UNICATA invests in building critical self-consciousness and social awareness that can lead to actions against discrimination and oppression, building a more just and sustainable society. As, both educators and students, waste pickers will become the agents of change. Experienced waste pickers are a fundamental element in the teaching and effective dissemination of knowledge.

UNICATA is focused on co-generating knowledge using participatory and human centred approaches and design, based on collective ways in defining the key gaps in education and training, ideating, and creating courses that respond to challenges, receiving input and feedback on course offerings, refining materials, and the delivery to better respond to the needs. The human centred design approach allows for the learner-experience to influence the development of each teaching module, and addresses change by thinking holistically about the social, economic, and environmental aspects regarding the work and workspaces of waste pickers and their livelihoods.

The course content for the pilot project includes the themes: historical and political approach to recycling and waste picking, role, and impact of key actors in the solid waste sector, waste management policy, Circular Economy and Reverse Logistics; effective communication and conflict resolution among other topics.

Waste pickers are the educators, coupled with academics or other experts and they help convey and create knowledge, using appropriate language and context.

The theory of change for this project is centred around the notion that tailored education will lead to higher incomes and better quality of life for waste pickers; improved interpersonal relations among the workers as well as greater gender equity; improved recovery of materials and better waste management; and more inclusive cities through greater collaboration between municipal authorities and WPOs. The development of an educational space for waste pickers (organized or autonomous) with thematic content based on local realities and necessities is critical to transforming the lives of waste pickers and their opportunities. These teaching methods are strongly focused on local contexts where students work and live, considering place specific aspects, to also stimulate interests on more general and interrelated subjects and to allow for knowledge sharing on these specific situations. This might help students to learn from different contexts, increasing the comprehension of more abstract or theoretical concepts and frameworks. Finally, this approach includes attention to issues of class, race, and gender diversity throughout the knowledge co-production process, particularly given that in countries such as Brazil the conditions of these social inequalities are widespread and deeply rooted in the colonial past throughout the territory.

The next section 2 describes our theoretical framework based on popular education and knowledge democracy. We discuss how UNICATA takes a decolonial approach to education (Zavala, 2016), using a social constructivist lens (Gerberry, 2023), which when applied to the context of waste management acknowledges the role of all actors in the waste value chain. In this approach the researcher takes an active role in constructing knowledge and investigating diverse points of view. This implies the active involvement of all participants; and learning takes place through interaction and the cognitive co-construction and co-production of knowledge (MacLeod, Burm & Mann, 2022). In section 3 we present the research and community outreach methodology which led to the creation of UNICATA. In section 4, first results of the pilot project are discussed, specifically hearing the voices of the participants. Finally, section 5 draws some first conclusions based on the interpretation of the results through the conceptual framework presented earlier.

2. MATERIALS: THEORETICAL FRAMEWORK

2.1 Popular education theory

Education is a multifaceted field, made up of different currents and conceptions that have moulded diverse educational practices. When considering waste pickers as a group of marginalised workers in situations of socio-environmental vulnerability, it is important to think about education strategies that are aligned with the context of these people's lives. For Piaget (1973), knowledge is understood as an activity that is constructive incessantly, learning takes place through the individual's interaction with their environment, as they organise their experiences. On the other hand, Vygotsky (1978) emphasises the importance of social interaction in learning, arguing that cognitive development is mediated by cultural tools and practices. These perspectives have influenced education, promoting student-centred and experience-based approaches that make sense in waste pickers' education.

Constructivism is an epistemology theory that underlines that learning is the process of constructing new knowledge on the foundations of existing knowledge and that knowledge construction is facilitated through interaction with the environment, with reality. Kolb (1984) for example describes learning and knowledge construction as a learning cycle which has four phases: concrete experience, reflective observation, abstract conceptualization, and active experimentation. Kolb's experiential learning cycle

allows apprehension, comprehension, intention, and extension (Yardley, Teunissen and Dornan, 2012).

Learning tied into experience builds critical thinking skills, by applying theory and academic content to real-world experiences, and local and traditional or indigenous knowledge within the classroom, the community, or the workplace. This could entail applied research projects, case studies, field visits, community/industry research projects, practica or placements, among other options widely described at many university websites (see for ex.: Carlton University, TLS Teaching Resources).

By applying an epistemology of inclusion, a constructivist lens strives to uncover historical realities. The legacy of modernity, capitalism, and colonialism, which created our current systems of dominance, exclusion and even erasure have shaped everyday lives. Historical realities marked by disparity, inequality, racism, and stigmatization are questioned and critiqued by an epistemology of inclusion, and action-oriented and participatory research and community engagement approaches are applied to understand the connections to contemporary capitalism (Pascale, 2018). Constructivism is not a method, but a conception of knowledge. From this perspective, it can be understood that there are some similar principles between constructivism and popular education, for example, the dialectical perspectives and the understanding that people are producers of culture and subjects who produce knowledge.

Popular Education is a pedagogical and political movement and a theory with Latin American roots that understands knowledge based on reality and that uses participatory methodologies to stimulate people's empowerment on a political basis for social transformation. The perspective of popular education seeks to contribute to a fairer society in defence of human rights, identities, and the environment. Popular education is a pedagogical approach that stands out for its emphasis on the active participation of the community in the educational process (Feitosa, 1999). This approach has been used widely, from adult literacy programmes to political training (Feitosa, 1999). The principles of popular education are: (a) horizontality, which emphasises equality between educators and learners, promoting the exchange of experiences and knowledge; (b) active participation, which involves the active engagement of participants in defining the themes and methods of learning; (c) contextualisation, which considers the importance of relating the content to the local reality and the issues faced by the community and; (d) dialogicity, which encourages critical dialogue and collective reflection as means of constructing knowledge (Feitosa, 1999).

Paulo Freire (2018) was one of the main authors to contribute to popular education. His work "Pedagogy of the Oppressed" outlines an educational approach centred on critical awareness and the emancipation of marginalised sections of society. Popular education is characterised by participatory pedagogical approaches, based on promoting reflective dialogues and valuing the lived experiences of learners. It also seeks to use teaching materials and practical activities that are related to local contexts. Furthermore, it provides democratic learning spaces in which participants are encouraged to question power structures and develop a critical awareness of their social reality (Freire, 2018).

On the other hand, the work "Pedagogy of Autonomy", also by Freire (2022), complements this perspective by emphasising the importance of students' autonomy and responsibility for their own learning. It promotes the idea that students should be active subjects in the construction of knowledge, encouraging creativity and active participation in the transformation of reality. Popular education therefore plays a fundamental role in promoting citizenship. The importance of Popular Education, influenced by Freire's principles, lies in its ability to empower individuals and communities to become agents of change. Freire's (2018) proposal breaks with the idea of compensatory and "banking" education generally offered by mainstream and conventional education. Freire (2018) believes in a critical education that should not represent a transmission of content, but a political act aimed at overcoming the contradictions and inequalities that determine society.

2.2 A decolonial approach to knowledge democracy

In the vein of grassroots learning, various discussions about education and power have emerged. One of these discussions concerns knowledge democracy, a concept that refers to the equitable distribution of access, production, and use of knowledge in a society (Nowotny et al., 2001). It assumes that knowledge should not be monopolised by academic or institutional elites but shared and shaped collaboratively by various social actors (Jasanoff, 2003). It argues that broad and inclusive participation in the production and dissemination of knowledge is essential for sustainable development and social justice (Nowotny et al., 2001). Knowledge democracy requires education, science and communication systems that empower ordinary citizens to participate effectively in the decision-making process, contributing to the construction of a more informed and democratic society (Stirling, 2008). In this context, the democratisation of knowledge emerges as a critical tool for tackling global challenges, promoting a more equitable distribution of intellectual resources, and fostering the inclusion of diverse perspectives in the creation and application of knowledge.

Another perspective applied to education and knowledge creation is decolonisation. Quijano (2000), in his influential theory of the "coloniality of power", has played a key role in critically examining the power structures and colonial legacy that persist in contemporary Latin American societies. Quijano (2000) argues that European colonisation has not only shaped political and economic relations in Latin America but has also resulted in profoundly structured forms of knowledge, identity and subjectivity. His analysis identifies coloniality as a matrix of global domination that encompasses not only direct colonial rule, but also the social and epistemic structures that emerged from it. Quijano's (2000) proposal is that decolonisation cannot be achieved through political or economic changes alone but requires a profound transformation in the forms of dominant knowledge and subjectivity that sustain colonial hierarchies. This approach requires a commitment to valuing and revitalising local and subaltern knowledge and entails

a profound critique of the categories of knowledge that underpin hegemonic Western thought (Mignolo, 2011).

The decolonisation of knowledge and power transcends the borders of former colonies and extends to global academic and institutional spaces. This involves a profound critique of hegemonic knowledge structures and the power relations that shape research, teaching and the dissemination of knowledge (Mignolo, 2009). Decolonisation is not just a symbolic issue, but requires concrete actions, such as restructuring academic curricula to include subaltern perspectives, supporting indigenous research and reconfiguring academic hierarchies (Tuhiwai Smith, 2012). The decolonisation of knowledge and power represents a movement of intellectual resistance that seeks to challenge the entrenched colonial structures that continue to shape the contemporary world. The decolonisation of knowledge and power demands a critical reflection on global institutions, such as international aid systems, and seeks to create spaces for the equitable participation of voices from the Global South in global decision-making (Grosfoguel, 2007).

It can be said that popular education is a critical dagogy that contributes to both the democracy of knowledge and decolonisation. Through emancipatory practices, popular education contributes to knowledge democracy by challenging the traditional hierarchies of power in education. In addition, popular education broadens access to knowledge and promotes the inclusion of historically marginalised groups through participatory approaches. This adds to the diversification of knowledge and strengthens the capacity of communities to influence the decisions that affect their lives. Popular education therefore plays a vital role in promoting knowledge democracy, as it makes knowledge more accessible, participatory, and relevant to a wide range of social actors (who often have been excluded in conventional education programs). Similarly, popular education contributes through empowering marginalised communities to understand and resist the forms of epistemic and structural domination inherent in the coloniality of knowledge and power, by questioning and discussing these relationships in the everyday lives of the community of learners. Grassroots education creates a space in which people can challenge dominant narratives and forge alternatives that are rooted in their own experiences and knowledge (Hooks, 2013). Popular education thus becomes an important tool in the decolonisation of educational thought and practice.

Considering that UNICATA aims to be a learning and training centre for waste pickers, both as students and as educators, popular education is in line with the principles of social transformation. For this reason, Paulo Freire's popular education underpins the institution's educational practices. However, UNICATA also intends to carry out research with waste pickers and train them to become researchers themselves. In this sense, participatory action research is another perspective that complements popular education in UNICATA's theoretical framework.

2.3 Participatory action-oriented research

Participatory Action Research (PAR) is a social research method that is widely recognised for understanding that research should not be a purely observational exercise, but rather an intervention tool that enables participants to understand and transform their own realities (Thiollent, 2011). PAR is based on a series of fundamental principles, including the collaborative and participatory nature of the process, in which researchers and community members work closely together to define problems, collect data, analyse results, and implement actions (Thiollent, 2011). In addition, PAR emphasises critical reflection as a central element, promoting the constant analysis of practices and the search for more effective and fair alternatives (Thiollent, 2011). It also calls attention to social transformation, where the results of research are not limited to the generation of knowledge but aim to bring about real change in social conditions and relations (Thiollent, 2011). These collaborative, reflexive and action-orientated principles make PAR a powerful approach for tackling complex issues and promoting the improvement of practices and conditions in diverse contexts.

PAR, developed by Orlando Fals-Borda, a Latin American pioneer in action research, proposed research that was sensitive to the local and cultural context, recognising people's knowledge and experiences as valuable resources for understanding and solving social problems (Fals-Borda, 2001). In addition, Fals-Borda emphasised the political dimension of action research, considering it a tool for challenging unjust power structures (Fals-Borda, 2001). Another central principle for the author is close collaboration between researchers and community members, promoting the co-creation of knowledge (Fals-Borda, 2001). These principles of collaboration, cultural contextualisation and political engagement are essential to Fals-Borda's PAR and contribute to its ability to promote meaningful and emancipatory change in communities. These notions also become the guiding principles in the proposed research activities integrated in UNICATA's curriculum and into the classroom.

In this way, the relationship between popular education and participatory action research is intrinsically linked to the search for active participation, awareness, and social transformation. Both approaches recognise the importance of valuing local knowledge and experiences. This synergy between popular education and action research creates for UNICATA a space where learning and research are seen as tools for social change and the promotion of justice, uniting theory, and practice in favour of the emancipation of waste pickers.

3. RESEARCH AND COMMUNITY OUTREACH METHODOLOGY

3.1 Background to UNICATA

UNICATA is a collaborative project, a partnership between researchers, academics, and professionals, including autonomous and organized waste pickers, the national waste pickers movement, non-governmental organizations, research centers and more. It is the result of long-term participatory research partnerships between waste picker cooperatives in São Paulo and researchers from the University of Victoria in Canada (UVic), from the

Federal University of ABC (UFABC) and from the University of São Paulo (USP). Since 2005, most of these partners have been involved in several initiatives, notably the Participatory Sustainable Waste Management project (also known as the Brazil-Canada project), the Waste Governance Mapping project and the Recycling Network project. These initiatives have allowed for long term co-creation of knowledge and expertise related to inclusive waste management. Some of these key actors are today the main drivers for UNICATA.

The governing bodies of UNICATA are the (1) Executive Council (EC), (2) the Management Council (MC) and the (3) Advisory Council (AC) (Figure 1). The activities of UNICATA are carried out under the direction of the Executive Council. The Management Council meets on a regular basis with the goal of establishing guidelines, policies and discussing significant projects and developments to advance UNICATA. The Advisory Council, which meets once a year, provides feedback and suggestions as well as offers improvements to UNICATA. Another classroom has been set up in Brasília, in August 2023 and additional classrooms will be established in other regions in Brazil. In the future, training could be made available also to waste pickers in other parts of the world.

3.2 Research and community outreach

The concrete initial steps to create UNICATA began with a rapid needs assessment followed by a participatory evaluation of the research results. From January to March 2022, we applied a detailed survey to 12 waste picker cooperatives in the metropolitan region of São Paulo, Brazil, representing 699 members. Our questions focused on four sections: (1) socio-demographic aspects of the participants, (2) educational experiences, (3) imaginary allowing to build a common language and vision for this university, and (4) practical and logistical aspects. In addition, we directed questions related to the overall situation of their organizations to cooperative leaders. The in-depth conversations with interviewees provided further evidence about the aspirations, ideas and challenges related to building an educational space directed towards the specific livelihood and work contexts of waste pickers. The data was analysed thematically and presented during a one-day long workshop, in April 2022, with waste picker leaders, to interpret the results collectively.

Social media and popular communication, using voice clips disseminated through WhatsApp, data visualisations and in-person meetings translating the academic results into accessible language, have played an important role in knowledge dissemination. The research has allowed us to develop a first draft curriculum consisting of 6 modules for the planned course, with 56 hours of classes per module and regular field visits. The modules of the first course are:

1. Introduction to the course
2. History, political education, and the waste picker as a social subject
3. Administration and cooperative management
4. Regulatory and legislative aspects
5. Sustainability and health at work
6. Research praxis focused on waste management contexts

While there are research-related activities in each of the first five modules, students will conduct in-depth research guided by the support of their mentors, during the sixth module. Community-based, participatory research methodology will be used as a major research paradigm. Cooperatives, governance, public policy, specifically Brazil's national solid waste legislation, circular economy and reverse logistics, solid waste and climate change, financial administration and accounting, environmental management, occupational health, human relations, and conflict resolution are some of the study areas that are covered in this course. These contents of the modules have been defined collaboratively with representatives of the waste pickers, based on key themes identified during the research. The introductory module (Figure 2) is a summary of the content that will be covered throughout the course. Therefore, the classes are organized into themes that represent the course modules and all classes are connected to each other.

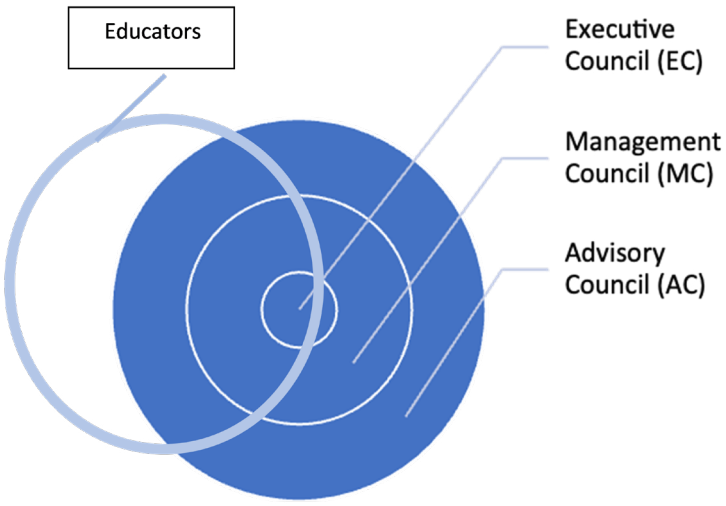


FIGURE 1: Proposed project governance structure.

FIGURE 2: Thematic content of the classes in module 1, representing the other 4 thematic modules.

3.3 Educational and pedagogic premisses

Before starting the first module, we invited all teachers (academics and waste pickers) to participate in a two-day workshop with the aim of sharing the pedagogical approach, the teaching methodology and philosophy, to collectively build a common basis of these important pedagogical dimensions. We emphasize the need for contextualization based on the concrete living conditions of the students and the adaptation to the specific situations encountered in each classroom. Between April and August 2023, the first module was delivered as a pilot project, with 22 waste pickers successfully finalizing module 1. This teaching modules can be adapted to different regional contexts and necessities.

An essential part of this proposal is that the project prepared by the teacher must also be a student project. To do this, right from the start, the teacher must look for what type of action would be interesting for that group of participants, and then develop their teaching plan, so that it becomes everyone's project. Therefore, when planning a series of classes to work on a topic, what we will look for, first of all, is the mobilization factor, which will give the opportunity to link the learning of that topic to activities that allow the participant to: (a) replicate activities learned in the classroom and apply to their own life and work, (b) understand whether they have learned something or not, (c) verify the need to know more about a certain subject. The mobilization factor of a didactic project therefore must be accessible and easy to understand. To be truly motivating learning must be practical, useful, concrete, tangible; or prompting, challenging, or even artistically stimulating. In a didactic project, the objective of the educator is to teach the contents, but the objective of the students is to achieve something that is meaningful to them.

This practice will allow certain skills to be developed by the students, which include communication, listening, organization and systematization of ideas, expression of thoughts in a synthetic way, active search for information and analysis of content and critical analysis.

4. RESULTS AND DISCUSSION

This completion of the pilot project for UNICATA provided first insight into the hurdles and requirements for setting up an educational space for vulnerable and socially excluded individuals, based on the premises of popular education and knowledge democracy. The implementation of this project presupposes a deep knowledge by the educators involved about the pedagogic, didactic, and methodological theoretical and practical foundations that foster the desired teaching practise and learning goals. We experienced the fact that it is not enough to understand the theory and concepts that support the desired educational approach, without bringing the praxis in experiential adult education and student-centered learning.

It proofed to be a necessary step to engage all educators in a workshop prior to teaching, to secure a democratic, inclusive, and participatory approach in teaching. The workshop also helped to transmit and discuss templates and examples that can help in the planning of activities and expected learning outcomes for each class. Meeting all educators before beginning the teaching of the module further had the benefit of building a common ground, connecting the teachers, and developing online means of communication to exchange experiences and transfer information.

The largest constraint in this process was the fact that there was not enough time to deepen the conversations, teasing out the real crucial issues, relevant to the teaching-learning process. Consequently, other preparatory workshops, the approach and thematic focus and planned activities for the workshop will be refined as the learning spiral will build on previous experiences.

Teaching in pairs and peer learning was a crucial step in the course delivery. For each class at least one academic and one waste picker were responsible for the preparation of teaching materials, based on the course content requirements defined collectively during previous workshops involving waste pickers and academics.

Teaching in pairs fosters reciprocity between those that bring practical work and life experience build over time and those that have accumulated theoretical knowledge. It means that everyone involved acts as both teacher and learner. This process permits greater cultural understanding and ethical development. It also builds deeper partnerships and more impactful learning outcomes. The students in the classroom will further benefit from greater diversity and, given that a waste pickers have been part in defining the course materials, there is greater likelihood that the content will be more relevant to their own experiences.

Over the 14 classes the students were exposed to the four phases of the learning cycle, as described by Kolb (1984), where students are exposed to "concrete experience, reflective observation, abstract conceptualization, and active experimentation", by engaging in a group research project elaborated throughout the module, taking part in a field trip visiting a successful waste governance project and by being exposed to new concepts and theory in classroom presentations and discussions.

At the end of the course a general evaluation form was applied to students to help ensure the success of the next module as a learning and community building experience. Sixteen waste pickers answered the evaluation form with multiple choice and descriptive questions. The results highlight that all participants rated the course positively, giving it scores of 4 and 5 on a scale of 0 to 5. All sixteen respondents would recommend the course to other people; believe that the course has had an impact on their lives; believe that the course has met their expectations; believe that the course has helped them in their daily lives; believe that it has improved their ability to find and analyse information; and that the course has helped them learn more about public policy, governance, and environmental issues. Only one person did not think that their understanding of waste picking and recycling had changed and only one person did not think the course had helped them learn more about occupational health.

In the open-ended answers, the waste pickers elaborated further about their learning perspectives. Monica mentions:

"What I thought of today's lesson, what had an impact on me, was the research that Luzia (another waste picker) brought to us about waste, where it all starts, what happens to it until it reaches us. I think that was very important for us because we don't know, at least I didn't know, right? And the other thing was when Dudu (National Waste Pickers movement (MNCR) leader) brought up the history [of the MNCR] and I had kind of gotten the history wrong in my head".

Pedro an autonomous waste picker shares his experience with the following words:

"I really enjoyed being part of this pilot project, … we go ahead, to leave a legacy for other people in situations that I found myself in and to have this study, to learn more, because we learnt things by force and now it is working out. The university of waste pickers is a reality that will last forever".

Luzia Honorato, a long-term leader among waste pickers comments on the 7th class which was on public policies:

"The importance of public policies in our field, the national movement of waste pickers, we all look forward to the construction of infrastructure and training. Public policy gives us a different kind of relationship with the government because a lens towards social inclusion is an approach that generates work and income, and it is immediate, it is necessary. So, today's lecture was brilliant because it brought us a huge range of knowledge on how to build this multi-handed project".

Dona Olinda had some specific comments about class 10 on governance:

"I thought this class evidenced the mission of UNICATA, to unite waste pickers and show that it is moving with waste pickers, the learning and teaching of waste pickers as well".

Maria Aparecida also commented on class 10 on governance:

"I'm also very grateful, firstly for being here. That one day I could be here speaking at the university for waste pickers, who until then had no value. I'm very grateful, and every day I learn and discover things that I didn't know yet and I take them [the learnings] into my daily life to empower myself".

UNICATA has the potential for creating social inclusion, increased socially just work relations with government and industry, preparing waste pickers for negotiations with government or industry, defending their rights and confronting injustices and unfair conditions or policies. The encounters in the classroom and during field visits empowers the waste pickers and creates opportunities to potentially amplify the voices of waste pickers as essential environmental and public service providers.

UNICATA has generated moments of critical self-reflection about stigma and marginalization. According to the autonomous waste picker Nanci Darcolete: "waste picking is the last decent job a person seeks before going into crime to survive. So, waste picking needs to be strengthened and supported by the government, because waste pickers are looking for opportunities and UNICATA can be this opportunity".

Some testimony speaks to the self-valuation because of the reflections during the classes. Mônica for example posits: "My degree came from the street and my doctorate from waste picking" and Pedro recognizes: "My father told me to go and study or I'd go and collect cans and today at the waste pickers' university I study to collect cans". These last two testimonies speak to a level of self-awareness and empowerment that can be achieved by waste pickers who have obviously also experienced deep stigma and exclusion from society, recognizing their value and contribution to society at the same time as a critique to the social and economic prevailing norms.

5. CONCLUSIONS

The experience of implementing the first module of the course titled "Solid waste, management, and governance with the inclusion of waste pickers for a sustainable and fair society" under UNICATA provides insights on a radically different model of grassroots education, delivered by waste pickers and academics working in pairs, linking popular ways of knowing with academic knowledge.

For the implementation of a decolonial course content and delivery it is a pre-requisite to recognize the existence of deep socio-economic gaps and disparities within society, colonial power structures that transect race, gender, and ethnicity, diminishing the value of a great part of the society in the global south context.

For transformative change to take place, UNICATA must apply a bottom-up approach grounded in pedagogical theories as articulated by Paulo Freire, Michel Thiollent, Fals Borda, among others. From the student perspective, problematizing concrete lived experiences of waste pickers in the classroom and during field visits are an essential teaching strategy, enabling critical understanding that can lead to critical action (Freire, 1974). We have witnessed many moments uncovering increased self-consciousness and social awareness, helping to understand society's oppressive forces. Experienced waste pickers represent a fundamental element in the teaching and effective dissemination of knowledge. As both educators and participants, waste pickers are agents of change in transforming their lives and societies.

UNICATA students have also been involved in the development of a research project, based on the topics discussed in class and their interests. These student projects have followed a participatory research approach, where the students have worked as researchers (citizen scientists), accompanied by academics. This approach has revealed research findings on cutting edge topics, which will also help push the edges of what we know about how to conduct better practice-driven and policy-oriented research.

UNICATA is a prime example of a grassroots initiated experience in popular education demanding and offering knowledge democracy. It suggests a solution to the problem of social exclusion and limited opportunities available to waste pickers, while waste management related work is becoming a pressing necessity, given the environmental and climate crisis increasingly penetrating our life. Investing in waste pickers' education not only prepares them better for the multiple work opportunities related to waste management but also establishes them as citizens and furthers their human development.

With the twofold purpose of UNICATA of teaching waste pickers and learning from them we hope to contribute to the design of a roadmap for the integration of waste pickers into the waste management sector. Finally, creating such an inclusive organization of knowledge cocreation and knowledge transfer brings waste pickers to the core of change, offering opportunities for mutual teaching and learning open for everybody.

ACKNOWLEDGEMENTS

We would like to acknowledge all the teamwork that has gone into this experience, particularly from members of the executive counsil of UNICATA, including Prof. Sylmara Goncalves Dias, Prof. Emeritus Angela Baeder, Prof. Adalberto Azevedo, Luzia Maria Honorata, Maria Mônica da Silva, Solanje Araujo Dias; as well as the graduate students: Daniele Tadeu de Oliveira, Felipe Palma and Gustavo Lira, involved in the pilot project, without whom this endeavour could never have taken off. We are also thankful to the editor and the reviewers of the Detritus jornal who have helped us further refine the article.

REFERENCES

Bulla, J., Rendon, M., & Trenc, J. (2021). Policing the stigma in our waste: what we know about informal waste pickers in the global north. Local Environment, 26:10, 1299-1312. Retrieved from: https://doi.org/10.1080/13549839.2021.1974368.

Carenzo, S. (2020). Contesting informality through innovation "from below": epistemic and political challenges in a waste pickers cooperative from Buenos Aires (Argentina). Tapuya: Latin American Science, Technology and Society, 3(1), 441-471.

Carlton University (2022). Experiential Learning. TLS Teaching Resources. Accessed at 10.9.2023. https://carleton.ca/tls/teachingresources/engaging-your-students/experiential-learning/

Dias, S. M. (2016). Waste pickers and cities. Environment and Urbanization, 28 (2), 375-390.

Fals-Borda, O. (1987). The Application of Participatory Action-Research in Latin America. International Sociology, 2(4), 329–347.

Fals-Borda, O. (2001). Participatory (Action) Research in Social Theory: Origins and Challenges. In P. Reason & H. Bradbury (Eds.), Handbook of Action.

Feitosa, S. C. S. (1999). Método Paulo Freire-Princípios e Práticas de uma Concepção Popular de Educação. Dissertação. Programa de Pós-graduação em Educação. Universidade de São Paulo: São Paulo, 156 p.

Freire, P. (2018). Pedagogy of the oppressed [s.l.] Bloomsbury Publishing USA.

Freire, P. (2022). Pedagogia da autonomia. Rio de Janeiro: Paz e Terra, 19897.

Gerberry, C. V. (2023). Developing self-efficacy through the social constructivist mentorship. Theory Into Practice, 62(1), 62-69.

Grosfoguel, R. (2007). The Epistemic Decolonial Turn: Beyond Political-Economy Paradigms. Cultural Studies, 21(2-3), 211-223.

Gutberlet, J., & Carenzo, S. (2020). Waste pickers at the heart of the circular economy: a perspective of inclusive recycling from the Global South.

Gutberlet, J., Carenzo, S., Kain, J. H., & Mantovani Martiniano de Azevedo, A. (2017). Waste picker organizations and their contribution to the circular economy: Two case studies from a global south perspective. Resources, 6(4), 52.

Gutberlet, J., Tadeu de Oliveira, D. & Rodrigues Costa de Castro, A. M. (Orgs.) (2023). Research production through citizen science by UNICATA students. Module 1 – Class 1. Vol. 1. ISBN 978-1-7776032-3-6.

Hooks, B. (1994). Teaching to Transgress: Education as the Practice of Freedom. Routledge.

Jasanoff, S. (2003). Technologies of Humility: Citizen Participation in Governing Science. Minerva, 41(3), 223-244.

Kolb D. (1984). Experiential Learning as the Science of Learning and Development. Englewood Cliffs, NJ: Prentice Hall.

Kopnina, H. (2020). Education for the future? Critical evaluation of education for sustainable development goals. The Journal of Environmental Education, 51(4), 280-291.

Lavagnolo M.C. & Grossule V. (2018). From 3R to 3S: An appropriate strategy for developing countries. Detritus 04: 1–3. DOI: 10.31025/2611-4135/2018.13749.

Mignolo, W. D. (2009). Epistemic Disobedience, Independent Thought and De-Colonial Freedom. Theory, Culture & Society, 26(7-8), 1-23.

Mignolo, W. D. (2011). The Darker Side of Western Modernity: Global Futures, Decolonial Options. Duke University Press.

Nowotny, H., Scott, P., Gibbons, M. (2003). Introduction: "Mode 2" Revisited: The New Production of Knowledge. Minerva, 41(3), 179–194. http://www.jstor.org/stable/41821245

Pascale, C.-M. (2018). Epistemology and Moral Economies of Difference: Transforming Social Research. International Journal of Critical Diversity Studies, 1(1), 45–57. https://doi.org/10.13169/intecritdivestud.1.1.0045

Piaget, J. (1973). To Understand Is to Invent: The Future of Education. Grossman Publishers.

Quijano, A. (2000). Coloniality of Power, Eurocentrism, and Latin America. Nepantla: Views from South, 1(3), 533-580.

Rutkowski, J. E., & Rutkowski, E. W. (2015). Expanding worldwide urban solid waste recycling: The Brazilian social technology in waste pickers inclusion. Waste Management & Research, 33(12), 1084-1093.

Stirling, A. (2008). ' "Opening Up" and "Closing Down": Power, Participation, and Pluralism in the Social Appraisal of Technology', Science, Technology & Human Values 33.2: 262–294, (17) (PDF) Grassroots innovations and democracy. Accessed on September 10th, 2023: https://www.researchgate.net/publication/315753103_Grassroots_innovations_and_democracy.

Thiollent, M. (2011). Metodologia da Pesquisa-Ação. (18th Ed.) São Paulo: Cortez.

Tuhiwai Smith, L. (2012). Decolonizing Methodologies: Research and Indigenous Peoples. Zed Books.

Vygotsky, L. S. (1978). Mind in Society: The Development of Higher Psychological Processes. Harvard University Press.

Yardley, S., Teunissen, P. W. & Dornan, T. (2012). Experiential learning: AMEE guide No. 63. Med Teach., 34: e102–e115.

Zavala, M. (2016). Decolonial methodologies in education. Encyclopedia of educational philosophy and theory, 1-6.

Extra contents

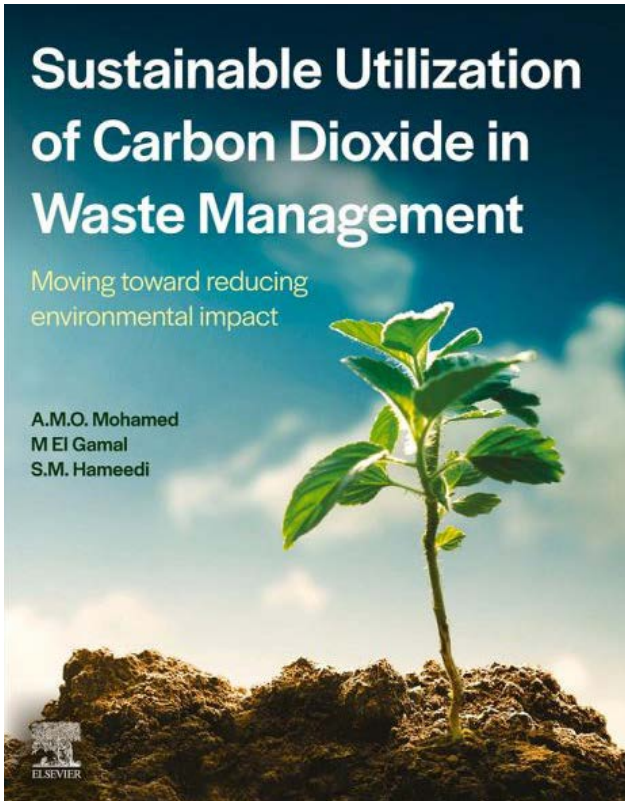
COLUMNS AND SPECIAL CONTENTS

This section comprises columns and special contents not subjected to peer-review

detritus | Multidisciplinary Journal for Circular Economy and Sustainable Management of Residues

CISA

BOOKS REVIEW



SUSTAINABLE UTILIZATION OF CARBON DIOXIDE IN WASTE MANAGEMENT

Edited by: A.-M. O. Mohamed, M. El Gamal, S. Hameedi and E.K. Paleologos

The book "Sustainable Utilization of Carbon Dioxide in Waste Management" illustrates several options for the sustainable use of carbon dioxide (CO_2) in the waste management sector. The authors highlight the main environmental impacts of waste generation and demonstrate the importance of applying carbon capture (CC) methods to improve the level of sustainability of waste management. They also provide the readers with the best available practices for CC, carbon storage (CS) and carbon utilization (CU) through the treatment of a wide range of waste types to improve the lifecycle benefits of waste treatments, with particular regard to the carbon footprint.

More specifically, the book is divided into 14 chapters. The first chapters introduce basic CC principles, with a critical view on their level of sustainability and the need for improvements, and present the methods to assess the benefits of CC following a Life Cycle Thinking approach. The second half of the book is a detailed survey on carbonation techniques that can be applied to a large variety of waste: from residues of industrial processes and air pollution control technologies to waste coming from extraction sites, construction and demolition activities and desalination processes.

Chapter 1 starts with an overview of carbon emissions worldwide by sector and the expected trend for the next future. The authors discuss the opportunities given by available markets for CC and CU, i.e. CO_2 reuse after sequestration, for instance in the beverage industry, in greenhouses, as a feedstock to produce value-added products, such as polymers, reprocessed aggregates, slags, ashes, chemicals, and synthetic fuels. The chapter also introduces basic principles related to the waste hierarchy, sustainable development, circular economy and end-of-waste concepts, showing the importance of defining appropriate end-of-waste criteria involving waste characterization, an assessment of technical, market, environmental and health impacts and the procedures for waste reprocessing. The authors present case studies on three waste streams to show the complexity behind the development of end-of-waste criteria: construction and demolition waste, industrial waste, and CC products. The end-of-waste status of the latter is particularly important to mitigate global warming and it depends on the related environmental impacts and the presence of an available end market.

Chapter 2 enters the details of carbon capture and storage (CCS) and CU processes. Both concepts require the separation of CO_2 from a waste gaseous stream originating from post-conversion (e.g., combustion), pre-conversion (e.g., syngas formation) or oxy-fuel combustion (which increase CO_2 concentration in the waste gas) processes. Despite the significant reduction in the global warming potential thanks to CC, the authors underline an increase in other environmental impacts (eutrophication, acidification, photochemical oxidant formation, human toxicity and ecotoxicity), stressing the need for cleaner technologies. In addition, the costs are related to the level of purity of the CO_2 emitted, which is the highest in fermentation processes and the lowest in oil refining. After separation, CO_2 is compressed, transported and injected into deep geologic formation and seabed or into oilfields for enhanced oil recovery (EOR). The chapter then presents the main applications of CU: carbonation/acidification of drinks and food, production of polymers, chemicals and fuels by chemical, biological and electrochemical conversion, and fixation in inorganic compounds, which is the main subject of the book. The authors then review examples of large-scale applications of CU projects worldwide and provide a list of

Managing editor:
Marco Schiavon
email: marco.schiavon.2@unipd.it

Detritus / Volume 26 - 2024 / pages I-IV
https://doi.org/10.31025/2611-4135/2024.18364

products with the largest estimated potential in terms of economic value in the European Union (EU), proteins from microalgae and synthetic fuels showing the highest values. Overall, CCS and CU are expected to contribute to 20–25% of the CO_2 emission reduction needed to comply with the 2050 targets of the International Energy Agency to halve energy-related CO_2 emissions. The chapter ends with an overview of the EU policies supporting CCS and CU, such as the Emission Trading System (EC/410/2018), the Renewable Energy (2018/2001/EU) and the Energy Efficiency (2012/27/EU) Directives.

Chapter 3 describes the basic principles of Life Cycle Thinking, with a focus on the necessary steps to perform a Life Cycle Assessment (LCA) of CO_2 utilization technologies and processes, in particular the aim and scope definition, the definition of boundaries, the inventory analysis, the Life Cycle Impact Analysis, the sensitivity analysis and the interpretation of the results. The authors point out the need for improvements in the LCA approach, specifically the need for a uniform LCA framework allowing the direct comparison between different technologies/processes and reducing the effect of the evaluator's choice.

In Chapter 4, the authors enter the technical details of waste carbonation, presenting carbonation reaction kinetics. More specifically, the chapter focuses on the factors that limit the reaction rates between an alkaline waste and CO_2, such as the diffusion of CO_2 and alkaline ions through the liquid film, diffusion through the boundary layer (product layer) and diffusive processes slowed down by changes in porosity.

Chapter 5 deals with mineral carbonation, i.e. the production of calcium- and magnesium-based carbonated as partial substitutes for Portland cement and aggregates. In particular, the accelerated carbonation (AC) process is described, which is characterized by low cost (due to the exothermic nature of the reactions involved), stability of the precipitated materials, high carbon fixation rates, ability to immobilize heavy metals, the pH neutralizing potential of the products and their possible use in the construction sector or in the chemical industry. Contrarily to natural carbonation, AC lasts from a few minutes to a few hours due to the higher concentration and purity of the CO_2 stream. The authors distinguish between direct and indirect AC, the latter involving the extraction of alkaline metals from the solid matrix. The chapter then describes the principles of mineral carbonation, showing the main chemical reactions involved, and the main parameters that influence the process: the type of surface activation (through grinding, heat/steam application, acidification, application of magnetic fields or sonication), the characteristics of the CO_2 stream, the reactor used, the reacting media (including process parameters like temperature, pH, liquid-to-solid ratio and pressure), and the product's nature. Finally, the main products and the several possible uses are described.

In Chapter 6, the authors discuss specific carbonation processes and related stages, with the available technologies ready for implementation from laboratory scale to industrial scale. In particular, the chapter focuses on multi-process aqueous processes, considered as more efficient than single-stage processes. Technologies for natural serpentine carbonation range from TRL3 to TRL7, while technologies for alkaline waste carbonation vary from TRL3 to TRL6. One of these processes, developed by some of the authors of the book for alkaline waste carbonation based on fluidized bed and CO_2 recirculation, is discussed with reference to case studies of potential implementation to process steel slags, to produce sewerage pipes from carbonated Ladle furnace slag and carbonated ground granulated blast furnace slag. The authors present the results of tests carried out in real underground sewerage systems and in saline and acidic environments.

The focus of Chapter 7 is on laboratory-scale methods, in particular fluidized-bed reactor, spouted-bed reactor, high-gravity rotating bed reactor and the use of ultrasound. The authors highlight that the fluidized-bed reactor is particularly advantageous compared to conventional methods because of the enhanced mass transfer and carbonation reactions, and the continuous detachment of the product layer from the reactive material bed. In the spouted-bed reactor, the inert particles enhance the gas-liquid interfacial area and mixing between the two phases. However, the best type of inert particles, the interaction with the gas stream, the degree of separation from carbonated materials and energy optimization strategies must be still investigated in detail. Similar benefits can be achieved with the high-gravity rotating bed reactor, but difficulties in modeling this process were pointed out. Ultrasound works by continuously removing the diffusion limiting layers and breaking up the particles through cavitation and enhanced turbulence. The main drawbacks are related to energy efficiency issues and to the reduced break-up of microparticles caused by cushioning effects related to high solid concentration. Some experimental methods to evaluate the CO_2 uptake are also reviewed.

The authors dedicate Chapter 8 to the carbonation of fly ashes. Different types of combustion fly ashes are reviewed: coal fly ashes, municipal solid waste incineration ashes and modern ashes, i.e. ashes produced with modern technologies such as oxy-fuel combustion. Direct (dry, semi-dry and aqueous) and indirect routes for carbonation are presented and their respective main fields of application: the construction industry and the production of valuable and high-purity precipitated calcium carbonates. Sequestration rates with these methods were reported to range between 50 and 100 g of CO_2 per kg of fly ash.

The sources and characteristics of different types of steel slags are presented at the beginning of Chapter 9. In general, steel and iron slags are depicted as excellent candidates for CO_2 sequestration because of their high amount of CaO. Slags are considered as attractive secondary materials especially for cement manufacturing, aggregate materials for concrete and asphalts. However, possible leaching of heavy metals and slag expansion due to free and unreacted CaO and MgO have slowed down their applications. Regarding the preferred carbonation methods, the authors suggest that dynamic systems (e.g., fluidized, rotating or ultrasonic beds) would increase the CO_2 uptake than static beds because of the increased mass transfer, breaking of the aggregated particles and the continuous detachment of the product layer.

Chapter 10 deals with the carbonation of calcium carbide residues, originated from the production process of acetylene, which is the raw material for polyvinyl chloride. The authors review the potential applications of calcium carbide residues and then focus on the applicable carbonation processes. Direct carbonation (especially the fluidized-bed process developed by two of the authors) and indirect carbonation to produce pure calcium carbonate are discussed. Finally, hydration, thermal pretreatment, material modification, and incorporation of inert materials are discussed as possible processes to apply for the production of effective CaO-based sorbents for CO_2 capture.

The carbonation of concrete cement waste, originating from hydrated or non-hydrated cement paste and particles from coarse sand aggregates, is the subject of Chapter 11. The authors focus on the cycle of absorption and release of CO_2 in the process of limestone calcination using concrete cement waste: the carbonation of hardened cement paste may be carried to uptake CO_2 and, meanwhile, produce calcite, which is the main ingredient in limestone production. The CO_2 released during limestone calcination can be recovered and supply again for the carbonation of cement waste. However, the authors stress the need for further studies on concrete production from cement waste, especially to improve the quality of the final products.

In Chapter 12, the authors present the possible strategies for the carbonation of mine tailing waste residues, namely the single-step direct aqueous carbonation and the two-stage carbonation. The chemistry of accelerated carbonation varies slightly depending on the dominant alkaline metal (Ca, Mg and Na). The authors then explain the carbonation processes for different residues (anorthosite, brucite, chrysotile and ophiolitic complexes). The carbonates and high-surface area silica can be used to produce cement and clinker. However, the processes involved are still not competitive on the market.

Chapter 13 provides interesting insights into possible ways to manage brine waste from desalination or the oil/gas industry. As a matter of fact, the discharge of brine waste into the environment has adverse impacts in terms of salinity and presence of heavy metals. Carbonation is applicable to brine waste too, allowing a two-fold opportunity: CO_2 sequestration and reduced impacts on water and soils. The authors present some available carbonation processes for brine waste: the Solvay process (aiming at the production of sodium bicarbonate and sodium carbonate from sodium chloride), methods involving alkanolamine liquefied absorbents or mixed metal oxides, and electrodialysis for absorption of CO_2 onto alkaline hydroxides to form bicarbonates and carbonates. Possible end products are cementitious construction materials and chemicals.

The last chapter (Chapter 14) deals with cement kiln dust and the applicable carbonation processes. Cement kiln dust composition is strongly related to the fuel used and the feeding material and is classified as hazardous waste with caustic properties. Cement kiln dust can undergo carbonation, whose reactions were modeled by the authors, who evaluated the effect of the many parameters involved. The carbonation degree and its efficiency also depend on the carbonation process: the authors discuss the use of fluidized-bed, ultrasonic, batch, column, rotating-tube and indirect processes, which may achieve > 70% carbonation efficiency.

Overall, the book provides detailed information on CCS methods and CU strategies for the simultaneous management of different waste types and the mitigation of carbon emissions from human activities. The book is directed to a specialized audience, i.e. environmental and sustainability scientists, engineers and academics in the field. Though mainly focused on mineral carbonation, the book provides insights into the application of other CCS and CU as well as a comprehensive overview of how these techniques fit in the general framework of waste management and the circular economy.

Marco Schiavon
University of Padova, Department of Agronomy, Food, Natural Resources, Animals and Environment (DAFNAE)
email: marco.schiavon.2@unipd.it

ABOUT THE EDITORS

Abdel-Mohsen O. Mohamed

Prof. Dr. Eng. Abdel-Mohsen O. Mohamed (known as A.M.O. Mohamed) earned his PhD from McGill University, Canada, where he was later employed as the Associate Director of the Geotechnical Research Centre and Lecturer at the Department of Civil Engineering and Applied Mechanics. He has 13 patents in areas of sustainable use of elemental sulfur and alkaline solid wastes, production of sulfur cement and concrete, carbon sequestration and utilization for treatment of solid wastes, and stabilization of sand dunes. He has authored and coauthored 20 scientific books and has published over 290 papers in refereed journals and international conference proceedings. He has been the recipient of several university and nationwide research accolades. He is the General Managing Director of EX Scientific Consultants, Abu Dhabi, UAE, Senior Advisor, Uberbinder, Inc., Seattle, Washington, USA, and an Editorial Board Advisor for number of Scientific Journals.

Maisa M. El-Gamal

Dr. Maisa M. El Gamal is currently employed by Zayed University as an Assistant Professor in the Environmental Science Department, College of Natural and Health Sciences. She holds a Doctorate degree in Chemical Science from Ta33nta University and a Master in Material Science from Alexandria University. She has worked for 20 years as a researcher with long experience in different areas like CO_2 capture and storage, soil stability, sulfur concrete production and solid waste management. More recently, her research activities are focused on the development of novel CO_2 adsorbent materials. Her record spans more than 100 publications in high impact journals, international and local conferences, patents, books, and book chapters. She has dedicated the working in these research fields beside her job as a teacher of Chemical and Environmental science and as supervisor to the students in their senior projects at Zayed University.

Suhaib Hameedi

Suhaib Hameedi gained his BSc. in chemical engineering from Mutah University-Jordan in 2005. His graduation training was in Jordanian phosphate mines company. He joined industries through chemicals manufacturing application in Jordan until 2010, and water treatment application until 2013 in United Arab Emirates. He earned his MSc. degree in chemical engineering from the United Arab Emirates University in 2016 with a thesis about CO_2 capture by steel-making residues. During his masters, he had duties as research assistant in CO_2 capture using industrial wastes. In addition, he was a teaching assistant to thermodynamics for a engineering students course. He joined Zayed University (ZU) in 2016 as a Researcher in environmental studies, mainly carbonation of industrial wastes. He participated in local and international conferences through papers, posters and oral presentation. Recently he is a member of the published patent of a new apparatus for carbon sequestration submitted by Prof. AMO Mohamed.

Book Info:

Editors: Abdel-Mohsen O. Mohamed, Maisa M. El-Gamal, Suhaib Hameedi
Imprint: Elsevier
Year of publication: 2022
Page Count: 606
Paperback ISBN: 9780128234181

detritus | Multidisciplinary Journal for Circular Economy and Sustainable Management of Residues

CISA

DETRITUS & ART / A personal point of view on Environment and Art

by Rainer Stegmann

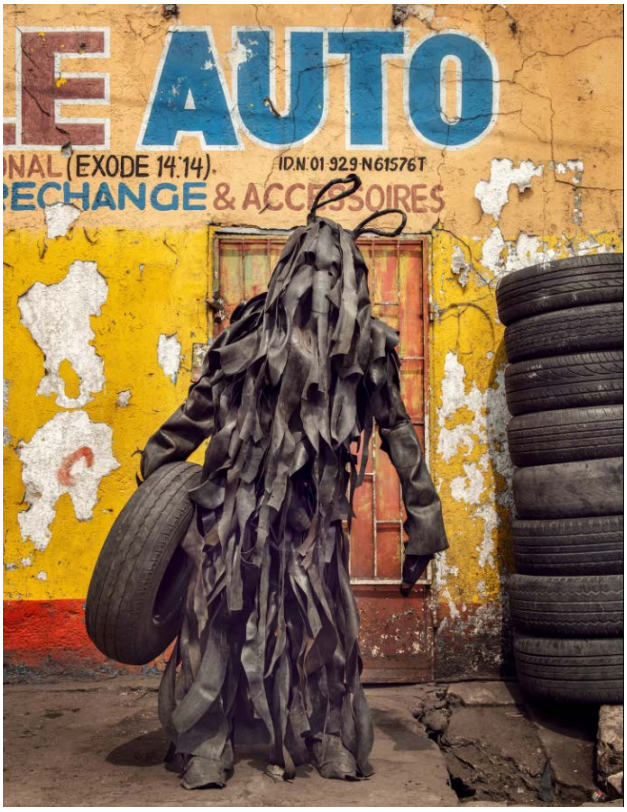
In this edition I want to introduce two examples of contemporary art from Kinshasa, Democratic Republic of Kongo (DRK), Africa. Young artists direct the attention about the severe waste problems in their country to the public by creating human waste sculptures. Kinshasa struggles with their own produced waste but also imported used goods from Western Countries that are already or become waste as e.g. used textiles and also flip flop shoes, and used cars.

The artist and social activist Eddy Ekete (*1978) from Kinshasa, DRK, founded in 2015 the artist collective "Ndaku Ya, La Vie Est Belle"; the name was intentionally chosen as a provocation. Ekete creates living installations on persons in their environment in Kinshasa highlighting specific waste problems that can be watched in the real world and on videos (www.eddyeketeblog.wordpress.com).

Stephan Gladieu (*1969) is a self-taught famous photographer who lives and works in Paris documenting the conflicts and social issues that agitate the world. "I chose to shoot their portraits in the streets of Kinshasa, with settings and characters that form a dialogue", said Stephan Gladieu (https://www.festivalphotolagacilly.com/en/photographes/stephan-gladieu). The two examples of the photographers work I present here are from his photo collection "Homo Detritus". The expressive Flip- Flop Man photo is in my view self - explaining, showing a person covered with Flip-Flop shoes as a symbol of an abundance society. The photo emits a special esthetics, showing the hidden beauty of a sad situation. Using these wasted shoes makes the dilemma of rich countries obvious that divert their used products to poorer countries. It is an outcry against the dramatic volumes of wastes present in the streets of Kinshasa and worldwide, an outcry against affluent societies in parts of the world and an outcry against the inaction of administrations to solve this problem.

Another piece of art from the "Homo Detritus" collection is the photo of a person that is covered with pieces of rubber tires carrying a used tire. He poses himself before a yellow wall which again provides this subtle esthetics.

Flip-Flop Man by Patrick Kitete from the Artist Collective "La vie est Belle" (photo by Stephan Gladieu, courtesy of the artist).



Tire Man by artist Savant Noir, (photo by Stephan Gladieu, from the photo collection "Homo Detritus", courtesy of the artist).

Managing editor:
Rainer Stegmann
email: stegmann@tuhh.de

Detritus / Volume 26 - 2024 / pages V-VI
https://doi.org/10.31025/2611-4135/2024.18365

This art photo shall make people aware of the inadequately managed large quantities of old tires; it protests also against the immense exploration of natural resources in the DRK. Beside several valuable metals as gold, copper, coltan and cobalt also huge amounts of extracted latex is used to produce rubber tires.

In my view, these photos find the right balance between the esthetical art work and the desired statement. This combination makes the photos very attractive to spread the message as a request for reducing/avoiding "waste" import and a more effective waste management. These art photos are relevant also for other countries in a similar situation but also for the rich export states.

In the coming issue I present to you a Chinese picture from the Museum in Zhangjiajie-Yongding with a very special technique I have not seen before.

detritus | Multidisciplinary Journal for Circular Economy and Sustainable Management of Residues

CISA

CONTENTS

VOLUME 26 / March 2024

ISSN 2611-4135 / ISBN 9788862650397