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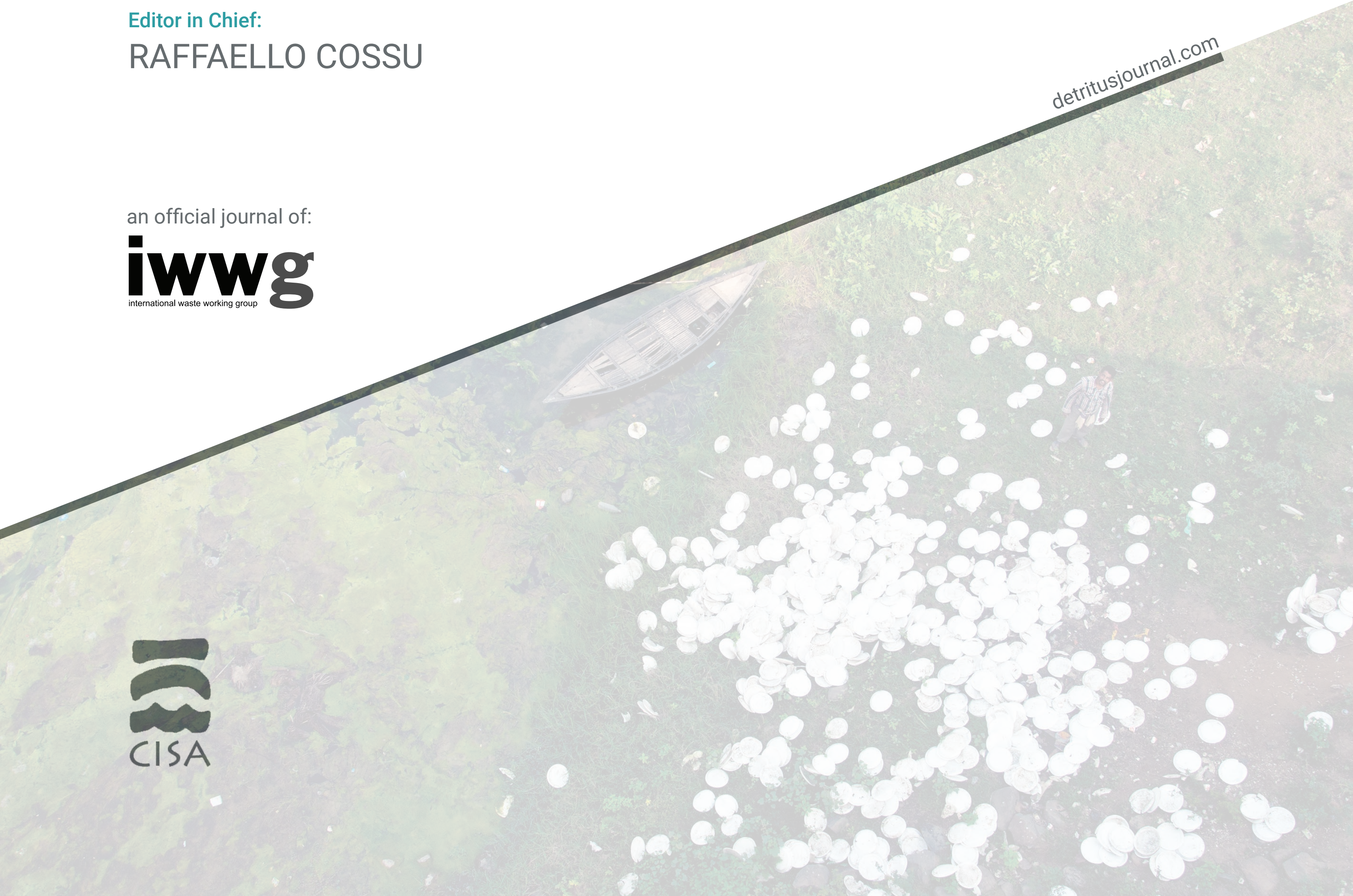

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Detritus - Multidisciplinary Journal for Waste Resources and Residues - is aimed at extending the “waste” concept by opening up the field to other waste-related disciplines (e.g. earth science, applied microbiology, environmental science, architecture, art, law, etc.) welcoming strategic, review and opinion papers. **Detritus is indexed in Emerging Sources Citation Index (ESCI) Web of Science, Scopus, Elsevier, DOAJ Directory of Open Access Journals 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.

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Editorial

CIRCULAR ECONOMY, METHANE EMISSIONS, WASTE MANAGEMENT, AND THE COURTS' ROLE

Normally defined as a new and sustainable model of production and consumption, circular economy involves sharing, leasing, reusing, repairing, refurbishing and recycling existing materials and products as long as possible. The obvious aim is to extend the life cycle of products.

Under the European Green Deal and in line with a proposed new industrial strategy, in March 2020 the European Commission presented the new circular economy action plan (EU Circular Economy Action Plan, 2020). It is about product design, reducing waste and empowering consumers (e.g., via the introduction of a right to repair).

In February 2021 the Parliament adopted a resolution on the new circular economy action plan, demanding additional measures to achieve a carbon-neutral, environmentally sustainable, toxic-free and fully circular economy by 2050, including tighter recycling rules and binding targets for materials use and consumption by 2030.

New EU Parliament strategy to reduce methane emissions

While circular economy is mainly based on reducing waste to a minimum, this is not the end of the story.

All sustainable strategies are also based on the reduction of greenhouse gases' emissions, or on carbon sequestration, to directly tackle climate change.

In this context, concern is growing on methane emissions, as their permanence in the atmosphere is long.

Landfills and waste management in general are one of the potential sources of such emissions.

Consequently, on 21 October 2021 the EU Parliament approved a new strategy to reduce methane emissions (European Parliament, 2021). This strategy also contains rules related to waste.

In general, the strategy is based on the fact that methane is a powerful greenhouse gas, 80 times more potent than carbon dioxide (CO2) over a 20-year period, making it the second most important greenhouse gas, as well as a precursor pollutant to ground-level ozone (O3) contributing to about a quarter of the global warming experienced today.

Thus, all scenarios aimed at meeting the 1,5°C target defined by the Intergovernmental Panel on Climate Change (IPCC) involve deep reductions of methane emissions. According to the UN Environment Programme (UNEP), reducing human-caused methane emissions by as much as 45 % will avoid nearly 0,3°C of global warming by the 2040s and complement all long-term climate change mitigation efforts mainly based on CO_2 emissions reduction. The European Green Deal (EU Green Deal, 2020) considers methane as the sector where the most cost-effective emissions savings can be achieved, while producing the quickest cooling effect.

Methane emissions and waste management

Agriculture still represents the largest share of anthropogenic methane emission sources in the EU. So much so that the use of agricultural waste and residues for biogas production is considered to be a driver for the circular economy, provided that the cascading use principle is adhered to and the appropriate sustainability criteria are applied.

Fugitive emissions from leaking equipment, infrastructure or closed and abandoned sites, as well as emissions from venting and the incomplete combustion of methane, represent the majority of methane emissions in the energy sector, by far the second most important methane emission source.

However, landfills of municipal solid waste have also been identified as a further significant source of methane, even if their role is much lower than that of agriculture and energy (Cossu et al., 2020).

Consequently, the EU Parliament new strategy on methane calls on the Commission to integrate a strong focus on methane emissions in the 2024 review of the Landfill Directive and the upcoming revision of the Industrial Emissions Directive. The strategy goes on by highlighting the need for measures to require landfill sites to use the bio-methane they produce until its energy content drops below a useful value and, once it is no longer viable to use the bio-methane produced at a landfill site, for the use of bio-oxidation and other technologies in hot spots in order to reduce the remaining methane emissions (Grossule and Stegmann, 2020).

After generally emphasizing that closure and after-care procedures for landfill cells are key to reducing leakages, taking into account the entire life cycle of landfill sites, the EU Parliament strategy generically affirms that "landfill disposal, which sits at the bottom of the waste hierarchy, is the most polluting way to manage waste both in terms of greenhouse gas emissions and other pollutants to air, soil and water".

Such an assertion seems to elicit – as Cossu (2020) puts it – "an idealistic order which is scarcely reliable to the real world" and to not take into account the virtuous role that, under strict conditions, sustainable landfills can

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play “in closing the material loop” as well as in working as a “carbon sink”.

Parliaments’ and Courts’ respective roles in tackling climate change

The regulation of greenhouse gas emissions is continuously adding new targets for the Member States to reach. Goals to be achieved in terms of maximum temperature grow, minimum percentage of waste recycling, maximum (and very low) percentage of waste disposal in landfills.

This poses a crucial question to modern democracies, which is easy to ask, but difficult to answer. What happens when the States do not meet the required standards? What happens, in other words, if one or several Governments do not implement environmental policies which fully reach the required goals?

The enforcement tools provided for by international law are weak. At their very best, both the Paris Agreement and other environmental Treaties only make it possible either to implement further consultations with the non-compliant State or to ask some International Court to apply an economic fine to that State.

In the context of the traditional political doctrine of the “separation of powers” - which assumes the division of the legislative, executive, and judicial functions of government among separate and independent bodies – no other role can be played by the Courts.

However, such doctrine is being slowly but continuously challenged. In the Netherlands, in the United States of America, in Germany and in several other countries, Constitutional and Administrative Courts have decided to change the pace of Courts intervention with respect to political law-making (Kahl and Weller , 2021).

In different ways, all these decisions imposed to a Government to change its politics in the direction of more effectively tackling climate change, also by improving waste management.

This trend – known as climate litigation, or environmental litigation – tries to “boldly go where no one has gone before” (as the famous StarTrek captain said). But it poses serious questions to scholars of both law and environmental management.

To what extent is a given environmental risk so serious and imminent as to require to the Courts to force the traditional separation of powers? And, coming again to landfilling, to what extent can Courts assess the environmental equilibrium of Final Sorage Quality of a given landfill, if and when they are asked to enforce the theoretical targets established by EU law for landfills closure rates?

These questions call for further research, as well as for joint efforts by legal, technical and environmental experts, in order to establish consensus on the relationship between environmental policy-making and the Courts’ role.

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TRANSITION TOWARDS A CIRCULAR ECONOMY: THE ROLE OF UNIVERSITY ASSETS IN THE IMPLEMENTATION OF A NEW MODEL

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ABSTRACT

Public awareness and relevant consumer behaviors are crucial in accelerating the transition to a circular economy (CE) model. This paper focused on exploring university activities for changing awareness and behaviors according to the principles of its new circular model to foster sustainable development. In this paper, a comprehensive literature review provides a holistic perspective on university CE-related activities in the implementation of the CE. The review revealed that the construction of a theoretical framework in universities with asset-based development is conducive to promoting the CE model through transformative learning. In light of recent academic insights into CE education, a theoretical framework for CE-related university activities was developed based on attributes of CE-related university assets, such as non-profit status, technology innovation, education, propagation, and efficient use of resources. We also introduce into scientific use the term CE-related university assets and provide a classification of these CE-related assets. The present findings contribute to a deeper understanding of universities' CE-related resources and assets to improve public awareness and behaviors, as well as to train and inspire the leaders (including engineers, managers, designers, etc.) of tomorrow, required for further implementing the CE model.

1. INTRODUCTION

Today, the circular economy (CE) model is increasingly recognized in many countries throughout the world as a sustainable alternative to the traditional linear model because of the CE model's contributions in sustainability with fewer resources consumed and lower environmental pollution (Zhang et al., 2019). Interestingly, the implementation of CE practices can support the achievements of several sustainable development goals (Schroeder et al., 2019). Since the 1970s, Germany (Shen, 2016) and other members of the European Union (Wysokińska, 2016), Japan (Liu & Du, 2019), the United States (Hu & Ji, 2017), Britain (Qiao & Wang, 2013) and many other countries have carried out practical explorations of the CE. After it was officially introduced in China in the late 1990s, the concept was generally accepted by all sectors of society and elevated to be a national development strategy (Ma, 2016). It is evident that although the CE has been implemented according to the federal law for years and provides numerous benefits, there is still a huge gap between theoretical research and practical processes (Shevchenko & Kronenberg, 2020; Zhai, 2017). To promote the implementation of the CE, many researchers have examined the drivers of and barriers to the CE, which could accelerate or derail the move to this new model (De Jesus & Mendonça, 2017). Generally, the government, enterprises, and the public are regarded as the three primary stakeholders in promoting the CE model (Dong et al., 2016). However, during the past decade, the implementation of the CE in China has been driven mainly by top-down promotion by the government. The Chinese government has not been satisfied with the implementation effect of CE policies because of the insufficient participation of stakeholders other than the government (Liu, 2014). In fact, the stakeholders that promote CE performance must be diversified and work together to prevent the implementation of CE from coming to a standstill (Gaidabrus et al., 2014; Telizhenko et al., 2016). Bottom-up promotion by the public has recently attracted researchers' attention; the main stakeholders are enterprise operators that pursue economic benefits and citizens who pursue ecological benefits (Zhu, 2017). Nevertheless, the public generally lacks CE awareness and behaviors (Guo et al., 2016; Shevchenko et al., 2019), while enterprise operators have insufficient CE-related knowledge and are unwilling to pay the high costs of implementation of the CE (Liu, 2015).

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Therefore, it is crucial to promote CE awareness and behavior by the public through effective CE education in transitioning to a CE model.

Higher education institutions have a particular social responsibility for the development of society, particularly in the proliferation of public awareness of sustainability, and in the training of future workforce in this topic (Amaral et al., 2015; Findler et al., 2019). The functions of higher education institutions, namely, the trinity of talent cultivation, scientific research, and social service, also determine that universities are one of the effective driving forces for promoting the bottom-up transition toward the CE model (Qu & Shevchenko, 2019). Moreover, the Circular Economy Development Strategy and Action Plan (PRC SC, 2013) and the Circular Economy Promotion Plan 2015 (PRC NDRC, 2015) explicitly stipulated the position and responsibility of higher education institutions in the implementation of the CE. However, the theoretical foundation of the development of higher education institutions in light of all possible circular activities and relevant assets is limited. To bridge this gap, this paper aims to carry out a systematic analysis of Chinese universities' activities contributing to the CE to propose a theoretical framework of university CE-related activities, so as to inspire commendable practices from one university to another as well as find a breakthrough to accelerate the CE transition in China.

In this paper, an extensive review of CE-related activities at the university level was conducted and has led to the need to construct a theoretical framework of CE activities with assets as the core for universities in the process of implementing the CE. To ensure that the review was comprehensive, articles published in the top-tier periodicals and peer-reviewed journals over the last 20 years in English and Chinese were selected. The literature was retrieved via Scopus, Web of Science, Google Scholar, and CNKI search engines based on the following keywords: "circular economy", "implementation model", "circular economy education", "circular economy practice", "stakeholder", "driving force", "barriers and challenge", "environmental education", "public awareness", "circular behavior" and "university assets". In addition, other papers and monographs were discovered from the references of selected articles based on relevance to the topic and popularity in terms of citations. A qualitative research method, informed by a critical literature review adopted from Ranjbari et al. (2021), is employed in this research to develop a theoretical framework for CE-related university activities based on attributes of university assets, such as non-profit status, technology innovation, education, propagation, and efficient use of resources.

2. LITERATURE REVIEW

2.1 Transformative learning theory and university CE activities

Studies of CE activities in colleges and universities include benefit analysis of the introduction of recyclable materials and recycling systems on campus (Barros et al., 2020; Tan & Li, 2016), the design of sustainable resource management schemes (Salguero-Puerta et al., 2019; Williams & Powell, 2019) and other applications of CE principles in campus development (Hopff et al., 2019; Mendoza et al., 2019). Among them, CE education in universities is expected and has been considered one of the most pivotal factors to realize the transition toward the CE model (Bugallo-Rodriguez & Vega-Marcote, 2020). CE specialty education and general education in universities have been a broad concern for researchers, involving the establishment of talent training mode (Cui et al., 2018; Weissbrodt et al., 2020), construction and evaluation of the CE curriculum system (Kirchherr & Piscicelli, 2019; Nunes et al., 2018; Rodriguez-Chueca et al., 2020), and CE education in specific fields (Kopnina, 2019; Rokicki et al., 2020). Moreover, China has incorporated the construction of a CE major and the cultivation of CE professional talent in universities in the national overall development strategy in recent years, which have led to some achievements (Qu et al., 2020).

However, university CE activities are fragmented and disconnected from each other and lack a system that can integrate them for an augmented effect. Moreover, there is no necessary correlation between higher education performance and sustainable behavior in society (Orr, 2002). Therefore, if universities want to improve the efficiency of the implementation of the CE, it is necessary to cultivate and pursue CE values and mindset that can completely change the inherent thinking and operation patterns of the linear economy. To this end, transformative learning is a credible alternative to solving this problem, because the effect in the field of adult education has been proven (Sokol & Shaughnessy, 2018). Furthermore, the significance of transformative learning in Education for Sustainable Development (ESD) has also been confirmed (Burns, 2018). Transformative learning implies profound structural changes in the basic premises of thought, emotion and behavior, and such a change in consciousness would dramatically and permanently alter self-cognition and our way of being in the world (Sterling, 2010-2011). In other words, different from the traditional manner of knowledge imparting and idea instilling, the CE concept and values can be internalized in the mind and manifested in practice through transformative learning.

To better understand the connotation of transformative learning, Bateson's hierarchy theory of learning should be reviewed. According to Bateson, learning should be separated into three levels, embracing learning, meta-learning, and epistemic learning (Blake et al., 2013). At present, the formal education implemented by higher education institutions generally advocates the first level of learning, which aims to improve intelligence by imparting knowledge through transmissive pedagogy (O'Neil, 2018). Meta-learning refers to the critical assessment and inspection process of the connotative ideas behind the learning content, which could cause changes in the beliefs and values of the subjective world. Epistemic learning is the process of thoroughly reconstructing the paradigm of learners, which will bring changes in people's worldview and the way they get along in the world. The three learning levels range from low to high, where the higher-level learning experience affects the mindset and action of lower-level learning; see Figure 1. The first level of learning is far from sufficient

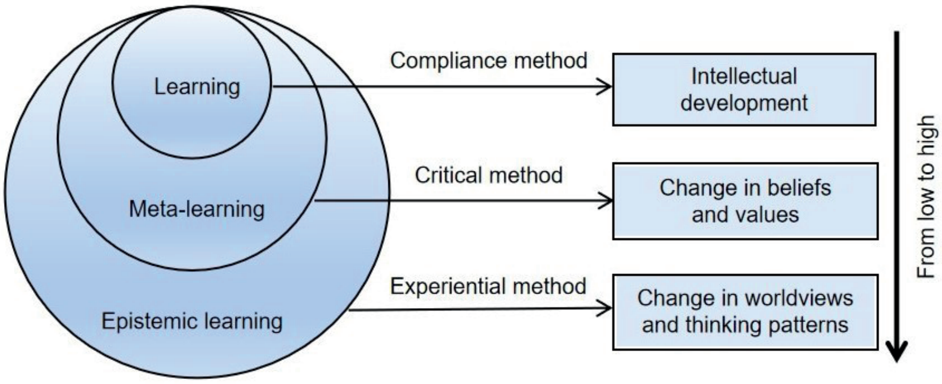

FIGURE 1: Hierarchy of learning and the transformation of different levels.

to establish CE values and patterns for improving the performance of CE education in universities. Higher levels of transformative learning and education are needed to improve the quality of CE education in universities, which not only could help learners acquire knowledge but also make them internalize CE values in their worldview and epistemology to stimulate the natural occurrence of pro-circular behaviors. With the combination of theoretical learning and practical experience, constructing a systematic CE theoretical framework in universities is a significant approach to realize transformative learning and education, which could integrate various isolated CE activities, thus enabling university administrators and students to change their epistemological presupposition and behavioral patterns to make the universities' effect truly prominent in promoting the implementation of the CE.

2.2 Development of university ESD and CE theoretical framework

Since the concept of sustainable development was first put forward in 1987, the international community has explored how to make education a supporting factor in sustainable development. Along with the continuous promotion of a series of activities, such as Agenda 21 (SDGKP, 1992), the United Nations Decade of Education for Sustainable Development (2005-2014) (UNESCO, 2003), the Global Action Programme on Education for Sustainable Development (2015-2019) (UNESCO, 2014) and the Education 2030 Framework for Action (UNESCO, 2015), ESD in universities has gradually formed systematic implementation and evaluation models. The most influential ones are the College Sustainability Report Card (CSRC) (ASEI, 2011) and the UI GreenMetric World University Rankings (UIGWUR) (UI, 2019), both of which concentrate on ranking or grading universities that strive to contribute to sustainability by evaluating their contributions to sustainable development to encourage universities' efforts to achieve the United Nations' Sustainable Development Goals (SDGs). The CSRC published by the American Sustainable Endowments Institute aims to grade the sustainability profiles of 322 colleges and universities in the United States and eight Canadian provinces in accordance with nine classification indicators. The UIGWUR, launched by Universitas Indonesia in 2010, has been widely recognized as the most authoritative assessment of sustainability efforts for universities all around the world. This tool mainly conducts an online survey and ranks the 912 participating universities in terms of their efforts at sustainability and policies through 6 classified indicators. The indicator categories of evaluation are shown in Figure 2.

Moving toward a CE model is one of the crucial approaches for delivering the SDGs (Schroeder et al., 2019). Therefore, a university CE theoretical framework should be established within the category of university sustainable development strategy. The analysis of the evaluation indicators above reveals that these sustainability implementation and evaluation systems contain many CE ideas and activities, which are a significant theoretical basis for forming a specialized CE theoretical framework for universities. The indicators and content of these systems that do not match the CE theoretical framework precisely reflect the disparity between them. In essence, the biggest disparity is mainly the difference between the concepts of sustainable development and CE. Sustainable development is a scientific development path that concerns the three-dimensional harmonious coexistence of economy, society and ecological environment. Therefore, the intentions of ESD are to promote the realization of the 17 SDGs by exerting the function of education in three levels below. The first level is to make the transition to a sustainable economic growth model, such as decent work and economic growth (SDG 8). The other is to foster the harmonious development and progress of society, such as no poverty (SDG 1) and zero hunger (SDG 2). The third level is to preserve and recover the ecological environment, such as climate action (SDG 13) and life under water (SDG 14).

Compared with the grandiose concept of sustainable development, the concept of CE is relatively concrete and realistic, which is viewed as an operationalization of sustainable development (Murray et al., 2017; Saidani et al., 2017). To the best of our knowledge, CE is a new economic system that replaces the "take-make-waste" linear model with the "cradle to cradle" concept in the whole life cycle of materials (Shevchenko et al., 2021) by reducing, alternatively reusing and recycling (3Rs) the resources and assets in the process of production and consumption (Ghisellini et al., 2016), aiming to decouple economic growth from finite resource consumption and environmental degrada-

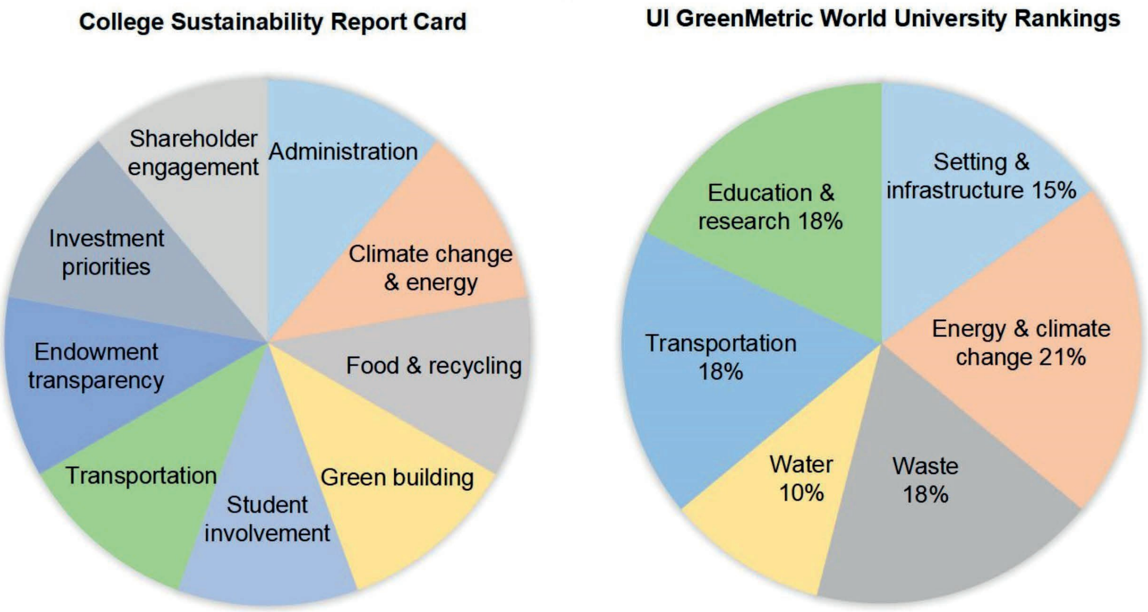

FIGURE 2: Indicator categories of the College Sustainability Report Card and the UI GreenMetric World University Rankings.

tion by reducing waste and maximizing resource utilization (EMF, 2021). Thereinto, the 3Rs are the dominant principles among the CE principle ranged from 3Rs to 10Rs in the previous literature (Reike et al., 2018; Saidani et al., 2019), from which three cyclic processes that run through the CE framework could be extracted (Morseletto, 2020). The first is the service cycle based on the Reduce principle. That is, by investing in a CE-oriented human capital support system, the top-level design and value reconstruction of CE service could be realized so as to reduce or even avoid the use of unnecessary resources to cut down the occurrence of new waste, for example, the CE training for educators, the Empty Plate Campaign launched in the campus canteens and the Plastic Limit Campaign initiated among student consumers. The second is the material cycle based on the Reuse principle. The material capital could be allocated efficiently to realize the most reasonable utilization of all materials through the transfer or sharing of the ownership or right to use of the resources, such as integrating idle bicycles to set up the shared cycling system on campus, transferring the ownership of idle office furniture and providing rental services for unused spaces such as classrooms during holidays. The third process is waste recycling based on Recycle principle. The valuable materials in the waste could be recycled and remanufactured to give new life to the materials to improve the utilization efficiency, such as establishing the domestic garbage sorting system and cartoon waste recovery system. In other words, the CE framework should focus on the goals of improving the utilization efficiency of resources and assets and reducing waste through the input of human capital and the diversified allocation of physical capital. In general, the university CE theoretical framework should be based on the overall layout of sustainable development for the university, aiming at ensuring the long-term implementation of the SDGs (Schroeder et al., 2019) by considering the most reasonable use of resources and environmental sustainability.

Furthermore, there is little participation in the UIGWUR by Chinese universities because the establishments of sustainable university are still in the initial stage in China. Many Chinese universities currently have no dedicated department responsible for implementing ESD or the CE to coordinate and organize these actions. Therefore, Chinese universities need to combine with their own characteristics to construct a systematic CE theoretical framework, rather than passively wait for all conditions to be mature before putting it into action. In this paper, the CE theoretical framework we propose based on CE-related university assets conforms to the realistic setting and practical convenience in China and could stimulate multiple subjects to make subjective initiatives, which is conducive to promoting the process of constructing sustainable universities and the realization of SDGs in universities.

3. RESULTS

3.1 CE-related university assets: definition and attributes

To better describe the CE theoretical framework for universities, we provide a definition of the university assets by considering the discourse on the CE (Kirchherr et al., 2017; Rossi et al., 2020) and the concepts of assets (Zhang et al., 2020; Ma, 2020). We define CE-related university assets as all types of resources that formed during the course of the university's development, owned or actually controlled by the university, and are expected to facilitate the transition to a CE model in the use process. CE-related university assets are the basis for universities to implement various CE activities, and an important indicator for measuring and evaluating a university's CE performance. Specifically, this novel concept contains four basic elements. The first is that the ownership subject of the CE-related university assets is the university. The second is that the forms of the assets are diverse. Examples include tangible assets, intangible assets, and fixed assets. The third is that the use process of the assets should follow the 3Rs principles of the CE. The fourth is the orientation of the assets should include universal CE policy goals.

Compared with other university assets, we argue that there are unique characteristics exclusive to CE-related university assets, including non-profit status, technological innovation, education, propagation and efficient use of resources. All of these attributes are significant factors for achieving the goals of a CE, see Figure 3.

- Non-profit attribute. It is stipulated that no organization or individual may establish educational institutions for profit in China (PRC MOE, 1998). Different from enterprises and other entities pursuing the goal of profit maximization, universities mainly focus on social benefits and public services as their ultimate goal. Therefore, CE-related university assets are non-profit.
- Technology innovation attribute. As one of the main execution subjects of research and development (R&D) activities in China, universities have a significant number of research teams, experts, scholars, and postgraduate students, who promote the vigorous development of scientific research assets in universities (Yin & Shen, 2005). It is evident that universities are the dominant contributors to the national scientific and technological output and achievements.
- Education attribute. Universities are significant bases for cultivating talent, which have abundant educational assets such as lectures and other teaching resources. These tangible and intangible educational assets could cultivate and transport a significant amount of talent for the society, and bring in a large number of practitioners with CE values and professional CE talent for various sectors of society. Also, CE practice in universities has an implicit education effect on students.
- Propagation attribute. Higher education institutions have great social influence in spreading culture and values, and their propagation activities for the values and value judgment could directly affect the thoughts, attitudes and behaviors of members of society (Zhao & Zhang, 2012). Universities can disseminate pro-circular values to society through lectures, teaching activities, students' social practice and volunteer service activities, and graduate employment in various industries.
- Efficient use of resources attribute. The essence of the CE model is to improve the efficient use of resources to achieve the goal of coordinated development of environmental protection and economic development. CE-related university assets are oriented by efficient use of resources; for example, textbook recycling and a paperless office system could improve the rate of resource utilization and reduce resource waste.

3.2 Classifications of CE-related university assets

To further clarify the extension and the specific orientation of CE-related university assets, we establish a multi-dimension classification system according to different features. This system is beneficial for decision makers to have a better understanding of the various categories and usage rules of CE-related assets, so as to conduct top-level scientific design and better propel the CE practice on campus. It could also help the participants of CE activities to cotton on the range of CE-related assets from multiple perspectives

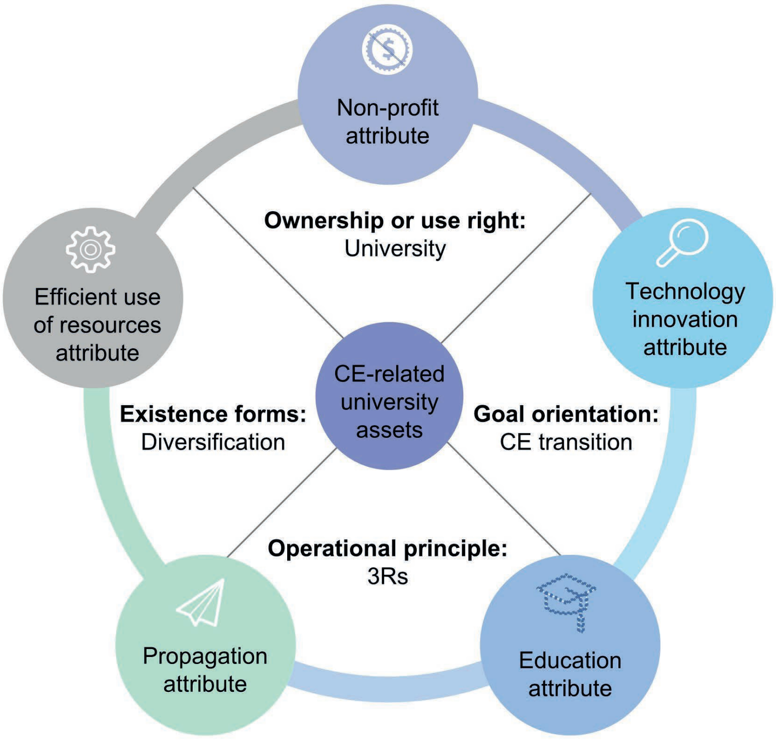

FIGURE 3: The elements of CE-related university assets.

TABLE 1: The classification of CE-related university assets.

Classification feature	Types of CE-related university assets
By application	1. Scientific research CE-related assets 2. Education CE-related assets 3. Operations CE-related assets
By morphology	1. Tangible CE-related assets 2. Intangible CE-related assets
By formation method	1. Innate CE-related assets 2. Developed CE-related assets
By cost level in the implementation of the CE	1. High-cost CE-related assets 2. Low-cost CE-related assets
By method of participating in the CE	1. Direct CE-related assets 2. Indirect CE-related assets

so that they could be able to clarify their responsibilities and striving direction in CE implementation. We argue that CE-related university assets can be classified into different types based on different standards; see Table 1.

First, according to the application, we propose to classify CE-related university assets into scientific research, education, and operations CE-related assets. Scientific research CE-related assets refer to scientific and technological support that can provide green and innovative technologies for the implementation of the CE through research and the integration of production, education and research. Education CE-related assets are educational resources that can cultivate CE professional talent for the national CE strategy, as well as improve CE awareness and knowledge of college students and the public. Operations CE-related assets are the physical campus resources that can be explored in CE practice that are managed by universities' operations departments, for instance, the development of shared cycling systems on a university campus. A large number of idle bicycles due to different reasons, such as abandoned by graduates, could be regularized and conducted with scientific management by the university logistics department to establish a free shared cycling system on campus. This system that reflects the attributes of CE-related assets could not only avoid the consumption of new bicycles to reduce resource waste but also realize the refurbishment and reuse of idle bicycles to improve the efficiency of resource utilization, see Figure 4.

In addition, we propose that CE-related university assets should be classified into innate and developed CE-related assets in line with different methods of formation. Developed CE-related assets must be created, developed or transformed artificially in a later use stage to meet the needs of the CE transition, such as research and creation of green materials and green products, and exploitation and construction of the CE curriculum. Different from developed CE-related assets, innate CE-related assets are assets that are pro-circular in the early stage of introduction or purchase, whose nature does not need to be acquired through post-processing and creation, such as green office supplies and textbooks and learning materials. Specifically, books and learning materials have distinct characteristics that include easy to preserve, high durability, easy to identify (unique ISBN code), so the second-hand book trade is always regarded as a typical representative of CE practice. Universities could apply the technical means to establish a free internet second-hand book trading platform for teachers and students with the adoption of a more flexible C2B2C (Customer to Business to Customer) model, so as to realize the reuse of books to improve the utilization efficiency. Meanwhile, CE information and ideas could be spread through this learning material recycling system to attract more users to participate in the recycling activities, see Figure 5.

Based on the morphology, we suggest dividing CE-related university assets into tangible and intangible CE-related assets; that is, the former has physical forms, while the latter is invisible. Intangible CE-related assets are unique non-physical resources, which can be used for personnel training, scientific research and external exchanges, including technological knowledge assets, human resources assets, institutional assets, reputation assets and other types.

Furthermore, we argue that CE-related university assets should be divided into high- and low-cost CE-related assets based on the costs of the CE-related assets involved in promoting the transition to the CE model. High-cost CE-related assets require universities to spend a certain amount of time and money or effort when developing this type of asset, for example, the construction of a bicycle sharing system and a reclaimed water recycling system. Low-cost CE-related assets do not cost too much time, money or effort, or are too inconvenient or even provide good benefits, such as the development of general CE education or recycling of learning materials.

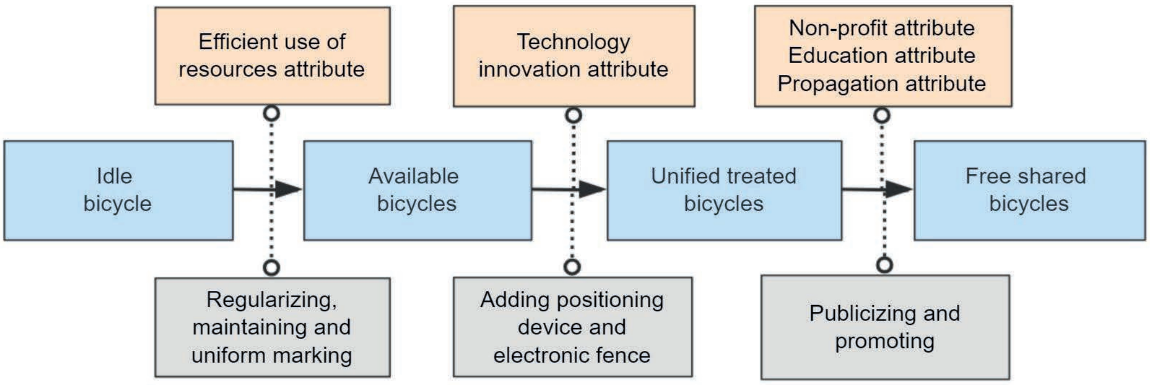

FIGURE 4: Flow diagram of the establishment of shared cycling system in university.

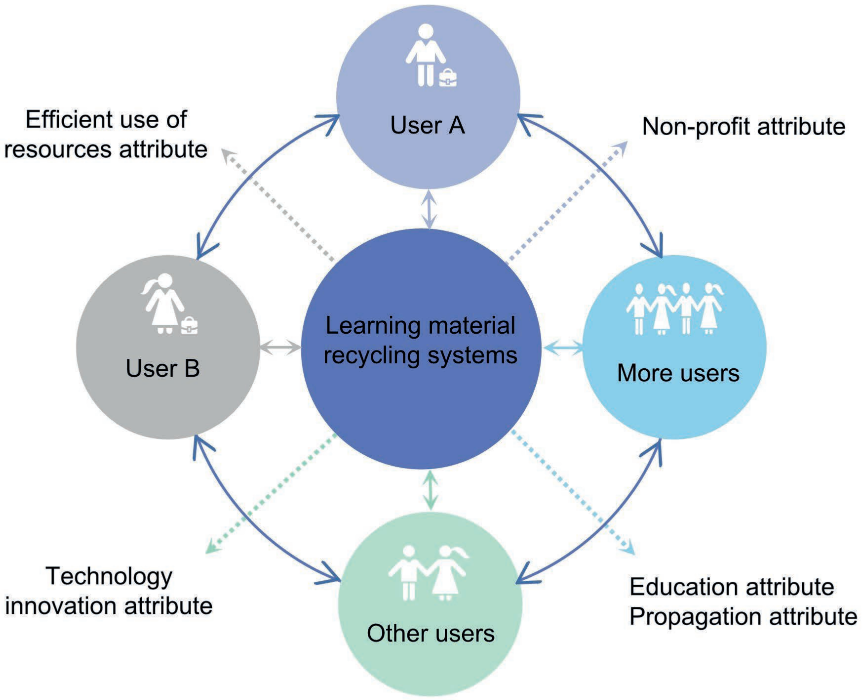

FIGURE 5: Learning material recycling system based on the internet trading platform.

Last, in terms of the different ways of promoting CE performance, we categorize CE-related university assets into direct and indirect CE-related assets. The former directly participates in or promotes the implementation of the CE, such as the CE practice carried out by the asset management department and the operations department. The latter is not directly involved in the implementation of the CE but can provide essential elements that can promote the implementation of the CE, such as educational assets that can improve people's CE awareness and knowledge. For instance, universities could cultivate CE professionals and implement general education about CE, and then students with professional knowledge and ideas can promote the implementation of the CE through their various pro-circular behaviors.

3.3 Content of CE-related university activities

Based on the definition and characteristics of CE-related university assets, CE-related university activities refer to the movements or actions that a university carries out to contribute to the transition toward the CE model with CE-related assets as the core. The essence of CE-related university activities includes scientific research, education and concrete practical activities based on the classification of CE-related assets by application, as shown in Figure 6.

Scientific research activities mainly focus on the research and application of CE technology, including research on green materials and green technology by researchers at the university and the transformation of green science and technology achievements from theory to practice through university–enterprise cooperation. China is making green technological progress the main driving force for sustainable development in the future (Jing & Zhang, 2014). Researchers have shown that the effect of guiding R&D toward green technology is significant in promoting the progress of green technology (You & Wang, 2016). In 2019, China invested 23.13 billion euros in R&D at higher education institutions, an increase of 23.2% from 2018 and accounting for 8.1% of the total expenditure. The proportion of the scientific and technological output of higher education institutions is much higher than the proportion of appropriation expenditure on R&D (NBSC, 2019). As the dominant contributors to the national scientific and technological output and achievements, universities can provide the necessary green technology support for the transition to the CE model by guiding researchers toward green technology innovation. Additionally, the application and transformation of green technological achievements are as important as the research on green technology. That is, achievements with practical value generated in the university laboratory should be put into practice for subsequent test, development, application and popularization. Cooperation between universities and industries is vital to realize the transformation of green technological achievements. With the increasingly common research on the coordinated development of green technology and economy, the combination of the scientific research advantages of universities and the industrial carrying capacity of enterprises can effectively promote the implementation of the CE to close the gap between theory and practice.

Educational activities mainly refer to the education and dissemination of the CE concept to students as well as society, which includes the cultivation of CE professionals and graduates with CE values for society, and the dissemination of the CE idea to the public. In 2019, there were 2,688 general higher education institutions, with a total of

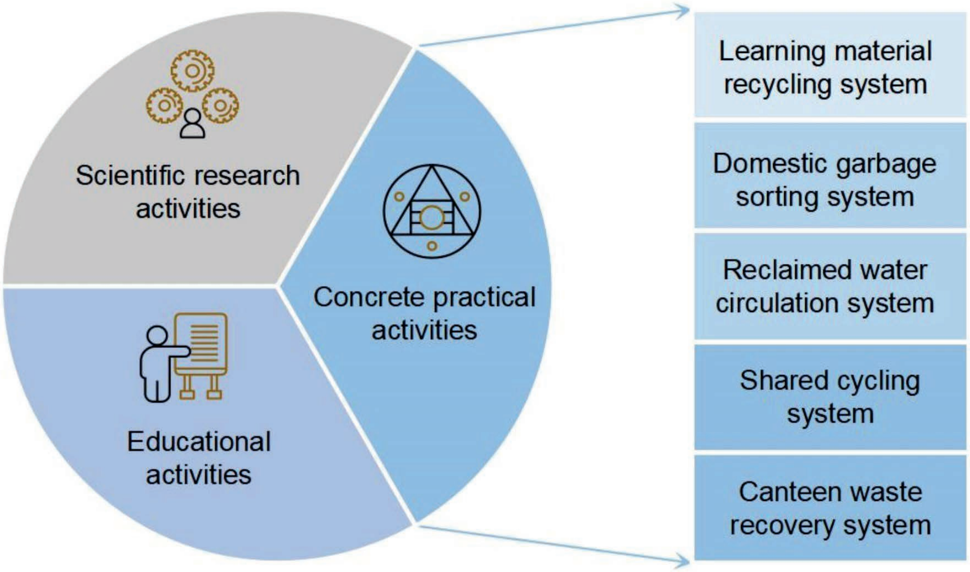

FIGURE 6: Illustrative content of the key types of CE-related university activities.

1.74 million full-time teachers, 30.315 million students and 7.585 million graduates at the undergraduate level, and 2.863 million students and 0.64 million graduates at the postgraduate level (NBSC, 2019). Colleges and universities play an irreplaceable role in environmental education by offering sustainability courses in a wide range of disciplines and departments (Coleman & Gould, 2019). However, according to the list of newly registered undergraduate majors published by the Ministry of Education every year, until 2019, only 49 colleges and universities in China offered a Resource Recycling Science and Engineering major, an emerging major approved by the Chinese Ministry of Education in 2010 to meet the urgent demand for talent in the implementation of the CE strategy in China (Qu et al., 2020). To solve the problem of the shortage of CE professionals, universities could attach importance to CE training for educators so that they could effectively convey the correct CE message by their course teaching. Moreover, it is necessary to strengthen the structure of the CE major and formulate scientific curriculum training programs to improve the training of CE talent. The graduates with CE degrees hired by enterprises can bring sufficient CE concepts and creativity to enterprises. Moreover, general education could be universalized to cultivate undergraduates with CE awareness and knowledge, who can spread CE values to surrounding communities through social practices in the community and guide residents to form green consumption habits. Graduates with CE awareness and knowledge are potential green consumers and CE practitioners, who can also disseminate CE values in their areas of expertise and their daily lives after they graduate.

Concrete practical activities refer to concrete CE practices on campus which consist of various resource recycling systems for achieving the CE, as well as direct use of a university's CE-related assets. Taking learning resources as an example, a survey of Wuhan University of Technology students showed that 85.6% of the respondents disposed of these post-use learning resources as waste paper rather than recycling them as reusable textbooks (Du, 2016). To advocate for recycling and reuse of textbooks and other learning materials, universities could organize on and offline learning material recycling systems (Guo, 2014). In addition, various resource recycling systems could be established on campus, such as a domestic garbage sorting system, a reclaimed water circulation system, a shared cycling system and canteen waste recovery systems. Additionally, an internal CE-related assets management network could be set up to monitor the efficient use of assets at every stage of their lifecycle according to CE principles. From the purchase of assets as a starting point, priority could be given to the use of environmentally friendly materials and products. In the process of using such products and processes, it is necessary to fully consider whether they pollute the environment and how to control pollution and other negative factors. The possibility of multi-level recovery of waste and other related factors would be considered in the process of asset scrapping and waste recovery. These both concrete and practical activities could exert an edifying influence on leaders and students and contribute to the realization of transformative CE learning and education.

3.4 Proposed framework to support the implementation of CE-related university activities

CE-related university activities involve a wide range of areas, including scientific research, education, undergraduate social practice and operations, so the subjects of CE-related university activities are more extensive, which means all university members need to be the subject of CE-related activities. Therefore, the CE theoretical framework would include all university members with wide spread knowledge as the key to successfully disrupting the linear system. In particular, the subjects mainly include researchers and lecturers of relevant teaching departments, undergraduate social practice departments and students with CE awareness and knowledge, as well as the operations department and its staff. It should be noted that not all university staff are born with the CE knowledge and ability to carry out CE-related activities, so CE training for them is the precondition for the implementation of all kinds of CE-related activities in this framework. On this basis, university researchers could take advantage of scientific research, set up teams to carry out CE policies and theoretical research, focus more on green technology design and technological innovation, and breakthrough the existing bottleneck of CE technology. Through curriculum teaching activities, lecturers could aim to cultivate CE professionals for enterprises and college students with CE awareness and knowledge who could disseminate CE education to society with routine social practices. In addition, operations managers and staff could explore CE practices on campus by constructing resource circulation systems and monitoring their operations. This practical exploration not only provides a direct and effective reference to the implementation of the CE in society but also affects the public's lifestyle in an all-around way, and forms the ecological culture within universities, thus contributing to the formation of a good ecological culture for society.

Based on the elaborations above, this paper proposes the theoretical framework of CE-related university activities that could provide many benefits for promoting the CE transition, including the construction of the CE culture in society, green manufacturing and technological innovation in enterprises, green consumption and participation in supervision of the public, see Figure 7.

In this framework, the subjects of CE-related university activities are the major factors, because their attitude and behaviors directly determine the effect of CE-related activities. Therefore, the CE training for university faculty and staff is of great significance. Fortunately, there is no need to impose excessive coercion or inducement for them except the training, because scientific research and teaching are crucial parts of universities' routine work. All they need to do is to integrate CE information into their daily work. Moreover, it is very convenient and effective to spread CE concepts to community residents by taking student social practice activities as an opportunity to implement education, because social practice activities during vacations and daily volunteer social service activities at every university in China has become a tradition (Wang, 2014). In addition, implementing CE practices on campus requires only the operations department to adjust the working concepts toward the goal of the CE to establish various resource recycling systems, which will not only make the operations work more efficiently but also form an intangible CE cultural atmosphere that can exert a subtle influence and implicit education to students. In other words, while participation in the CE practice is the responsibility of all members of the university, they will not suffer additional work stress or role load but can obtain many benefits in the process. In any case, the theoretical framework of CE-related university activities is a low-cost and high-profit way to promote the transition to a CE model.

4. DISCUSSION AND CONCLUSIONS

As an engine of knowledge and technology, universities can have a significant impact on the public's CE awareness

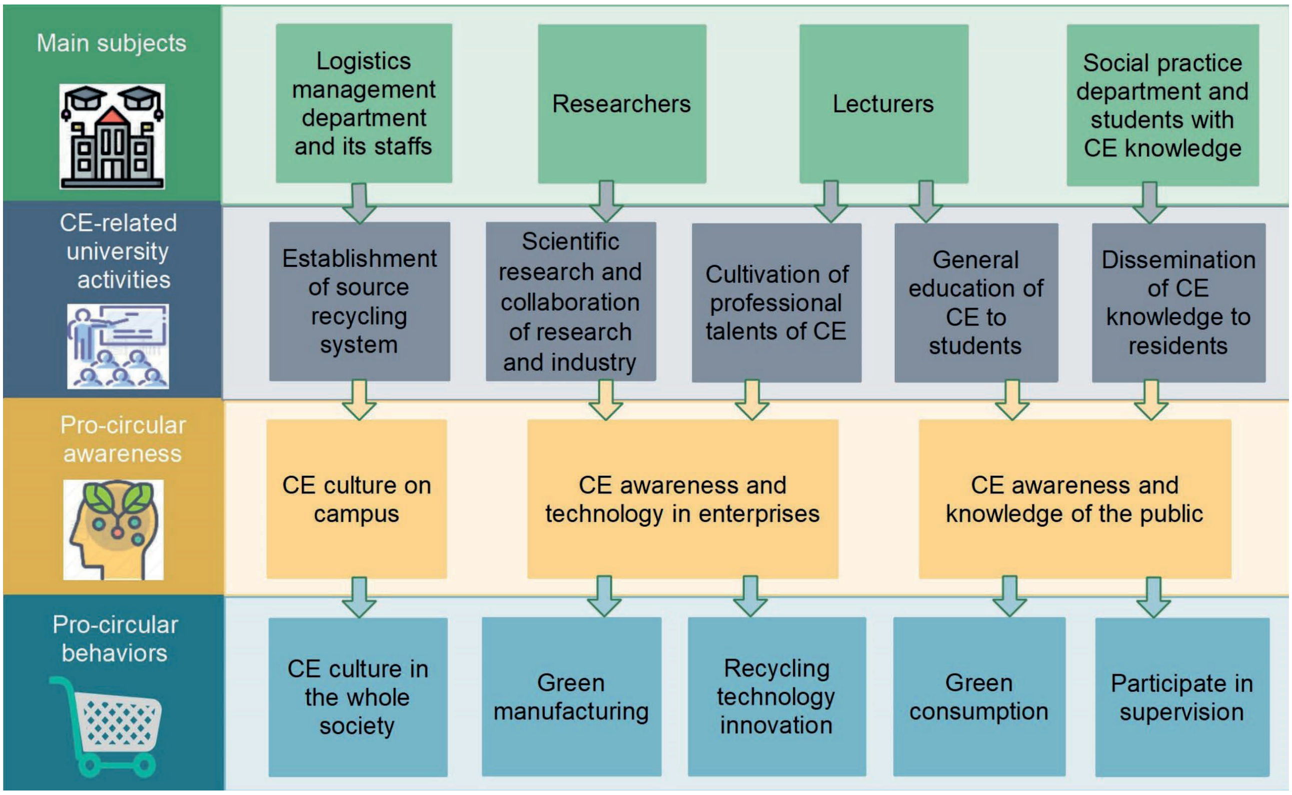

FIGURE 7: Theoretical framework of CE-related university activities toward the CE transition.

and behavior of the workforce of tomorrow through CE education to drive the CE from theory to reality, and even raise standards for sustainable performance (Nunes et al., 2018). For early realization, this paper provided the definition of CE-related university assets as a novelty, which mainly refers to university assets involved in and which could be developed in the application of the 3Rs principles to contribute to universal CE policy goals. Further, we developed a theoretical framework for CE-related university activities based on the classification and attributes of CE-related university assets, such as non-profit status, technology innovation, education, propagation and efficient use of resources.

There have been many theoretical research and practical explorations of the contribution of higher education institutions to the CE. However, these implementations are fragmented, and separate operations or simple splicing cannot have an impressive impact on CE promotion, and may even cause friction and obstruction. We proposed a systematic theoretical framework for CE-related university activities, which integrates various CE activities in a unified management system rather than simply patching them together, to achieve transformative learning and education to expand the university influence in the CE transition, which can make up for the deficiencies of previous studies. Additionally, this paper expounds the connotation and extension of the concept of CE-related university assets to make CE-related university activities concrete and close to reality, which is helpful for university implementation of the CE in practice.

In the theoretical framework of CE-related university activities, we proposed four kinds of activities toward the transition to a CE model on the basis of CE training for university faculty and staff. The first is scientific research CE-related activities, which take researchers as the main subject in the implementation and can provide CE technical support for enterprises based on scientific research CE-related assets. The second is education CE-related activities, which take lecturers as the central implementation subject who can cultivate CE professionals and implement general CE education for college students. The third is derived from the previous one, which takes college students as the main subject who can diffuse the CE concept to society through their routine social practices and other volunteer activities. The fourth is concrete CE practical activities with operations managers and staff members as the main subject, who could provide the reference for CE practice at the social level and contribute to the construction of CE culture in society based on operations CE-related assets.

Compared with the dimensions of sustainable universities (Cortese, 2003) and the pertinent themes of university CE assessment (Nunes et al., 2018), we provide a clearer explanation of the content of CE-related university activities in this CE theoretical framework, including a detailed process of activity implementation and specific responsible departments and subjects. It makes this framework more operable and feasible in practice, and can be used as a reference for other universities that would like to make contributions to the CE. However, it is a limitation that this framework leans on the implementer to exert their subjective initiative to promote the various CE-related university activities from the bottom up. Thus, the effect and durability of implementation must be evaluated. Therefore, the formation of a university management model that transitions toward the CE transition must be investigated in future research to guarantee the implementation and development of this theoretical framework in universities, to more effectively foster the transition to a CE model.

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BIOCHAR PRODUCTION FROM WASTE BIOMASS: CHARACTERIZATION AND EVALUATION FOR AGRONOMIC AND ENVIRONMENTAL APPLICATIONS

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ABSTRACT

This study focused on the valorization of different types of waste biomass through biochar production at two pyrolysis temperatures (400 and 600°C). The different feedstocks being used included three materials of municipal origin, specifically two types of sewage sludge and the organic fraction of municipal solid waste, and three materials of agroindustrial origin, specifically grape pomace, rice husks and exhausted olive pomace. The scope of the research was to characterize the resulting materials, in order to evaluate their possible uses in agronomic and environmental applications. Biochar characterization included the determination of several physical and chemical parameters, while germination assays were also carried out. Under the investigated conditions, both pyrolysis temperature and feedstock type appeared to significantly affect biochar characteristics, leading to the production of versatile materials, with many different possible uses. Specifically, results implied that biochars of both municipal and agroindustrial origin have the potential to effectively be used in applications including the improvement of soil characteristics, carbon sequestration, the removal of organic and inorganic contaminants from aqueous media, and the remediation of contaminated soil, with the degree of suitability of each material to each specific use being estimated to differ depending on its particular characteristics. For this reason, with these characteristics in mind, before proceeding to larger scale applications a cautious selection of materials should be conducted.

1. INTRODUCTION

In recent years, the continuous increase of wastes has directed global interest to the development of sustainable waste management strategies. One of the most representative examples of rapidly increasing waste production is that of municipal waste (Elkhalifa et al., 2019). In fact, both municipal solid waste (MSW) and sewage sludge (SS) obtained from municipal wastewater treatment plants constitute two priority waste categories which, as a result of the increasing population in urban centers, are continuously generated in large quantities. The importance of these wastes comes not only from their high production rates, but also from their particular composition, since they often contain various potentially toxic elements (e.g. potentially toxic metal(loid)s, pathogens, organic contaminants, etc.) (Agrafioti et al., 2013; Ahmad et al., 2014; Gunarathne et al., 2019; Rybova et al., 2018).

Waste and by-products originating from agroindustrial activities represent another category of residual materials with a quite elevated generation rate, especially in countries where agriculture and agro-industries represent important sectors of the economy (Fountoulakis et al., 2008). The wine and olive oil production and the rice processing industries are among the most profitable agroindustries, yet they generate considerable quantities of wastes and by-products. In EU-28 in 2019, the production of grapes for wine, olives for oil, and rice, reached 22,370, 10,255 and 2,841 thousand tonnes, respectively, with Greece accounting for 466, 935 and 222 thousand tonnes, respectively (EUROSTAT, 2020).

Lately, more and more attention has been focusing on the use of waste as resources for both energy and added-value materials, in the framework of a circular economy (Elkhalifa et al., 2019). In this context, waste biomass of not only municipal, but also of agroindustrial origin, could prove quite promising due to both composition and availability.

Converting waste into biochar through pyrolysis is considered a viable method for valorizing such residual

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resources (Gunarathne et al., 2019). The reason for the increasing interest in biochar comes from the fact that, apart from being an effective method for reducing health and environmental hazards associated with waste biomass, it can find various beneficial applications, including its use as an adsorbent for contaminant removal from water or wastewater, as an amendment for improving soil characteristics and for remediation of contaminated sites (Ahmad et al., 2014; Aller, 2016). This high versatility of biochar is attributed to its wide variety of properties, which depend not only on the pyrolysis conditions being adopted, but also on the type of feedstock being used (Aller, 2016; Fryda et al., 2019; Rehrah et al., 2016).

Biochar characterization usually includes the investigation of several properties, with each one of them playing a different role in the potential biochar applications. For example, proximate and ultimate composition can give insights regarding biochar stability in soil. High fixed carbon contents, as well as high aromaticity and hydrophobicity have been associated with greater carbon stability and thus a greater ability of biochars to act as carbon sequestration agents (Ahmad et al., 2012; Tag et al., 2016). Such biochars are usually produced at higher temperatures and are more resistant to microbial degradation and mineralization. On the other hand, biochars that are produced at lower temperatures are more hydrophilic and can contribute to increasing soil water holding capacity (Rehrah et al., 2016; Zhao et al., 2017). Determining the electrical conductivity of biochars can reveal their effect on soil quality and fertility (Rehrah et al., 2016; Zhao et al., 2017), while biochars with a large amount of surface functional groups and a high cation exchange capacity can be used in soils for enhancing nutrient exchange sites and for preventing nutrient leaching (Tag et al., 2016; Zhao et al., 2017). Biochar pH can be very important for both agronomic and environmental applications. Since biochars are often moderately to highly alkaline, they can exert liming effects resulting in acid soil amelioration, immobilization of metals in contaminated soils and removal of them from aqueous media (Ahmad et al., 2014). The point of zero charge (pH_{PZC}) is another very important characteristic in terms of contaminant removal from water and wastewater. It represents the pH value at which the surface charge of biochar is zero. More specifically, when the pH of the solution is greater than pH_{PZC}, the biochar is negatively charged and tends to attract cations, while when the pH of the solution is lower than pH_{PZC}, the biochar is positively charged and tends to attract anions (Li et al., 2017; Tan et al., 2015). Moreover, while biochars produced at higher pyrolysis temperatures tend to be more effective for sorbing organic contaminants, as a result of their usually higher surface area, microporosity and hydrophobicity, those generated at lower temperatures are more prone to sorbing inorganic and polar contaminants through electrostatic interactions, precipitation/co-precipitation, as well as interaction with surface functional groups (Ahmad et al., 2014). All the above, highlight the importance of a comprehensive characterization, and of the use of such information to thoroughly evaluate biochars for their use in more than one types of applications at the same time. Such an approach will be helpful in directing research towards the most efficient, effective and profitable solutions. In the literature there is a limited number of studies (Ibn Ferjani et al., 2019; Oh et al., 2012; Pariyar et al., 2020; Stylianou et al., 2020; Taskin et al., 2019) referring to biochar characterization aiming at both agronomic and environmental uses.

The present study contributes to this regard, by characterizing and investigating biochars of different natures regarding their potential environmental and agronomic uses Six different waste biomass feedstocks, specifically three of municipal origin, namely two types of sewage sludge and the organic fraction of municipal solid waste, and three of agroindustrial origin, namely grape pomace, rice husks and exhausted olive pomace, were used to produce biochar through pyrolysis at two different temperatures, i.e. 400 and 600°C. The resulting carbonaceous materials were then characterized through a series of physical and chemical analyses, and used in germination assays, in order to reveal eventual beneficial, inhibitory or toxic features. The objective of the study is to ultimately be able to assess, on the basis of the obtained results, the potential uses of each biochar for either agronomic or environmental purposes.

1.1 Nomenclature

CEC	cation exchange capacity
EC	electrical conductivity
EOP	exhausted olive pomace
FC	fixed carbon
FT-IR	Fourier Transform Infrared spectra
GP	grape pomace
OF	organic fraction
OFMSW	organic fraction of municipal solid waste
pHPZC	point of zero charge
PTMs	potentially toxic metal(loid)s
SS	sewage sludge
SSC	sewage sludge from Chania
SSP	sewage sludge from Psyttalia
RH	rice husks
VM	volatile matter

2. MATERIALS AND METHODS

2.1 Waste biomass feedstocks

Six types of biomass were used as feedstocks for biochar production, namely two types of digested sewage sludge (SS), the organic fraction of municipal solid waste (OFMSW), grape pomace (GP), rice husks (RH) and exhausted olive pomace (EOP). The first SS sample (SSC) was obtained from the Municipal Wastewater Treatment Plant of Chania, Crete, Greece and consisted of anaerobically digested SS that had been mechanically dewatered. The second SS sample (SSP) was obtained from the Psyttalia Wastewater Treatment Plant, Athens, Greece and consisted of anaerobically digested SS that had been dewatered through drying. OFMSW originated from the Inter-municipal Enterprise of Solid Waste Management (DEDISA) of Chania. GP was obtained from a local winery in Chania, while RH originated from a rice mill in northern

Greece. Finally, EOP was obtained from the local food industry Mills of Crete.

Prior to pyrolysis the six materials were subjected to a preparation procedure, which differed slightly depending on the material. More specifically, SSC was initially oven dried at 60 ± 5°C for 3 days and then ground to a particle size lower than 500 μm, while for SSP the procedure included only the grinding step, since the material was already dry when received. In the case of OFMSW, the sample was initially manually screened, aiming at removing any unwanted materials (e.g. inert, plastic, metallic and/or hazardous materials) and at leaving only putrescibles and (tissue) paper. Afterwards, the sample was oven dried at 60 ± 5°C for 3 days, further screened for unwanted materials that may have remained after the first screening, and finally ground to a particle size lower than 500 μm. GP was prepared through oven drying and grinding, as earlier mentioned, while RH and EOP were received as agro-industrial productsand were not further processed. The grinding procedures were carried out using either a food processor or a universal cutting mill (Pulverisette 19, Fritsch). After the above mentioned preparation procedures, all biomass feedstocks were stored in closed containers until further use.

2.2 Biochar preparation

The pyrolysis process was carried out in a muffle furnace (Linn High Therm) at two different temperatures, 400 and 600°C, with a heating rate of 3°C/min and a residence period (at the target temperature) of 1 h. These two pyrolysis temperatures were chosen on the basis that below 300°C pyrolysis of biomass may be incomplete, while above 700°C the amount of carbon left on char is minimum. Inert conditions were ensured by purging nitrogen in the furnace interior with a flow rate of 200 L/h. After cooling, the resulting materials were subjected to a washing procedure with the purpose of removing excess ash and eventual organic substances that may have been produced during pyrolysis. This procedure was adopted as a step in the production process aiming at limiting potential toxic effects of the biochars in future environmental and agronomic applications. In brief, the samples were mixed with deionized water at a solid/liquid ratio of 1/15 g/mL and agitated on an orbital shaking table at 200 rpm for 1 h. The solid and liquid fractions were then separated through vacuum filtration and the solid fractions were finally rinsed with deionized water and oven dried. The final products were homogenized using a mortar and ultimately stored in closed containers until use. Twelve types of biochar were obtained through the above-mentioned procedure, which are presented in Table 1.

2.3 Characterization and analytical methods

The biochar materials were characterized regarding certain basic properties, aiming at evaluating their potential use in agronomic and environmental applications. These include proximate (ash, volatile matter (VM), fixed carbon (FC)) and ultimate (CHNS%) composition, contents in mineral elements and major oxides, pH, electrical conductivity (EC), point of zero charge (pH_{PZC}), cation exchange capacity (CEC), zeta potential, bulk density, specific surface area, as well as determination of surface functional groups. The pyrolysis yields were calculated as well, by taking into consideration the initial mass of feedstock and the final mass of carbonaceous material obtained at the end of pyrolysis. Moreover, all biochars were used in germination assays, with Lepidium sativum as a test plant.

Waste biomass feedstocks were also characterized, albeit focusing on proximate and ultimate analyses, pH and EC determination, as well as compositional analysis regarding mineral elements.

2.3.1 Proximate and ultimate analyses

Proximate analysis of biochars was carried out on the basis of ASTM method D1762-84, while for biomass feedstocks APHA (American Public Health Association) method 2540G and ASTM method E897-88 were used. Ultimate analysis was determined by flash combustion at 1,020°C using a EuroVector EA300 series elemental analyzer.

2.3.2 pH, EC, pH_{PZC}, CEC, zeta potential

pH and EC were measured in the slurry obtained after agitating the materials with the respective liquid media. In the case of biochars, the materials were agitated both in deionized water (for pH and EC) and in KCl (1N) (only for pH), with a solid/liquid ratio of 1/20 g/mL for 1.5 h (Rajkovich et al., 2012). For the biomass agitation took place in deionized water with a solid/liquid ratio of 1/10 g/mL for 24 h. In order to determine the pH_{PZC} of the different biochars, the pH 'drift' method was adopted, as reported by Uchimiya et al. (2011). On the other hand, CEC was determined according to EPA method 9081 using sodium acetate and ammonium acetate (EPA, 1986). Zeta potential was measured following the methodology reported by Yao et al. (2011). The measurements were conducted by using a Zetasizer Nano-ZS (Malvern Instruments).

2.3.3 Bulk density and specific surface area

Bulk density was determined according to the method reported by Ahmedna et al. (1997), while the specific surface area of carbonaceous materials was determined

TABLE 1: Biochar codification.

Feedstock	Pyrolysis temperature (°C)	Biochar coded name
SSC	400	SSC400
	600	SSC600
SSP	400	SSP400
	600	SSP600
OFMSW	400	OFMSW400
	600	OFMSW600
GP	400	GP400
	600	GP600
RH	400	RH400
	600	RH600
EOP	400	EOP400
	600	EOP600

using a Nicolet 380 (Thermo), after degassing all samples at 200°C.

2.3.4 Mineral elements and major oxides contents

Mineral element contents of the produced carbonaceous materials and their precursors were determined via Inductively Coupled Plasma Mass Spectrometry (ICP-MS) (CX 7500, Agilent) after sample acid digestion with HNO_3. On the other hand, major oxides contents were determined via Energy Dispersive X-ray fluorescence (XRF) (S2 Ranger, Bruker) after fusion (Claisse Fluxer M4) of ignited (1,050°C) biochar samples (ash samples) with Li-tetraborate.

2.3.5 Surface functional groups

The presence of surface functional groups on the biochars was evaluated by recording the materials' FT-IR spectra with a Fourier transform infrared spectrometer (Perkin Elmer Spectrum 1000) using the KBr pellet technique (sample:KBr = 1:100).

2.3.6 Germination assays

Germination assays were conducted in order to assess the eventual phytotoxic effect of the investigated biochars on Lepidium sativum seed germination and early seedling growth in terms of root elongation. In order to conduct the assays, the twelve biochars were mixed at a 1% rate, on dry basis, with Phytotoxkit™ (MicroBioTests Inc.) reference soil (85% sand, 10% kaolin and 5% peat, according to the supplier). The amendment rate value (1%) was selected as a representative intermediate value that would provide an indication of the potential effects, either positive or negative, that the investigated biochars may have on higher plants. Briefly, equal quantities of each soil-biochar mixture were placed in circular Petri dishes (90 mm diameter) and wetted with a quantity of deionized water equivalent to 80% of the water holding capacity of the soil (Mumme et al., 2018). The same procedure was also followed using the reference soil with no amendments (Control assay). Afterwards, a piece of filter paper, which was also wetted to 80% of its water holding capacity, was placed inside each dish, on top of the soil mixtures and 10 seeds of Lepidium sativum were arranged in line on the filter paper, at a distance of at least 1 cm from the edge of the dish. Finally, both test (soil-biochar mixtures) and control dishes were covered with their lids and placed inside an incubation chamber set at 25°C at a 50-60° angle. After 3 d, digital images of the dishes were acquired and root lengths were determined through image analysis, using the ImageJ software. All assays were conducted in triplicates.

In order to evaluate the results, two parameters, i.e. the Germination Index (GI) and the Root Growth Inhibition (RGI), were calculated, according to literature (Nieto et al., 2016; Oleszczuk and Hollert, 2011):

$$GI=G\cdot(RL_t/RL_c) \quad (1)$$

$$RGI=(RL_c-RL_t)/RL_c \quad (2)$$

where G is the percentage of seeds germinated in the test assays (germination rate), RL_t is the mean root length of the seeds germinated in the test assays, and RL_c is the mean root length of the seeds germinated in the control assays.

3. RESULTS AND DISCUSSION

3.1 Yield and proximate analysis

As shown in Figure 1 the pyrolysis yield was negatively correlated with the increase in pyrolysis temperature. In fact, while the yield obtained at 400°C ranged between 30.4 and 54.9%, the yield obtained at 600°C varied from 26.3 to 46.2%. Moreover, when comparing different feedstocks, higher yields and thus higher biochar quantities were obtained from the two sewage sludge types, SSC and SSP, followed by OFMSW, RH and GP. The lowest yields were associated with EOP pyrolysis.

Proximate analysis (Figure 2) showed that the carbonaceous materials produced at 400°C contained less ash and more volatile matter, as compared to those produced at 600°C. As far as the FC contents are concerned, the results depended on the material origin. For biochars obtained from feedstocks of municipal origin, FC appeared to be decreasing as a function of pyrolysis temperature, while the opposite was observed for biochars obtained from feedstocks of agroindustrial origin.

The decrease in pyrolysis yield with increasing temperature has been associated with decomposition of organic matter, as well as with dehydration of hydroxyl groups (Rehrah et al., 2016; Stefaniuk and Oleszczuk, 2015). This phenomenon was corroborated by the analogous reduction in VM contents (Zhao et al., 2017), which in turn resulted in an increase in the concentration of inorganic matter (Suliman et al., 2016; Tag et al., 2016; Zhao et al., 2017) and thus, in increased ash content. As far as FC is concerned, the trends observed in the present study, i.e. both increasing and decreasing trends as a function of temperature, has also been reported by other authors (Ahmad et al., 2012; Ahmad et al., 2014; Gómez et al., 2016; Hossain et al., 2011; Jin et al., 2014; Pellera and Gidarakos, 2015; Rajkovich et al., 2012; Suliman et al., 2016; Taherymoosavi et al., 2017; Zhao et al., 2017), and they may be associated with the ash content of the investigated materials. In fact, Enders et al. (2012) noticed that for materials with ash content above 20%, FC decreased as a function of pyrolysis temperature, while the opposite happens for materials with ash contents below 20%. These authors attributed this phenomenon to

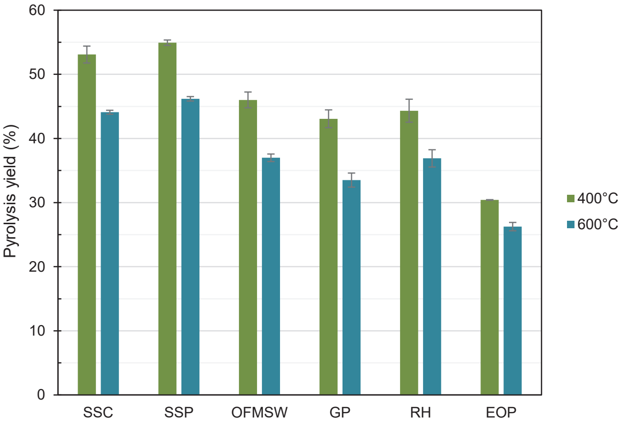

FIGURE 1: Pyrolysis yields for the six feedstocks at two temperatures (error bars represent standard deviation).

interactions between organic and inorganic constituents of the pyrolyzed materials during thermal treatment (Enders et al., 2012).

As far as the influence of feedstock type is concerned, the ash and VM contents of the six feedstocks exerted a significant effect both on the pyrolysis yield and on the proximate composition of the resulting biochars. In fact, pyrolyzing the material with the highest ash content, i.e. SSP, yielded not only a higher amount of biochar, but also higher-ash-containing materials. Such a relation between yield and ash content was highlighted also in previous studies (Song and Guo, 2012; Suliman et al., 2016).

3.2 Ultimate analysis

Ultimate analysis results (Table 2) demonstrated that feedstock origin played an important role in biochar composition. This was particularly evident when observing the biochar C content. Indeed, while biochars of municipal origin were characterized by C content ranging from 25.9 to 39.5%, for biochars of agroindustrial origin a much higher range of values was noticed, from 42.2 to 93.7%. H and N contents also presented differences in their range of values for different materials, with biochars of agroindustrial origin being characterized by generally lower values. As far as the influence of pyrolysis temperature is concerned, higher temperatures seemed to be generally associated with lower H and N contents, while in the case of C, reduced and increased values were observed for materials of municipal and agroindustrial origin, respectively.

The decrease in H and O contents with increasing pyrolysis temperature is quite common in the literature and is usually attributed to breakage of weak bonds in the biochar structure (Al-Wabel et al., 2013; Rehrah et al., 2016). As far as the C content is concerned, the most commonly observed behavior is its increase as a function of temperature (Colantoni et al., 2016; Gómez et al., 2016; Ibn Ferjani et al., 2019; Tag et al., 2016) and it is usually an indication of an intensified carbonization (Rehrah et al., 2016). On the other hand, C loss has also been reported (Cao and Harris, 2010; Kah et al., 2016; Lu et al., 2013). This phenomenon can most likely be associated with the composition of the biomass feedstocks being used, and particularly with their relatively high ash content, as was also concluded by Kah et al. (2016).

The ratios H:C and O:C are often used in order to determine the degree of aromaticity and polarity of biochars, respectively, with lower H:C ratios characterizing more aromatic materials and lower O:C ratios characterizing less hydrophilic materials (Ahmad et al., 2012; Rehrah et al., 2016). As it is observed in the Van Krevelen diagram (Figure 3), in this study both ratios decreased with increasing pyrolysis temperature, a behavior that has previously been associated with the occurrence of dehydration reactions during pyrolysis, as well as with a higher degree of carbonization for the obtained materials (Rehrah et al., 2016; Tag et al., 2016; Zhao et al., 2017). The highest H:C and O:C values were observed for biochars produced from the two sewage sludge feedstocks, i.e. SSC and SSP, at 400°C. Such elevated values may be attributed to the existence of residual organic material in the biochar (Ahmad et al., 2012; Rehrah et al., 2016). Moreover, the lower H:C values of biochars produced at 600°C suggest higher aromaticity, thus higher recalcitrance for these materials, while higher O:C values of biochars produced at 400°C indicate lower hydrophobicity, which could result in a higher water retention ability (Rehrah et al., 2016). Apart from the two abovementioned ratios, (O+N):C is also used as a polarity index (Ahmad et al., 2012; Oh et al., 2012). This ratio presented a generally decreasing trend with pyrolysis temperature (Table 2), indicating a progressive loss of polar surface functional groups (Ahmad et al., 2012).

3.3 pH, EC, pH_{PZC}, CEC, zeta potential

Pyrolysis resulted in materials with higher pH values (Table 4) compared with their respective precursors (Table 3), while biochar pH also increased with increasing

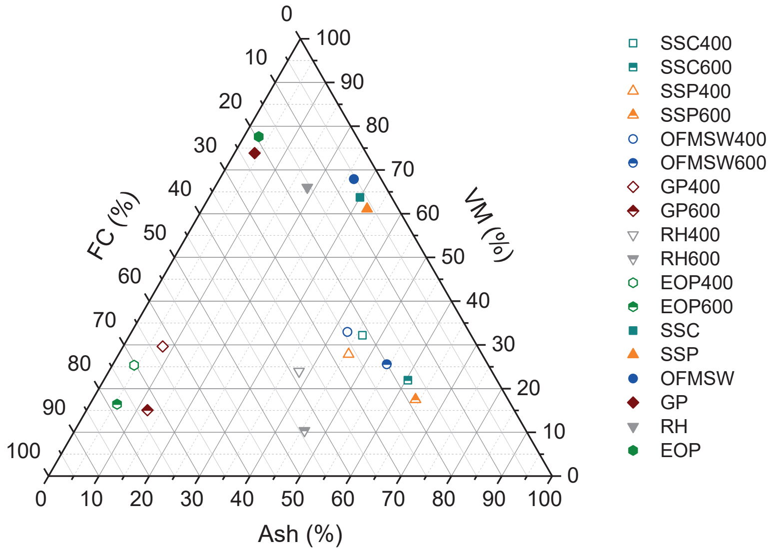

FIGURE 2: Proximate analysis of feedstocks and biochars.

TABLE 2: Ultimate analysis of feedstocks and biochars, on a dry basis.

Element	Municipal feedstocks			Biochars						
	SSC	SSP	OFMSW	SSC400	SSC600	SSP400	SSP600	OFMSW400	OFMSW600
C (%)	35.8 ± 0.0	36.4 ± 0.5	37.3 ± 0.3	29.3 ± 0.8	27.5 ± 0.3	27.3 ± 0.2	25.9 ± 0.4	39.5 ± 1.8	30.3 ± 0.8
H (%)	11.9 ± 0.0	12.4 ± 0.3	9.33 ± 0.25	3.01 ± 0.99	1.88 ± 0.03	2.77 ± 0.18	0.56 ± 0.09	2.06 ± 0.02	0.75 ± 0.03
N (%)	4.84 ± 0.38	4.71 ± 0.10	1.49 ± 0.06	3.64 ± 0.14	2.57 ± 0.11	3.07 ± 0.11	2.23 ± 0.22	1.57 ± 0.08	1.13 ± 0.05
S (%)	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< 0.4
O * (%)	17.4 ± 0.4	13.8 ± 0.3	25.2 ± 0.4	17.8 ± 1.4	7.65 ± 0.38	21.1 ± 0.4	7.15 ± 0.32	14.0 ± 1.8	13.0 ± 0.9
H:C	3.98 ± 0.01	2.50 ± 0.01	3.01 ± 0.08	1.24 ± 0.40	0.82 ± 0.02	1.22 ± 0.08	0.26 ± 0.05	0.63 ± 0.03	0.30 ± 0.00
O:C	0.36 ± 0.01	0.22 ± 0.00	0.51 ± 0.01	0.46 ± 0.05	0.21 ± 0.01	0.58 ± 0.01	0.21 ± 0.01	0.27 ± 0.05	0.32 ± 0.03
(O+N):C	0.48 ± 0.00	0.39 ± 0.01	0.54 ± 0.01	0.56 ± 0.05	0.29 ± 0.01	0.68 ± 0.01	0.28 ± 0.01	0.30 ± 0.05	0.35 ± 0.03

Element	Agroindustrial feedstocks			Biochars					
	GP	RH	EOP	GP400	GP600	RH400	RH600	EOP400	EOP600
C (%)	48.1 ± 0.7	40.0 ± 0.6	47.3 ± 0.2	69.1 ± 5.3	83.9 ± 1.3	42.2 ± 1.2	43.4 ± 1.8	83.2 ± 0.9	93.7 ± 0.4
H (%)	9.23 ± 0.56	8.62 ± 0.13	9.84 ± 0.06	5.34 ± 0.08	2.17 ± 0.19	2.05 ± 0.10	1.19 ± 0.02	1.84 ± 0.90	1.32 ± 0.13
N (%)	2.53 ± 0.20	0.54 ± 0.06	1.00 ± 0.19	2.82 ± 0.57	0.71 ± 0.12	0.38 ± 0.02	0.27 ± 0.03	0.02 ± 0.00	< DL
S (%)	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL
O * (%)	36.2 ± 0.6	32.5 ± 0.5	38.9 ± 0.3	14.9 ± 4.8	1.10 ± 1.06	17.6 ± 1.3	9.54 ± 1.78	10.6 ± 1.0	<0.1
H:C	2.30 ± 0.16	2.59 ± 0.06	2.50 ± 0.01	0.93 ± 0.06	0.31 ± 0.03	0.58 ± 0.02	0.33 ± 0.02	0.27 ± 0.13	0.17 ± 0.02
O:C	0.56 ± 0.01	0.61 ± 0.02	0.62 ± 0.01	0.16 ± 0.06	0.01 ± 0.01	0.31 ± 0.03	0.17 ± 0.04	0.10 ± 0.01	0.00 ± 0.00
(O+N):C	0.61 ± 0.01	0.62 ± 0.02	0.64 ± 0.01	0.20 ± 0.07	0.02 ± 0.01	0.32 ± 0.03	0.17 ± 0.04	0.10 ± 0.01	<0.01

*DL: Detection Limit , *determined by difference , values are expressed as average ± standard deviation*

production temperature. This behavior may be attributed to phenomena occurring during pyrolysis, such as the progressive loss of acidic functional groups from the materials surface (Mukherjee et al., 2011; Stefaniuk and Oleszczuk, 2015), as well as the separation of alkali salts from the materials organic matrices (Al-Wabel et al., 2013). It has also been previously associated with the increase in ash content of the biochars during pyrolysis (Rehrah et al., 2016; Tag et al., 2016). According to the obtained data all tested carbonaceous materials can be characterized as alkaline, with biochars of agroindustrial origin generally showing higher values, with the exception of RH400, which not only was associated with the lowest pH values among all materials, but it was also characterized as acidic.

In terms of pH_{PZC}, the results were consistent with pH data, with values being lower compared with the respective pH values. The differences were more significant for biochars of agroindustrial origin. On the contrary, CEC of the tested materials decreased with increasing production temperature. CEC presented relatively high values ranging from 119 to 494 meq/kg. This behavior for both parame-

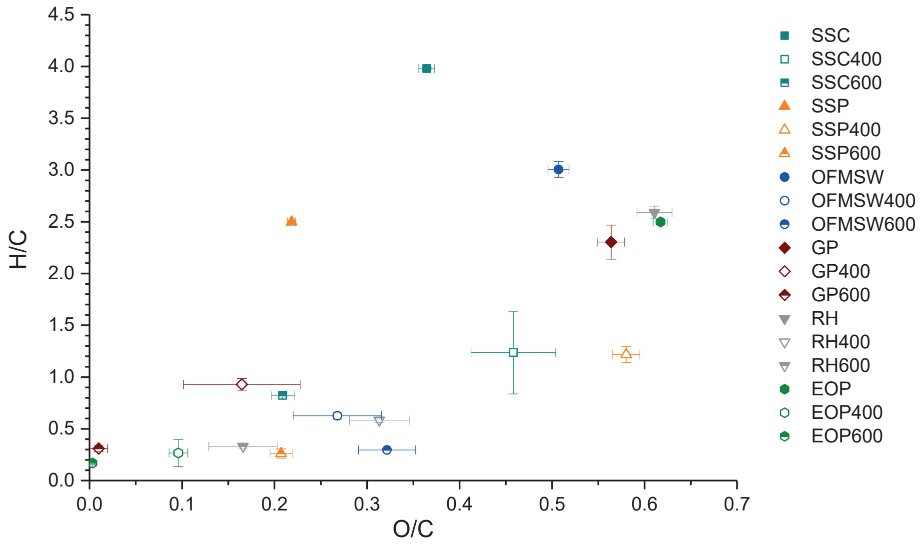

FIGURE 3: van Krevelen diagram (error bars represent standard deviation).

ters was a consequence of the intensified removal of surface functional groups at higher pyrolysis temperatures (Inguanzo et al., 2002; Lu et al., 2013; Suliman et al., 2016; Tag et al., 2016; Zhao et al., 2017).

In the case of EC, its variation as a function of pyrolysis temperature followed a different behavior for materials of different origin (Table 4). Specifically, for biochars of municipal origin a decrease was observed, while for those of agroindustrial origin the values were found to increase. Most studies refer to a positive correlation between EC, pH and ash contents (Rehrah et al., 2016; Song and Guo, 2012), which in turn comes as a result of volatile material loss (Stefaniuk and Oleszczuk, 2015); however an opposite behavior has also been observed in previous studies (Hossain et al., 2011; Luo et al., 2014; Manolikaki et al., 2016; Oh et al., 2012). In addition, biochar EC values were lower compared with those of their respective precursors (Table 3).

EC is often used to estimate salinity and as an index for evaluating the quality of fertilizers. More specifically, if a biochar is characterized by high salinity, it is usually not recommended for soil applications, due to potential harmful effects on plants, while very low salinity is also undesirable (Tag et al., 2016). According to a classification reported by Belyaeva et al. (2012), materials with EC values (determined with a 1:5 soil:water ratio) between 500 and 1500 μS/cm are considered moderately saline, those in the range 1500-2000 μS/cm, extremely saline, while those above 2000 μS/cm, too saline for most plants. Assuming that the dilution factor between the above mentioned ratio and the one used in the present study (1:20) applies for EC values (Singh et al., 2017), most biochars might be characterized as moderately saline, whereas SSC400, GP400 and GP600 as extremely saline, and OFMSW400 and OFMSW600 as too saline for most plants.

As far as zeta potential is concerned, negative values for all biochars revealed the negative surface charge of the materials (Yargicoglu et al., 2015), while the increasing electronegativity with increasing pyrolysis temperature is in agreement with previous results (Mukherjee et al., 2011).

TABLE 3: pH and EC of feedstocks.

Properties	Municipal feedstocks			Agroindustrial feedstocks		
	SSC	**SSP**	**OFMSW**	**GP**	**RH**	**EOP**
pH	7.09 ± 0.03	7.10 ± 0.08	6.11 ± 0.04	3.82 ± 0.06	5.91 ± 0.02	5.50 ± 0.23
EC (mS/cm)	2.00 ± 0.01	2.18 ± 0.06	7.95 ± 0.12	2.53 ± 0.02	0.79 ± 0.01	2.01 ± 0.04

TABLE 4: Chemical and physical properties of biochars.

Properties	Biochars of municipal origin					
	SSC400	**SSC600**	**SSP400**	**SSP600**	**OFMSW400**	**OFMSW600**
Chemical properties						
pH (DW)	7.53 ± 0.04	7.45 ± 0.04	7.94 ± 0.05	8.63 ± 0.06	8.50 ± 0.06	9.76 ± 0.04
pH (KCl)	7.40 ± 0.05	7.43 ± 0.02	7.27 ± 0.01	8.05 ± 0.01	8.38 ± 0.03	9.50 ± 0.04
pH_{PZC}	7.14 ± 0.05	7.20 ± 0.05	7.11 ± 0.05	7.41 ± 0.05	8.30 ± 0.05	9.47 ± 0.05
EC (μS/cm)	429 ± 7	326 ± 12	333 ± 9	199 ± 2	1785 ± 80	871 ± 7
CEC (meq/kg)	176 ± 1	126 ± 2	371 ± 2	180 ± 2	388 ± 17	257 ± 10
Zeta potential (mV)	-9.84 ± 1.24	-11.5 ± 1.8	-10.2 ± 2.8	-11.9 ± 1.7	-9.97 ± 1.93	-13.8 ± 2.9
Physical properties						
Specific surface area (m^2/g)	2.87 ± 0.03	23.8 ± 3.4	14.4 ± 0.1	52.5 ± 5.9	8.03 ± 0.82	101 ± 4
Bulk density (kg/m^3)	711 ± 12	945 ± 11	652 ± 9	751 ± 3	400 ± 2	464 ± 0
Properties	**Biochars of agroindustrial origin**					
	GP400	**GP600**	**RH400**	**RH600**	**EOP400***	**EOP600***
Chemical properties						
pH (DW)	9.05 ± 0.04	9.93 ± 0.22	6.49 ± 0.06	9.23 ± 0.03	9.52 ± 0.16	10.05 ± 0.04
pH (KCl)	7.76 ± 0.04	9.23 ± 0.10	4.44 ± 0.03	7.36 ± 0.06	8.02 ± 0.27	9.03 ± 0.06
pH_{PZC}	7.45 ± 0.05	8.14 ± 0.05	6.33 ± 0.05	7.72 ± 0.05	7.32 ± 0.05	7.75 ± 0.05
EC (μS/cm)	422.7 ± 26.2	468.0 ± 55.7	179.6 ± 3.2	190.5 ± 3.7	267.3 ± 7.8	341.3 ± 7.4
CEC (meq/kg)	196 ± 28	134 ± 3	494 ± 25	212 ± 2	203 ± 4	119 ± 2
Zeta potential (mV)	-20.4 ± 1.3	-19.3 ± 1.7	-12.2 ± 0.4	-13.4 ± 1.1	-11.2 ± 1.5	-15.7 ± 2.7
Physical properties						
Specific surface area (m^2/g)	1.29 ± 0.05	21.8 ± 5.4	59.4 ± 2.3	215 ± 7	6.85 ± 2.76	128 ± 7
Bulk density (kg/m^3)	515 ± 22	516 ± 12	303 ± 27	312 ± 11	357 ± 23	365 ± 29

** these materials were analysed in particle form in all cases except specific surface area analysis (materials ground in mortar), values are expressed as average ± standard deviation*

3.4 Specific surface area and bulk density

In terms of physical characteristics (Table 4), specific surface area and bulk density, a positive effect of pyrolysis temperature on these two parameters was observed. Increased surface area for biochars produced at 600°C is in agreement with the findings of other authors (Cao and Harris, 2010; Randolph et al., 2017) and is most likely a result of the progressive decomposition of organic matter and the more intense formation of micropores and channels within the structure of the biochars (Ahmad et al., 2012; Zhao et al., 2017). However, in the present study, the differences between lower- and higher-temperature biochars were very pronounced, or in other words, the specific surface areas of all materials produced at 400°C were comparatively quite low. Such a phenomenon has been previously reported in the literature and has been associated with partial blockage of pores by condensed volatile materials (tars), inorganic compounds (ash), and/or other amorphous decomposition products (Rehrah et al., 2014).

As far as bulk density is concerned, this parameter is often determined for biochar materials, especially when they are intended for soil applications, since it affects soil quality, particularly in terms of porosity and compaction (Rehrah et al., 2016). In this study there was a positive relation between bulk density and pyrolysis temperature, in agreement with Rajkovich et al. (2012) and Rehrah et al. (2016).

3.5 Mineral elements contents

Table 5 presents the results regarding the mineral elements content of the twelve biochars, obtained after acid digestion. Generally, biochars of municipal origin were richer in mineral elements compared with biochars of agroindustrial origin, with total concentrations ranging at levels of approximately 47-91 g/kg and 3.4-20 g/kg, respectively. For the former biochars, the most abundant element was Ca, with particularly elevated concentrations ranging from 32 g/kg (SSC400) to 82 g/kg (OFMSW600). Among other elements found also at relatively elevated concentrations, in the region around 1-10 (±2) g/kg, were, for SS-derived biochars Fe, Mg and Al, plus K and Na for SSP400 and SSP600, and for OF-derived biochars Mg, K, Na, Fe and Al. All the other tested elements, including potentially toxic metal(loid)s (PTMs), were found in concentrations not exceeding 0.8 g/kg (or even 0.2 g/kg in certain cases). Nevertheless, to this regard, the fact that in SS-derived biochars there was a more pronounced presence of Zn, Pb, Cu, Mn and Cr, compared with OF-derived biochars, is noteworthy. As far as agroindustrial biochars are concerned, the elements with the two highest concentrations were Ca and K, with the former being the most abundant for GP-derived biochars (max. ~11.6 g/kg), and the latter for RH- and EOP-derived biochars (max. ~4.6 g/kg). Intermediate concentrations, with values around 0.1-1.2 (±0.02) g/kg depending on the material, were measured for elements such as Mg, Fe, Mn, Al and Na. Finally, in this case, all elements found in lesser quantities reached values below 0.1 g/kg. It is worth mentioning that the orders of magnitude, as well as rank orders in each case, varied depending on the biochar feedstock.

Regarding the mineral elements detected in more significant amounts, i.e. Ca, Fe, Al, Mg, K, Mn and Na, pyrolysis resulted in increase in their concentrations (Table 5), while further increase in pyrolysis temperature led to mostly increased and mostly decreased concentrations for municipal and agroindustrial biochars, respectively. The results of the present study agree, in general, with similar findings reported elsewhere (Al-Wabel et al., 2013; Cao and Harris, 2010; Hossain et al., 2011; Jin et al., 2014; Lu et al., 2013; Rehrah et al., 2016; Shen et al., 2017; Song and Guo, 2012; Zhao et al., 2017). Regarding PTMs, their values were in general terms comparable to those in the literature (Domene et al., 2015; Jin et al., 2014; Kah et al., 2016; Pituello et al., 2015), while they did not exceed the limit values set by the Council Directive 86/278/EEC on the use of sludge in agriculture (EC, 2009). As far as the effect of pyrolysis temperature on these elements is concerned, their behavior was characterized by high variability, with both increasing and decreasing trends being noticed. This is most likely due to the ability of certain elements to volatilize at high temperatures (Hossain et al., 2011; Li and Jiang, 2017; Luo et al., 2014; Pituello et al., 2015; Zhao et al., 2017).

3.6 Surface functional groups

The presence of surface functional groups on biochars was evaluated through the FT-IR spectra illustrated in Figure 4. At first glance, it is evident that there is a high degree of pattern similarity between the spectra of the two sewage sludge-derived biochars, as well as between those of GP- and EOP-derived biochars. Moreover, the spectra of the OFMSW-derived biochars, although presenting bands at similar wavenumbers as the SS-derived biochars, differ in terms of band intensity.

In more detail, biochars of both municipal and agroindustrial origin, all presented distinct bands with highest points in the range 3418-3350 cm^{-1} and 3442-3328 cm^{-1}, as well as 1616-1558 cm^{-1} and 1614-1574 cm^{-1}, respectively. The former broad bands indicate the presence of hydrogen bonds and may be assigned to O-H stretching (Coates, 2000). As far as the latter bands are concerned, they are usually associated with the presence of aromatic compounds (Coates, 2000) and may be assigned to C=C stretching (Chen et al., 2008) and/or to carboxylate, which is especially likely in the cases of GP400 and EOP400, for which weak peaks at 1384 and 1372 cm^{-1}, respectively, were also observed (Coates, 2000). Moreover, all biochars, except those derived from RH, presented peaks around 1434 and 874 cm^{-1}, which may be assigned to carbonates (Coates, 2000). Specifically in the case of biochars of municipal origin, these peaks combined with weak peaks at 712 cm^{-1}, are consistent with the possible presence of calcite, whose typical peaks are found around 1433, 874 and 713 cm^{-1} (Jimoh et al., 2017; Nasir et al., 2019). In addition to the above mentioned bands which were common to all biochars, some others were common only among certain materials. Indeed, weak bands with highest points between 2954 and 2864 cm-1, as well as medium to strong peaks between 1046 and 1034 cm^{-1}, were observed only for biochars of municipal origin. The former bands indicate the presence of aliphatic groups, with specific assignments to

TABLE 5: Mineral element content (mg/kg) of feedstocks and biochars, on a dry basis.

Element	Municipal feedstocks			Biochars					
	SSC	SSP	OFMSW	SSC400	SSC600	SSP400	SSP600	OFMSW400	OFMSW600
B	7.27 ± 0.09	6.91 ± 0.12	9.23 ± 0.43	9.17 ± 1.47	8.30 ± 0.33	8.82 ± 0.02	8.24 ± 0.87	11.9 ± 0.4	15.7 ± 1.7
Na	274 ± 28	722 ± 9	1931 ± 8	314 ± 50	340 ± 8	700 ± 8	890 ± 102	1044 ± 61	1236 ± 9
Mg	1165 ± 8	2521 ± 15	1222 ± 84	1773 ± 284	1930 ± 62	3838 ± 7	4423 ± 505	1949 ± 59	2496 ± 8
Al	689 ± 8	4503 ± 65	395 ± 38	1070 ± 181	1593 ± 54	7293 ± 116	8074 ± 844	869 ± 14	1996 ± 35
K	212 ± 7	641 ± 6	3999 ± 123	314 ± 54	348 ± 10	992 ± 8	1181 ± 128	1788 ± 130	1890 ± 14
Ca	20637 ± 360	31035 ± 523	38679 ± 4658	32123 ± 5619	36036 ± 1205	51945 ± 411	55461 ± 6504	65207 ± 2162	81895 ± 793
Cr	12.1 ± 0.0	156 ± 2	5.34 ± 0.80	18.9 ± 3.1	16.3 ± 0.4	237 ± 5	191 ± 19	6.72 ± 0.35	9.13 ± 0.25
Mn	65.6 ± 0.1	55.9 ± 1.8	42.6 ± 10.7	109 ± 16	129 ± 3	102 ± 1	107 ± 11	85.9 ± 11.2	94.0 ± 4.2
Fe	9987 ± 153	2282 ± 8	716 ± 42	10462 ± 1404	10521 ± 396	2862 ± 82	3027 ± 175	905 ± 31	1213 ± 133
Co	0.52 ± 0.00	1.02 ± 0.01	0.40 ± 0.04	<1.37	<1.37	<1.37	<1.36	<1.36	<1.37
Ni	7.38 ± 0.15	22.4 ± 0.0	13.5 ± 15.0	16.4 ± 2.4	10.1 ± 0.2	34.1 ± 0.7	27.7 ± 3.5	5.29 ± 0.53	9.05 ± 0.14
Cu	87.1 ± 12.5	195 ± 7	30.0 ± 3.0	94.5 ± 8.9	102 ± 2	225 ± 2	205 ± 17	35.1 ± 0.3	59.7 ± 35.5
Zn	283 ± 0	379 ± 10	71.1 ± 3.7	515 ± 61	546 ± 21	705 ± 2	688 ± 63	127 ± 4	125 ± 0
As	1.18 ± 0.01	2.16 ± 0.04	0.20 ± 0.06	1.17 ± 0.11	1.06 ± 0.02	1.87 ± 0.03	1.68 ± 0.11	0.39 ± 0.01	0.54 ± 0.04
Se	<0.33	<0.32	<0.33	0.50 ± 0.22	<0.33	<0.33	<0.33	<0.33	<0.33
Mo	5.07 ± 0.08	3.73 ± 0.04	0.91 ± 0.06	6.97 ± 0.76	6.81 ± 0.13	4.92 ± 0.04	4.69 ± 0.44	0.89 ± 0.32	1.45 ± 0.06
Cd	0.28 ± 0.03	0.46 ± 0.09	<0.030	0.57 ± 0.06	0.58 ± 0.06	0.89 ± 0.03	0.94 ± 0.06	0.059 ± 0.005	0.060 ± 0.004
Hg	1.69 ± 0.05	1.45 ± 0.02	0.32 ± 0.00	0.35 ± 0.07	0.32 ± 0.08	0.44 ± 0.04	0.65 ± 0.14	0.34 ± 0.02	0.30 ± 0.01
Pb	55.9 ± 0.3	74.3 ± 1.7	23.3 ± 6.4	104 ± 13	110 ± 1	148 ± 1	148 ± 16	37.0 ± 3.0	40.4 ± 1.1

Element	Agroindustrial feedstocks			Biochars					
	GP	RH	EOP	GP400	GP600	RH400	RH600	EOP400	EOP600
B	21.6 ± 0.1	2.29 ± 0.15	3.98 ± 0.08	35.2 ± 1.7	10.1 ± 0.3	2.69 ± 0.04	2.34 ± 0.12	6.83 ± 0.12	1.44 ± 0.07
Na	52.5 ± 24.1	54.3 ± 10.9	170 ± 55	49.9 ± 0.5	32.1 ± 6.8	82.0 ± 40.8	60.1 ± 4.6	196 ± 5	88.6 ± 1.1
Mg	589 ± 20	302 ± 77	104 ± 0	1296 ± 71	522 ± 22	470 ± 5	277 ± 20	199 ± 3	42.1 ± 1.3
Al	<0.059	151 ± 118	<0.059	37.4 ± 4.9	36.7 ± 4.0	100 ± 20	128 ± 14	14.3 ± 12.5	4.47 ± 1.26
K	3721 ± 130	1199 ± 47	2935 ± 248	6899 ± 255	2472 ± 72	2074 ± 83	2136 ± 86	4616 ± 68	1908 ± 123
Ca	5407 ± 195	<471	<311	11551 ± 189	8780 ± 339	833 ± 265	520 ± 97	2469 ± 438	636 ± 98
Cr	1.19 ± 1.01	2.88 ± 2.99	0.33 ± 0.05	4.43 ± 5.16	0.38 ± 0.02	1.16 ± 0.36	0.88 ± 0.09	0.33 ± 0.06	0.26 ± 0.00
Mn	7.62 ± 0.16	176 ± 105	4.56 ± 1.91	18.2 ± 0.5	7.22 ± 0.21	202 ± 12	161 ± 8	4.51 ± 0.18	1.69 ± 0.18
Fe	78.4 ± 13.0	61.7 ± 49.7	48.3 ± 27.5	144 ± 22	56.3 ± 6.7	43.5 ± 1.4	73.3 ± 12.5	55.4 ± 17.3	29.5 ± 11.4
Co	<0.22	<0.21	<0.21	<1.36	<1.37	<1.36	<1.37	<1.37	<1.37
Ni	0.24 ± 0.14	0.46 ± 0.49	<0.12	0.57 ± 0.10	0.30 ± 0.17	0.56 ± 0.19	2.10 ± 0.45	1.07 ± 0.86	<0.082
Cu	30.3 ± 1.2	32.4 ± 40.0	26.6 ± 33.2	41.2 ± 0.9	7.77 ± 1.12	4.52 ± 0.03	4.60 ± 0.16	4.81 ± 0.12	1.66 ± 0.13
Zn	14.9 ± 2.1	19.1 ± 7.0	5.86 ± 1.50	32.4 ± 4.3	12.7 ± 3.6	30.8 ± 7.6	23.5 ± 1.7	7.19 ± 2.35	3.36 ± 0.18
As	<0.040	0.12 ± 0.03	<0.040	<0.017	<0.017	0.22 ± 0.01	0.10 ± 0.01	<0.017	<0.017
Se	<0.33	<0.33	<0.32	<0.33	<0.33	<0.33	<0.33	<0.33	<0.33
Mo	0.39 ± 0.09	1.19 ± 1.25	0.20 ± 0.01	0.20 ± 0.01	0.31 ± 0.05	0.21 ± 0.09	0.30 ± 0.02	0.19 ± 0.02	0.22 ± 0.01
Cd	<0.029	<0.029	<0.029	<0.075	<0.068	<0.029	<0.030	<0.030	<0.030
Hg	0.37 ± 0.00	0.35 ± 0.06	0.38 ± 0.08	0.56 ± 0.02	0.55 ± 0.03	0.91 ± 0.04	0.64 ± 0.00	0.49 ± 0.02	0.53 ± 0.00
Pb	0.65 ± 0.40	1.51 ± 1.86	<0.002	1.08 ± 0.08	0.51 ± 0.20	0.63 ± 0.26	0.56 ± 0.16	0.31 ± 0.26	0.13 ± 0.04

values are expressed as average ± standard deviation

$-CH_3$ and $-CH_2$ symmetric and asymmetric stretching (Ahmad et al., 2012; Coates, 2000; Hossain et al., 2011), while the latter peaks are most likely attributed to C-O stretching (Zhao et al., 2017). Similarly, weak bands in the range 1698-1694 cm^{-1} appeared only in the spectra of biochars of agro-industrial origin and could be assigned to C=O groups (Gai et al., 2014; Tran et al., 2016), possibly associated with the presence of carboxylic acids on these materials (Coates, 2000). In turn, both RH-derived biochars also presented a characteristic set of peaks, at 1096, 800 and 468 cm^{-1}, which may be assigned to Si-O-Si groups (Wang et al., 2018). Finally, weak bands around 750, 780 and 800 cm

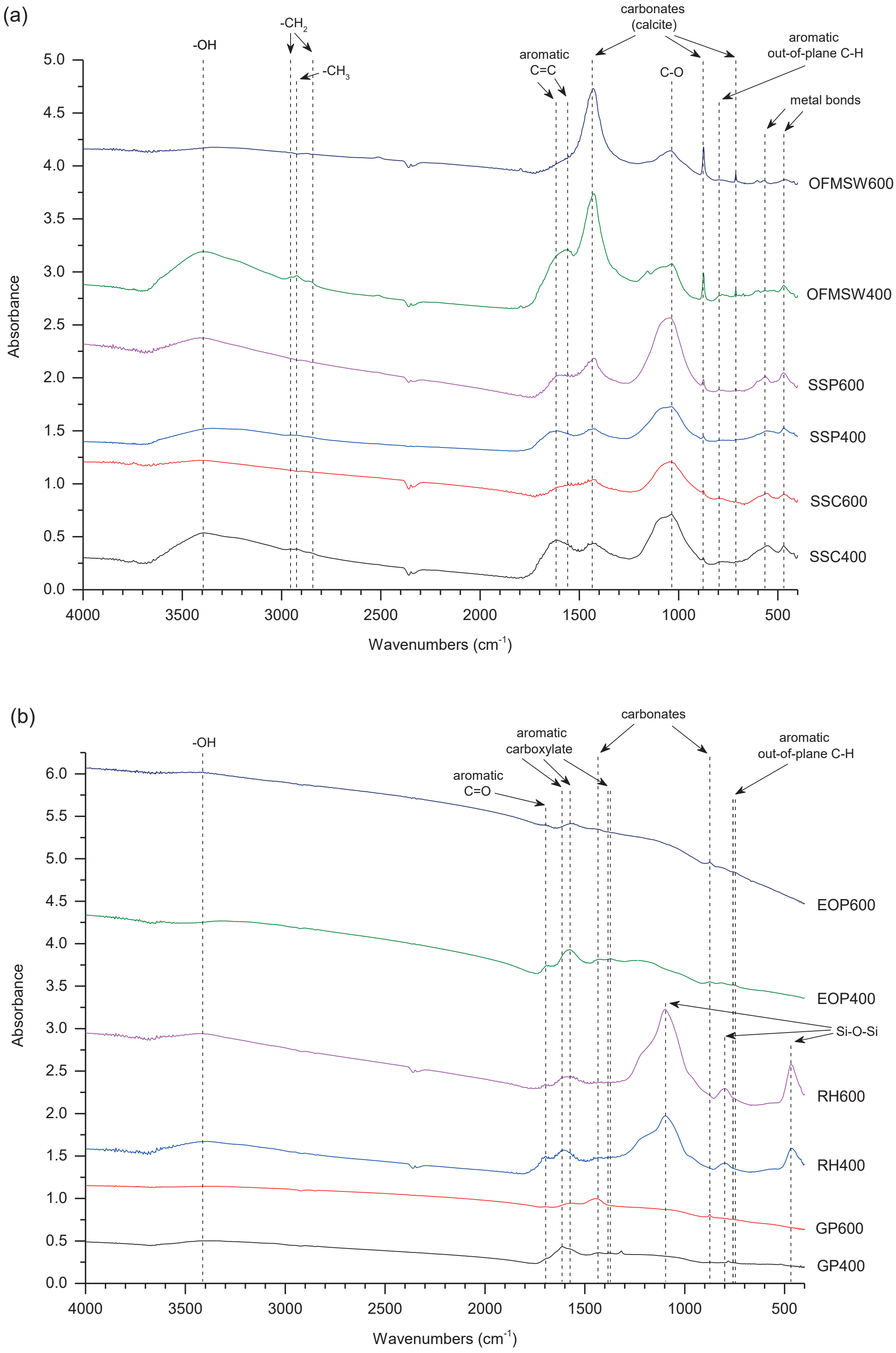

FIGURE 4: FT-IR spectra of (a) municipal and (b) agroindustrial biochars.

^{1}, and below 600 cm^{-1}, could probably be associated with aromatic out-of-plane C-H bending (Coates, 2000), and the presence of metal bonds (Hossain et al., 2011), respectively. FT-IR spectra patterns and bands similar to those of the present study have also been observed in previous studies investigating materials of similar origins (Chen et al., 2014; Lu et al., 2013; Mitchell et al., 2018; Yi et al., 2016; Taherymoosavi et al., 2017; Trakal et al., 2017; Zhang et al., 2018).

As far as the influence of pyrolysis temperature is concerned, it was noticed that the increase to 600°C resulted in a general intensity reduction for O-H bands around ~3000 cm^{-1}, as well as for aromatic bands around ~1600 cm^{-1}. On the other hand, the peaks attributed to carbonates were preserved, with slight intensity variations. Moreover, while $-CH_3$ and $-CH_2$ bands, present on municipal biochars produced at 400°C, were completely eliminated with the increase in temperature, such an effect was not noticed for C-O peaks being observed for the same materials, with them being preserved. At the same time, while there was no significant change in the carboxylic acid bands of agro-industrial biochars, the increase in temperature most likely caused a reduction in carboxylate groups on the same materials, manifested by the elimination of peaks around ~1380 cm^{-1}. Finally, the bands being observed below 800 cm^{-1} were maintained only for municipal biochars produced at 600°C.

3.7 Germination assays

According to the results, none of the biochars had a negative effect on Lepidium sativum germination, since in all assays a 100% germination rate was noted (data not shown). As far as root growth is concerned, according to a scale reported by Nieto et al. (2016), phytotoxicity is indicated when GI values are below 80%, while values above 100% are an indication of phytostimulatory effects. Consequently, none of the examined biochars could be considered as phytotoxic at a 1% amendment rate, since GI values were all above 80% (Figure 5). Moreover, six biochars, specifically SSC600, SSP600, GP400, GP600, EOP400 and EOP600 could be considered as phytostimulant under the examined conditions, as a result of their corresponding GIs being greater than 100%. Nevertheless, some degree of inhibition, manifested by positive RGI values (Figure 5), was noted for the remaining six biochars, specifically SSC400, SSP400, OFMSW400, OFMSW600, RH400 and RH600.

In the literature, root growth inhibition has been mainly associated with the effect that the addition of biochar can exert on the soil solution salinity, by inducing osmotic stress (Buss et al., 2016; Intani et al., 2018; Mumme et al., 2018). This was most likely the reason for the inhibition no-

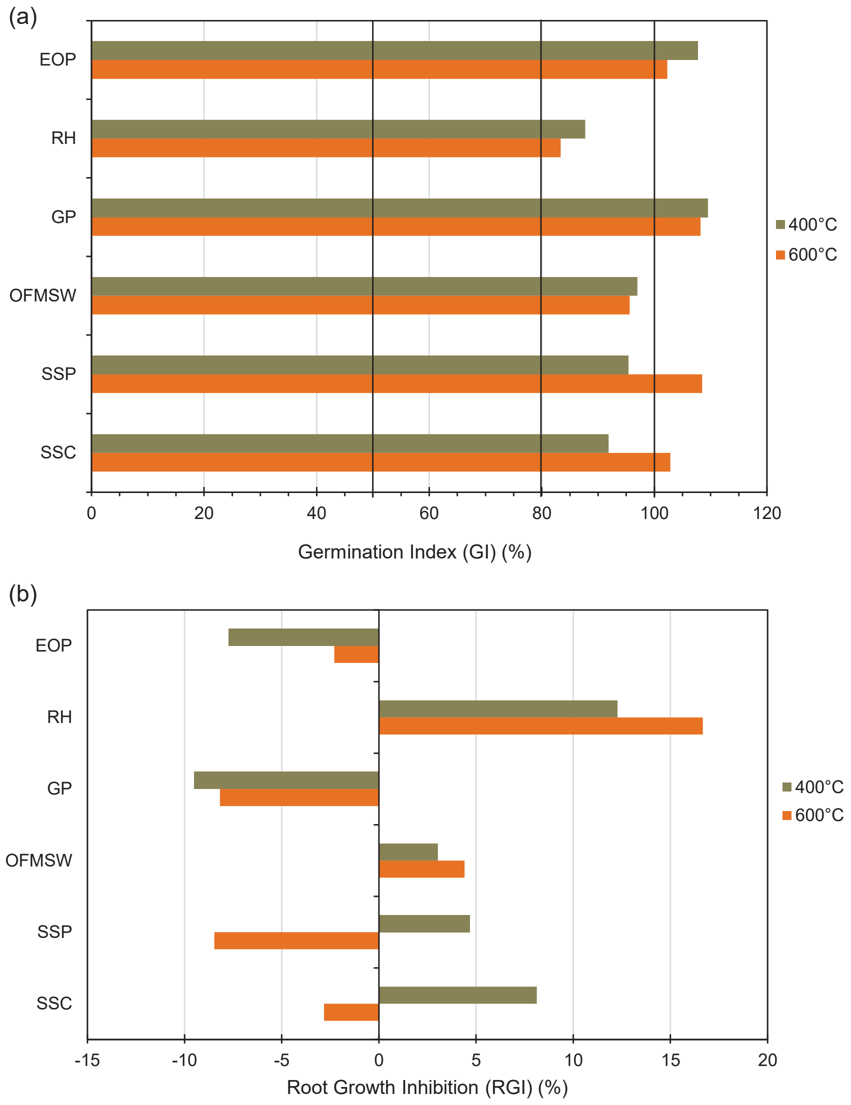

FIGURE 5: (a) Germination Index (GI) (%) and (b) Root Growth Inhibition (RGI) (%) obtained from germination assays with biochar amendment rate 1%.

ticed in the present study for the four biochars of municipal origin, even if this negative effect was quite moderate. Although EC values corresponding to these biochars could suggest such an effect, in reality they could only partially predict the outcome. More specifically, if only EC was considered, the municipal biochars OFMSW400, OFMSW600 and SSC400 would be more likely to cause some inhibition, as mentioned earlier (§3.3.). Nevertheless, SSP400 also showed similar results, although its EC was not equally elevated. Therefore, EC values should not be used as the sole indicator for salinity levels. Such a conclusion was also drawn in a previous study (Buss et al., 2016). What indeed contributed to the increased salinity was most probably the elevated mineral load of the biochars in question (Table 5), especially in terms of PTMs. In fact, the elevated presence of such elements, including PTMs, in more soluble form has been previously associated with osmotic stress (Rucińska-Sobkowiak, 2016). Interestingly, OFMSW-derived biochars appeared to cause a lower degree of inhibition compared with the other materials. This could be attributed to the counterbalancing between their high EC and their low cumulative PTMs content, high pH and high macro-nutrient (Ca, K, Na, Mg) content. Indeed, it has been previously reported that at low amendment rates biochars with high pH and K concentrations could have a positive effect on root growth (Buss et al., 2016). Moreover, although SSC600 and SSP600 were also characterized by quite elevated PTMs loads, they showed no inhibiting effects. This could be related to their production temperature, since it has been shown that the bioavailability of PTMs is reduced for biochars produced at higher pyrolysis temperatures (Zeng et al., 2018).

As far as biochars of agroindustrial origin are concerned, the only materials that appeared to cause some inhibition were the two RH-derived biochars, which in fact were those ultimately being associated with the highest RGI values among all tested biochars. These results are not consistent with EC data, since GP400 and GP600, which presented higher EC values than RH400 and RH600, did not cause inhibition, but instead they exerted a phytostimulant effect on Lepidium sativum seeds, as did EOP400 and EOP600. The positive effect of GP- and EOP-derived biochars may most likely be attributed to their pH and macro-nutrient contents (Buss et al., 2016), as well as probably to their comparatively lower PTMs content. On the other hand, the inhibition caused by RH400 and RH600 may be mainly related to the quite pronounced SiO_2 content of these biochars (Table 6), considering that SiO_2 has been reported to eventually have toxic effects on root elongation at elevated concentrations (Lee et al., 2010).

It is worth mentioning that some authors have linked root growth inhibition with the presence of organic water-soluble potentially toxic elements (e.g. PAHs, phenolic compounds, etc.) on biochars (Buss and Mašek, 2014; Gell et al., 2011; Intani et al., 2018). In the present study it was unlikely that such a phenomenon took place, since all biochars were washed before being used in germination assays and this procedure would have removed toxic or inhibitory water-soluble substances (Intani et al., 2018).

3.8 Major oxides contents

XRF results presented in Table 6 refer only to selected biochars, chosen on the basis of the other characterization analyses and germination assays. Specifically, the selected materials were biochars of municipal origin and RH-derived biochars. According to the data, CaO was present in all biochars derived from SS and OFMSW, which is consistent with the FT-IR spectra regarding the presence of calcite in biochars before ignition (Leontakianakos et al., 2015), especially in the case of OFMSW400 and OFMSW600. Other oxides being detected in considerable amounts in municipal biochars include Fe_2O_3, SiO_2, P_2O_5 and Al_2O_3, while lower

TABLE 6: Major oxides content (%) in ash samples of selected biochars, on a dry basis.

	SSC400	SSC600	SSP400	SSP600	OFMSW400	OFMSW600	RH400	RH600
Al_2O_3	2.37	3.66	9.35	10.8	1.85	5.02	0.79	0.78
CaO	21.6	27.7	28.9	29.3	48.7	47.1	0.73	0.89
Cr_2O_3	1.18	0.41	0.80	0.56	0.48	0.14	0.002	0.007
CuO	0.09	0.08	0.13	0.12	<0.005	<0.005	<0.005	<0.005
Fe_2O_3	42.5	28.5	14.2	10.7	8.98	4.59	1.17	1.21
K_2O	0.75	1.04	1.84	2.14	2.01	3.20	0.06	0.20
MgO	0.80	<0.005	2.90	2.90	2.00	3.67	0.84	0.82
MnO	0.43	0.15	0.15	0.11	0.17	0.11	0.15	0.17
Na_2O	<0.005	<0.005	<0.005	2.10	<0.005	2.55	0.78	0.54
NiO	0.73	0.14	0.25	0.15	0.21	0.06	0.02	0.02
P_2O_5	11.4	15.0	16.0	16.0	2.57	2.48	0.13	0.24
PbO	<0.005	<0.005	0.25	<0.005	<0.005	<0.005	<0.005	<0.005
SiO_2	15.4	20.7	22.5	22.8	23.3	25.3	89.2	97.1
SO_3	0.50	<0.005	0.28	0.22	7.27	5.40	<0.005	<0.005
TiO_2	0.90	1.13	1.13	1.12	0.63	0.85	<0.005	<0.005
ZnO	0.28	0.24	0.38	0.38	0.11	0.12	<0.005	<0.005

percentages of metal oxides in these materials are consistent with the considerations regarding metal bonds made in §3.6. Similarly, the results obtained for RH400 and RH600 confirmed the highly significant presence of SiO_2 in these materials, again corroborating the FT-IR analysis.

4. CONCLUSIONS

The present study focused on the characterization of twelve biochars derived from six types of biomass and produced at two temperatures, aiming at evaluating their potential use in agronomic and environmental applications. Both pyrolysis temperature and feedstock type appeared to have a significant effect on biochar characteristics, with the data implying various potential applications for the examined materials.

In terms of agronomic application, based on the characterization results, biochars generated at 400°C may be more able to improve soil characteristics, as well as enhance nutrient and water retention, compared to higher-temperature materials, due to their lower bulk density, as well as higher CEC and hydrophilicity, respectively. On the other hand, biochars obtained at 600°C could offer greater carbon stability due to their higher aromaticity, and thus be more suitable for carbon sequestration. Moreover, almost all biochars of agroindustrial origin, as well as some biochars of municipal origin may be good candidates for ameliorating acid soils, as a result of their high pH values. Although the germination assays showed no phytotoxic effects of the investigated biochars on Lepidium sativum seeds, under the examined conditions and at a soil amendment rate of 1%, prior to real-case use of these materials at rates >1%, a thorough assessment of their potential inhibitory or toxic effects should be performed in relation to the specific application for which they are intended (type of soil, type of plant, etc.). Attention should be given on the biochars' salinity and mineral contents, especially in terms of bioavailability.

As far as environmental applications are concerned, higher CEC as well as the stronger presence of surface functional groups in biochars produced at 400°C, suggest that these materials may be more suitable for metal retention in both soil and aqueous media compared with those produced at 600°C. Moreover, the presence of functional groups coupled with the higher polarity of the low temperature biochars is an indication of a potentially better performance with polar organic contaminants. On the contrary, biochars produced at 600°C, being characterized by higher specific surface area and higher hydrophobicity, may be more effective in remediating contamination by non-polar organic compounds. Furthermore, pH values suggest that several of the studied biochars could be effectively used to induce metal precipitation, while pH_{PZC} values reveal a potential affinity of OFMSW400, OFMSW600 and GP600 also for anionic contaminants.

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SAMPLING AND SUB-SAMPLING OF GRANULAR WASTE: SIZE OF A REPRESENTATIVE SAMPLE IN TERMS OF NUMBER OF PARTICLES

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ABSTRACT

This paper elucidates the theoretical principles behind the calculation of the size of a representative sample of granular solid waste. The key concept is the number of particles that must be present in a sub-portion of matter to be representative of a larger portion of matter. This depends on the fraction of particles in the waste batch showing the properties of interest, which shall be measured. A representative sample must include a fraction of particles of interest reliably similar to that of the waste batch to be characterized, with a controlled variability. In this context, it is demonstrated that the number of particles of interest that must be collected in a representative sample is 100. From this requirement, the mass of a representative sample can be calculated based on the knowledge of the frequency of particles of interest of the waste lot to be characterized. Data on particles concentrations in different samples of WEEE plastic scraps exemplifies how the presence in the sample of enough rare particles showing the property of interest is key to ensure reliable measurements. Further, the assumptions made on the controlled degree of variability to determine the minimum number of particles are discussed based on data on achievable intra- and inter-laboratory variability of analytical standards for waste characterization. Accordingly, the mass of laboratory samples and test portions recommended in published sampling plans or analytical standards are assessed for the occurring number of particles.

1. INTRODUCTION

Reliable data on characterization of granular solid wastes are needed to allow informed decisions on the appropriate way in which they should be treated (or not), recovered or disposed of. However, for practical and economical reason, it is impossible to analyse the entire batch of waste to be managed. Therefore, smaller portions, also known as samples, shall be collected, and brought to the laboratory to be further analysed. Similarly, the lab operators will investigate smaller fractions, usually defined as test portions, derived from the sub-sampling of the laboratory sample. Data reliability is thus ensured i) when the specific analytical standard is correctly performed and ii) when laboratory samples and test portions can be thought as "representative", i.e., their composition is "reliably" similar to the one of the waste lot to be characterized.

From the prospective of analytical chemistry and chemical metrology, the degree of reliability linked to an analytical result is determined by the magnitude of its uncertainty, calculated based on the achieved variance from repeated analysis performed on a set of identical samples (EURACHEM and CITAC, 2012; 2019). Similarly, the so-called "Theory of Sampling" (ToS) refers to the variance originating from different specific types of "errors" (Gy, 2004a; 2004b; 2004c; 2004d). Despite being developed independently, both approaches agree on describing the total variance as constituted by the sum of several sources, the main being the analytical step and the sampling activity.

While much effort is usually provided to the correct performance of the analysis, the theory (and practice) of representative sampling is still not mastered in the waste community.

Indeed, the EU technical standards on waste sampling provide qualitative information on how to perform representative sampling and quantitative methods to determine the mass of a representative laboratory sample or test portion: these instructions are resumed, for each waste stream, within a so-called "sampling plan" (EN 14899, 2016; CEN/TR 15310-1, 2007; EN 15002, 2015). Nevertheless, the aforementioned standards do not explain the theoretical principles behind these formulations. Notably, only Khodier

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et al., (2019), remarkably addressed this topic, but focusing on a specific waste type sampled according to a national Austrian standard, which was judged not optimal for the type of analysis performed (i.e., material composition analysis).

In this context, this paper addresses the theoretical bases behind the proposed formulas for the determination of the size of a representative sample of granular solid waste in the related EU technical standards. In doing so, it introduces the key concept of the "number of particles" that should be present in a sample to be representative of a bigger batch of granular solid material, assuming a wanted/controlled variability between equivalent samples, and a skewed distribution, among particles, of the parameters to be quantified (this latter to be known a priori or estimated). In particular, the equations presented in sampling standards are revisited here starting from that distribution. Here, the word "particle" refers to the physically distinct portion of solid mater not bound to the other portions at the time of sampling. It is equivalent to part, piece or scrap.

Sampling plans address the waste heterogeneity/variability at the scale of a population (for instance annual production or daily stream of waste) by considering factors that influence ("stratify") the constituents in the population (EN 14899, 2016). More "homogeneous" populations or sub-populations are then sampled. Several mono- or composite- (i.e., made of increments) representative samples are taken and analysed. However, this paper addresses only the heterogeneity/variability occurring in laboratory samples taken from a population or sub-population of solid waste, as well as the test portion. In other words, only the variability of the properties of individual particles making up the sample are considered here and used to calculate the mass of representative samples. This is referenced as "fundamental variability" in the ToS. This implies that the contributes to variability derived from both the so-called "incorrect" sampling errors (i.e., originating from blunders in sampling performance) or the unavoidable "grouping and segregation error" (Gy, 2004a; 2004b; 2004c; 2004d), that covers the spatial heterogeneity (due to particle size distribution) of the waste, are not considered in this study. However, a method to calculate the size of a representative sample considering both the particles properties distribution and the possible size-property relationships will be proposed by the authors in a following paper.

Further, this paper presents data about the occurring distributions among particles of wastes of parameters of interest. The influence of these distributions on the results measured in the lab is also discussed.

The assumptions made to derive the number of particles in a representative sample are then evaluated based on the variability monitored in real cases. In particular, the analytical variability (intra- and inter-laboratory) from the analysis of i) reference materials, ii) laboratory samples and iii) standards validation trials were used.

Finally, the size of several samples and test portions, as indicated by published sampling plans and analytical standards usually applied for waste, are assessed in terms of number of particles to check if the requirement proposed in the theoretical part can be fulfilled.

2. REPRESENTATIVE SAMPLING IN TERMS OF NUMBER OF PARTICLES

2.1 Theoretical basics: binomial probability distribution

Sampling performance allows to produce, from a population of discrete material (e.g., a waste lot) a subset (i.e., a "sample"), the elements of which reliably resemble the population itself in terms of several characteristics of interest. Also, a sampling action can be conceptualized as a selection, from a batch, of a number n of different elements ("particles"). In these terms, a sample can be thought as the sum of n particles individually drawn from a lot. The sample will be considered representative if characterized by a reliably similar proportion, occurring between its elements, of the properties of the population (i.e., the batch of materials to be characterized).

Given this background, the probability to get a specific number x of particles showing a researched characteristic, within n repeated drawings (of 1 particle) from a lot characterized by a fraction p of the researched feature (or, better, the fraction of particles in the lot showing the presence of the researched characteristic), can be mathematically interpreted by the binomial distribution B(x; n, p):

$$B(x; n, p) = \frac{n!}{x!(n-x)!} p^x (1-p)^{n-x} \qquad (1)$$

The distribution B(x; n, p) is characterized by an expected value μ (i.e. the value of x characterized by highest probability) and by a variance σ^2 (i.e. how far a set of recorded x_i - derived from a set of identical samples constituted by n drawn particles- are spread out from the expected value μ):

$$\mu = np \qquad (2)$$
$$\sigma^2 = np(1\text{-}p) \qquad (3)$$

Consequently, each sample (intended as n collected particles) is characterized by a specific $\acute{p}_i = x_i / n$, which is the estimator of p in the sample itself. By definition, the more $\acute{p}_i$ will resemble p, the more representative of the lot will be the collected sample.

The resulting squared coefficient of variation $CV_p{}^2$ (also known as Relative Standard Deviation) is therefore

$$CV_p{}^2 = \frac{\sigma^2}{\mu^2} = \frac{np(1-p)}{n^2p^2} = \frac{(1-p)}{np} \qquad (4)$$

Here, CV_p is the coefficient of variation indirectly identifying the extent of variability between different $\acute{p}_i$, observed on a set of identical samples, in relation to the true value p. In other words, the lower the CV_p, the more $\acute{p}_i$ will resemble p, i.e., the more representative will be the collected samples. In particular, as CV_p decreases with increasing n, the exact value of p can only be more and more precisely approached in samples containing higher and higher numbers of particles.

Finally, from Equation 4 we can derive n, the number of particles constituting the sample characterized by a fraction $\acute{p}_i$ of particles of interests, as:

$$n = \frac{(1-p)}{CV_p{}^2 p} \qquad (5)$$

Indeed, the calculation needed to estimate n is therefore based on the values of the parameters p and CV_p, which must be known, measured or assumed for the lot to be characterized.

2.2 Practical implications: meaning of p and CV_p in granular waste

Notably, Equation 5 is incorporated in the equations indicated in the technical standards giving the mass of the laboratory or test samples for wastes (i.e., CEN/TR 15310-1, 2007; EN 15002, 2015).

In the cited standards, p is defined as the “fraction of particles with a specific characteristic” (CEN/TR 15310-1, 2007) or “fraction of the particles with the property of interest” (EN 15002, 2015), this latter being the sole referring to the concept of “number of particles” in the lot with the characteristic of interest which should be present in a representative sample with the same proportion.

To achieve this goal, granular waste lots are conceptually modelled as a population of particles, each one showing or not a given property of interest. This latter can be defined as a chemical concentration, geometrical size (i.e., granulometry) or generic quality occurring in the X-th percentile of the population to be analysed. In the waste field, particles with the “property of interest” are often intended as being characterized by a chemical concentration (e.g., trace elements, PolyAromatic Hydrocarbons, Flame Retardants, etc.), which is seldom 100% on the particle weight base. The concentration of constituents in a waste particle is rather a continuous function from the limit of quantification to the maximum, depending on the genesis of the particle (i.e., from solid fractionation, multi-mineral solid fraction, massive precipitation, surface precipitation, surface complexation, particles aggregation, etc.). Consequently, continuous variables such as chemical contents are conceptually transformed into a binary property defined by the sampler: e.g., each particle could or could not be characterized by a chemical concentration greater than an arbitrary value.

Given this background, the measured value of a characteristic of interest in a sample of granular solid waste (but this could be valid also beyond the sole waste field) can be assumed as the mean value of that characteristic as measured between all the particles making up the sample. Therefore, knowing or assuming how it is distributed within particles in the lot is crucial. If the distribution of concentrations among particles can be considered normal, as it is the case for industrial products, the last centiles are much less concentrated relatively to the mean, and their contribution is less critical. This implies that, where all particles making up the lot to be analysed contain almost the same individual concentration of the measurand, p can be set to 1. Therefore, sampling and analysing one single particle would be enough.

On the contrary, where the properties of interest are characterized by distributions skewed by some highly concentrated and rare particles (i.e., 10 to 100 times the mean), up to the “nugget” distribution (e.g., one 100% particle in thousands or millions of 0% particles), the fraction of these “rare” particles collected in the sample will enormously affect the mean concentration measured, finally determining the reliability (or, better, the representativeness) of the measured data. These latter conditions are the more expected in the waste field, where particles composition is usually not generated under controlled design criteria, as instead happens for industrial production. In these cases, p should be assumed much lower than the unity: this is reflected in EN 15002, which suggests using 0.1 to 0.001, respectively for parameters of interest present at a “major” (e.g., dry matter) or “minor” (e.g., trace metals) level in the sample.

The coefficient of variation CV_p is referred by the standards solely by using the term CV (i.e., without explicit mention to the relationship with $\acute{p}_i$) and defined as “the desired coefficient of variation caused by the fundamental error”. The fundamental error is not further defined, but well the fundamental variability as “the inherent variability shown by a material and its analysis at the smallest scale of measurement”. The expression “fundamental error” of the standard could result quite confusing, as it just implicitly refers to the “fundamental sampling error” of the TOS (Gy, 2004a; 2004b; 2004c; 2004d), whose calculation in the waste field is seldom performed, being based on many assumed parameters, not easily measurable as operational factors.

However, the standards likely suggest assuming CV (or CV_p, equivalently) as due to the analytical variability obtained with the smallest possible (“homogeneous”) test portion in the same laboratory by the same operator, i.e., under “repeatability” conditions. Lower variability can simply not be obtained: in other words, a higher degree of representativeness cannot be provided by the sample. The minimum measurable CV is thus simply fixed to the CV_r, defined as the lowest variability that can be achieved only due to material heterogeneity and analysis variability at the lowest scale of measuring (i.e., matching with the definition of the fundamental variability):

$$min\ (CV_p \approx CV) = CV_r = 0.1 \tag{6}$$

The value of CV_r for specifical analytical protocols are routinely measured in laboratories as part of their quality control system. For the sake of sampling, in CEN/TR 15310-1 and EN 15002, it is simply suggested to generally use CV = 0.1 as respectively “well accepted value” or “typical value”, without further explanations (as assumed by the authors and stated in Equation 6).

In the normal distribution, given the mean x and the standard deviation s, the confidence interval of the mean (i.e., covering 95% of the data set) is the interval [x – 1.96 s ; x + 1.96 s] or equivalently [x – 1.96 CV*x ; x + 1.96 CV*x], which can be rounded to x ± 2 CV*x . By applying Equation 2, the confidence interval of the estimator of p obtained by repeated sampling of samples (which is a normal distribution) is $\acute{p}_i \pm 0.2\ \acute{p}_i$ (or $\acute{p}_i \pm 20\%$).

2.3 From the number of particles to the mass of a representative sample

As p can be assumed <<1 for waste, and according to Equation 6, Equation 5 can be rearranged as:

$$np = \frac{(1-p)}{{CV_p}^2} \approx \frac{1}{CV_r^2} \approx 100 \tag{7}$$

In Equation 7, np is the "number of particles showing the property of interest" that must be in a representative sample. Equation 7 simply demonstrates that the hypothetical number of particles of interest in a representative sample is 100, whatever p is. This result is called the "number of target particles" by Bunge (2019) and was a conclusion from the same author (starting from another approach) and confirmed empirically (Bunge and Bunge 1999). Otherwise, the other extremely simple conclusion is that a representative sample must contain a total number n of 100/p particles, without assumptions on concentrations and size. It must be noted that in cases where p cannot be considered << 1 (e.g., chemical waste macrocomponents, general waste material fractions, etc.), the simplified formula of Equation 7 will determine higher number of particles than the sole Equation 5 and thus it can be considered as a conservative approach (i.e., leading to samples characterized by higher n).

Furthermore, Equation 7 is based on the theoretical variability imposed in terms of CV_r: here, assuming a larger variability in the results (i.e., $CV_r > 0.1$) will lead to fewer particles in in the sample (as can be easily recalculated from Equation 7) together with a consequent lower degree of sample representativeness. In other words, samples containing less than 100 particles of interest could lead to a higher uncertainty/variability associated with the measurement of the parameter of interest.

As previously introduced, in the horizontal standards for waste sampling and test portions preparation from laboratory samples (CEN/TR 15310-1, (2007) and EN 15002, (2015), extended with the f factor in EN 15413, (2011) for solid recovered fuel), Equation 5 (therefore also Equation 7) results incorporated in the equation giving the mass of the laboratory sample or of the test portion:

$$M_{sam}(kg) = \frac{\pi}{6}(D_{95})^3 * \rho_{solid} * g * f * \frac{(1-p)}{CV^2 p} \tag{8}$$

Where, D95 and D05 are respectively the 95th and 5th mass percentiles of particles diameters, ρ_{solid} is the particles solid density, g is a correction factor for particle size distribution (for uniform distribution, i.e., $D95/D05 \leq 1$, g=1; for narrow distribution, i.e., $1 < D95/D05 \leq 2$, g = 0.75; for medium distribution, i.e., $2 < D95/D05 \leq 4$, g = 0.5; and for broad distribution, i.e., $4 < D95/D05$, g = 0.25) and f is a form factor, defined as the ratio of the volume of the D95 particles as a multiple of their three dimensions, divided by the volume of a cube of D95 size. In this respect, Equation 8 allows to calculate the mass of the laboratory sample as the number n of particles needed in the sample i.e., $(1-p)/(CV_p^2\ p)$, multiplied by the mean mass of particles (i.e., $\pi/6\ (D_{95})^3 * \rho_{solid} * g * f$), approximated as the mass of a sphere with the diameter of the largest particles averaged among the particle size distribution. In particular, the g factor takes partially into account the fact that many particles are finer than D95, while the f factor is used to have a more realistic approach of the volume of the large particles (EN 15413, 2011).

In this context, it should finally be highlighted that the standards used for waste sampling introduce a further requirement, needed to avoid particle segregation during practical sampling performance. This comes from the fact that the use of the binomial probability distribution to model sampling is justified only if each sampling action can be considered probabilistic, i.e., each particle is characterized by a uniform non-zero probability to be caught. This condition is included in the definition of correct sampling given by Gy (2004a), as mandatory to derive reliable (i.e., representative) samples.

In practice, individual samples are the result of several extractions of equivalent increments, considered as a subset of neighbouring particles of the lot. In this regard, we can interpret the requirements laid down in the standard CEN/TR 15310-1, (2007), which are i) on the actual size of the sampling instrument (i.e., width, height and length must be at least 3 times the size of the largest particles) and ii) on the consequent minimum increment mass M_{inc} (Equation 9), as conditions to perform probabilistic sampling and avoid large particles segregation:

$$M_{inc} = (3*D_{95})^3 * \rho_{bulk} \tag{9}$$

where D95 is the 95-percentile particle diameter and ρ_{bulk} the bulk density of the material. It must be kept in mind that Equation 8 and Equation 9 are only approximations.

2.4 Estimation of p for some granular waste for compliance assessment

The fraction of highly concentrated particles of interest (p) that must not be exceeded in waste to not trespass a concentration limit (CL), intended as the mean concentration among all particles, can be calculated from the functional concentration (FC) of the analyte in the products that became waste. Here, a CL is a concentration that must not be exceeded for compliance with waste regulation or (secondary) product specifications. In this respect, the particles of interest can be assumed as those with the recommended FC. FC can be found in producer's catalogue and in technical literature or product safety data sheets.

Consequently, if the other particles of the lot have a null concentration and all particles are characterized approximately by the same mass, the mean concentration of the lot of particles is equal to pFC + (1-p)0 = pFC. That concentration must be lower or equal to the CL, thus leading to $pFC \leq CL$ or $p \leq CL/FC$. Therefore, the fraction of particles of interest is simply lower or equal to the ratio of the CL in waste and the FC in products.

Indeed, this approach is limited to waste originating from products with a known composition, and with all the particles having approximately the same mass (e.g., plastic scraps after shredding). Examples are additives of fire-protected plastics: the CL for the persistent organic pollutants polybromodiphenylethers (PBDEs), the hexabromocyclododecane (HBCDD) and the short-chain chlorinated paraffins (SCCPs) under consideration are 200 mg kg^{-1}, 100 mg kg^{-1} and 540 mg kg^{-1}, respectively. As their maximal reported FC are 180,000 mg kg^{-1}, 40,000 mg kg^{-1} and 30,000 mg kg^{-1}, respectively, the samples must be large enough to capture particles with a frequency of p = CL/FC = 0.0011, 0.0025 and 0.0140. In other words, 11 particles with a concentration of 180,000 mgPBDE kg^{-1} and 9989 particles with a zero concentration have a mean concentration of 200 mgPBDE kg^{-1}, which is the concentration that a representative sample must be able to measure for compliance assessment, here with a relative variability of 10% when the sampling and analysis operations are repeated. The corresponding n for the three cases above = 100/p = 100,000, 40,000 and 7,000 particles (Vencovski et al. 2021).

3. MATERIALS AND METHODS

For the aim of this study, three types of data or information were collected from published documents in the scientific or technical literature and here used for three different analyses.

3.1 Assessment of concentration distributions at particle scale

First, single particle concentrations of Br were collected from Hennebert, (2020) as analyzed through portable XRF, calibrated with reference material for Br, on three samples of plastic scraps originated from shredding of waste from electric and electronic equipment (WEEE). The first sample was composed by a total of 200 particles and was collected immediately after shredding of one lot of WEEE; the second, counting 200 particles, was sampled after shredding and further density sorting (usually applied to sort out the denser brominated scraps). The third sample consists on 350 sorted dense plastic scraps from waste of cathode ray tubes (CRD). Descriptive statistics (mean, median, maximum value, standard deviation and CV) was performed on the collected single particles concentrations of Br from the considered samples. Further, histograms were built for datasets together with cumulated histograms to graphically summarize the occurring distributions among the collected particles concentrations. All statistical work and graphical representations were performed using Microsoft Excel® 2016.

3.2 Assessment of the observed variability at analytical scale

Then, data on observed CVs were collected as calculated from 6 sets of analytical results obtained by the performance of different analytical methods (i.e., measuring different parameters) applied to specific materials:

- Br and Sb concentrations obtained from repeated XRF analysis performed by the authors on a certified reference plastic material;
- Elemental and Brominated Flame Retardants (BFR) concentration determined through Ion Chromatography (IC) on certified reference plastic material (Haarman et al. 2018);
- Br and Sb concentrations derived through IC and Inductively Coupled Plasma (ICP) analysis performed on laboratory samples of plastics from small household appliances (SHA) and screens (Hennebert and Filella 2018);
- Concentrations of Polyaromatic hydrocarbons (PAH), Polychlorobiphenyls (PCB) and Dioxins (PCDD/PCDF) derived from an intra and inter-laboratory ring test validating the related methods EN 16181, (2018), EN 16167, (2018) and EN 16190 applied on samples of sludge, compost and soil (Kalbe et al., 2019);
- Elements concentrations determined through ICP and IC on water extracts derived from standardized leaching tests applied on waste materials and presented as validation data in the dedicated technical standard (EN 12457-2, (2002));
- Results from ecotoxicological bioassays involving different organisms (marine bacteria, freshwater algae, soil bacteria and earthworms) performed on reference test media (i.e., liquid or solid media spiked with known concentration of contaminants), proposed for assessment of the hazard property HP 14 of waste (Pandard and Roembke 2013, Hennebert 2018) (EN ISO 11348-3, (2008), EN ISO 8692, (2012), ISO 18187, (2018), ISO 17512-1, (2020)).

The collected data on analytical CVs were first used to compare the achievable inter-laboratory and intra-laboratory variability by the considered different analytical methods. These results were then used to assess the reliability of the assumption made on the value of the CV_r in Equation 6 to derive the requirement on the needed number of particles of interest in a representative sample (i.e., Equation 7).

3.3 Assessment of number of particles in laboratory samples and test portions

The values of size (mass or volume) of samples were collected as indicated in 6 sampling plans, designed for different waste materials, and already published in technical reports or standards. The main general instructions are described as follows:

- Waste wood from furnitures. Increments of 5 m^3 are taken. Their number is 20 + 0.06 times the mass of the batch (in tons). This composite sample is shredded on site and sieved in two fractions (80 – 15 mm, and < 15 mm). Each fraction is sampled in order to make a laboratory sample of 2 kgs (Eco-Mobilier and Valdelia, 2018);
- French municipal solid waste incinerator bottom ashes (both maturated and un-maturated). Six to one hundred increments of 10 liters are taken, mixed and quartered until a laboratory sample of 2 to 8 kg is obtained (SVDU, 1995);
- Shredded plastics of WEEE from SHA (Wäger et al. 2011);
- Shredded plastics of WEEE from SHA (CENELEC TS 50625-3-1, (2015));
- Waste from plastic lamps (CLC/TS 50625-3-2, 2016);
- WEEE plastic scraps (Maris et al. 2015).

Finally, the values of size (mass or volume) of test portions were gathered from 7 among the most used analytical standards for waste characterization: waste percolation test EN 14405, (2017), granular waste leaching test EN 12457 parts 1-4, (2002), XRF elemental analysis EN 15309, (2007), waste acid digestion for subsequent determination of elements EN 13656, (2020), PCB analysis in waste EN

15308, (2017), Polybrominated biphenyls and polybrominated diphenyl ethers analysis in polymers of products EN 62321-6, (2015) and waste EN 16377, (2013).

The reported sample sizes were then analysed to assess the number of particles present in the samples themselves. Where granulometric and physical information were available in the cited reference, number of particles were calculated as follows (according to Equation 8):

$$n = \frac{M_{sp}}{\frac{\pi}{6}(D_{95})^3 * \rho_{solid} * g * f} \tag{10}$$

Where n is the number of particles in the sample, M_{sp} is the mass (kg) of sample as indicated in the published sampling plan or test portion preparation standard, while the definitions of D_{95}, ρ_{solid}, g and f are the same used for Equation 8. However, not all considered references reported in detail the needed information on these latter parameters. In these cases, authors or professional unions related with the management of the specific waste material were contacted to collect (or estimate, based on personnel's experience) the missing information.

4. RESULTS AND DISCUSSION

4.1 Observed distribution of concentrations at particle scale

Three examples of single particles concentrations of Br in WEEE are presented in Figure 1 (Hennebert, 2020): at first sight, the normal distribution does not fit with the data.

Data of Br concentration from plastic scraps after shredder were characterized by median value of 5 mg/kg, a mean of 3,536 mg Br kg^{-1}, a maximum value of 139,300 mg Br kg^{-1}, a standard deviation of = 16,968 mg Br kg^{-1} and a CV of 4.80. Furthermore, shredded WEEE plastic particles undergone density sorting showed a median value of 8 mg Br kg^{-1}, a mean of 995 mg Br kg^{-1}, max = 31,664 mg Br kg^{-1}, a standard deviation of 4,683 mg/kg and a CV of 4.70) (Hennebert, 2020). Accordingly, the last percentiles tremendously influence the mean concentration. The median and the mean are in fact very different.

The normal distribution underestimates the contribution of the last centiles to the mean. For instance, among the 200 measured Br concentrations in shredded plastic particles, the two more concentrated particles increase the mean concentration of 1,000 mg Br kg^{-1} and represent about 25% of the total bromine present in the batch of particles. Here, by considering also the trivial hypothetical case of 999 particles with 0 mg Br kg^{-1} and one particle with 100,000 mg Br kg^{-1} resulting in a mean concentration of 100 mg Br kg^{-1}, the measured data clearly suggest that these few particles must absolutely be "captured" (be present) in a representative laboratory sample. If they are not (if there are not "enough" particles of interest in the sample), different laboratory samples will give highly variable mean concentration per sample (as measured in the laboratory). Also, the concentration of individual particles cannot be predicted with mean and standard deviation, as usual, with the normal distribution.

Sometimes the distribution is trimodal, as exemplified in the bromine concentration of sorted dense plastic scrap of cathode ray tubes (Figure 1). There are three groups of concentration that can be observed in Figure 1: < 1 000 mg Br kg^{-1}(no bromine, but probably other additives used to increase density of the plastic), 15,000-45,000 mg Br kg^{-1} (insufficient concentration for fire protection, probably the result of improper recycling), and 50,000-150,000 mg Br kg^{-1} (fire protected plastics). It should be noted that such skewed distributions are frequently observed at population scales. This point is briefly mentioned here because it is not the topic of this paper, dealing with particle scale.

4.2 Observed analytical variability

In Equation 6, CV_p is assumed equal as CV_r, which is the variability of the measurement at the smallest analytical scale (on the smallest test portion that can be analyzed). This paragraph discusses the collected data of several CV_r with granular solid waste, to assess the reliability of this assumption.

Results from the collection of variability values are presented in Table 1. Here, two cases are distinguished: analysis without extraction (e.g., direct analysis like XRF or direct analysis of liquid extracts), and extraction followed by the analysis (i.e., typical analysis performed for solid materials). The analytical variability of homogeneous liquid samples or liquid extracts of solid waste is well known as "low" (typically $CV_r \approx 0.03$). The variability of analysis involving extraction from solids is higher. For the measurement of the total content (of element or substance), the extraction is done under extreme conditions (fine powder, acids or base, solvent, high temperature, etc.), potentially until the total dissolution of the solid matrix, which can be easily verified by the analyst. These strong conditions guarantee that total extraction occurs. But regarding the measurement of partial content of element or substance (like leaching tests, percolation tests, (bio)available concentrations…), the extraction is done under milder conditions (coarser particles or aggregates, deionized water or mild extractant like EDTA or sodium dithionite, room temperature, mild solid/liquid separation at the end of the extraction, etc.). The extraction must follow exactly the protocol, and the protocol itself should not have variants; otherwise the extraction ratio could be higher or lower. Due to this two-step-procedure, and since partial extraction is more variable, the analytical variability of solid samples is typically higher than the one of liquids.

The intra-laboratory variability (repeatability) of chemical (total) analysis is low: the specific resulting mean is 0.04 for analysis without extraction, and 0.10 with extraction (light green cells). The inter-laboratory variability (reproducibility) of chemical analysis of reference material or prepared "homogeneous" samples is (logically) higher: here, the mean CV is 0.21 for analysis without extraction, and 0.24 with extraction (light orange cells).

Leaching tests and biotests have higher variability. It should be noted that they make use of only partial extractions (i.e., of the leaching fraction or the bioavailable fraction), more sensitive to changes of results when the methods are not strictly followed. For leaching tests (EN 12457-2), the variability of inter-laboratory tests of prepared solid samples is clearly higher (CV = 0.37) (yellow cell). In this respect, the inter-laboratory variability could

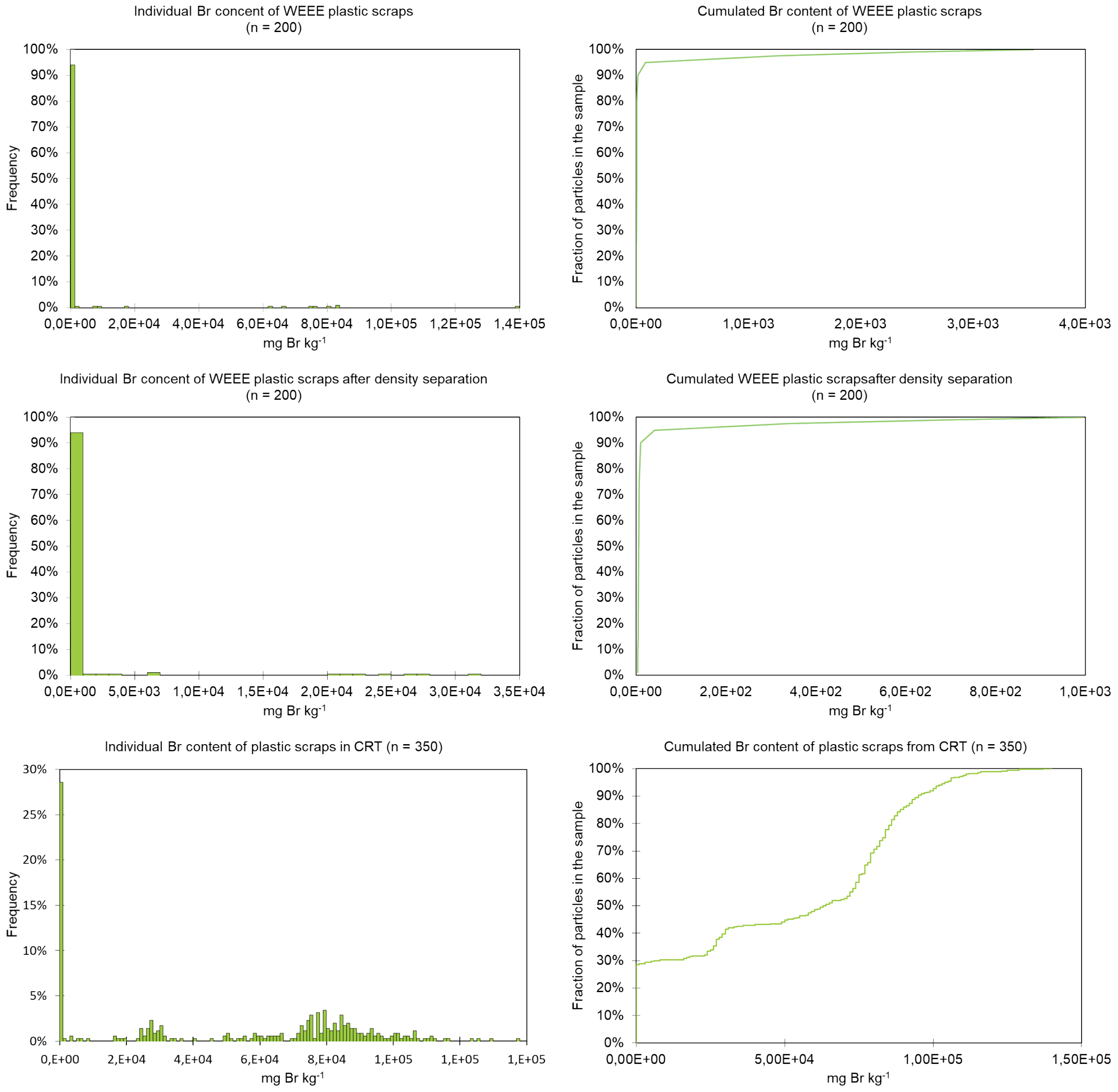

FIGURE 1: Histograms of Br particles concentrations (left) and cumulated mean Br concentration (right) in samples of in WEEE plastic scraps before (top) and after density separation (middle) and in plastic scraps from CRT (bottom).

originate from the different options available in the standard for liquid-solid contact (e.g., rolling, tumbling, etc.) and liquid-solid separation (e.g., decantation, filtration, centrifugation), that should instead be fixed in the standard to reduce the inter-laboratory variability. The influence of all these parameters was discussed with the results from an inter-laboratory test (Van der Sloot et al. 2001).

Only data of biotests whose related technical standard provides validation data were considered (Table 1). The CVs are calculated from the intra-laboratory variability on one reference substance (1 spiked solid media), and the inter-laboratory variability on prepared matrices (2 liquid solutions and 1 spiked solid media). However, the variability could be calculated only from intra-laboratory repetitions (i.e., CV of 0.20). There are not enough data of inter-laboratory trials on true waste samples in the standards, including sample preparation and leaching for the aquatic tests on solid leachates, to calculate a representative CV for inter-laboratory variability.

In summary, possible reasons are resumed in Table 2 explaining the (too high) CVs observed in Table 1.

4.3 Number of particles in samples and subsamples

4.3.1 Laboratory samples

Six cases of sampling plan from technical reports or standards (i.e., present in the data section) are compared with the optimal size of a representative sample, as expressed as n in Equation 7, (Table 3). For waste wood

TABLE 1: Observed CVs in results from the performance of different analytical methods on sets of samples of different materials. Light green: CV ≤ 0.10, green: CV ≤ 0.20, light yellow: CV ≤ 0.30, yellow; CV > 0.30.

Sample	Reference	Target Parameters	Methods	Intra-laboratory						Inter-laboratory					
				Analysis (no extraction)			Analysis (with extraction)			Analysis (no extraction)			Analysis (with extraction)		
				n	CV mean	CV max	n	CV mean	CV max	n	CV mean	CV max	n	CV mean	CV max
Plastic reference material	Original data	Br	XRF	25	0.01										
		Sb	XRF	25	0.03										
Plastic reference material	Haarman et al. 2018	Elements	Combustion, IC										n.a.*	0.06*	0.13*
		BFR	EN 62321-6										12	0.20	0.36
Plastic scraps from SHA and screens	Hennebert and Filella 2018	Br	Combustion, IC				33 t	0.10	0.27						
		Sb	Combustion, ICP				33 t	0.10	0.25						
		BFR	EN 62321-6				178 t	0.16	0.64						
		All					244 t	0.14	0.64						
Sludge, compost and soil	Kalbe et al. 2019	PAH	EN 16181	31	0.04	0.08	75	0.10	0.17	31	0.15	0.34	75	0.39	1.23
		PCB	EN 16167	77	0.07	0.09	76	0.06	0.09	77	0.32	0.38	76	0.27	0.39
		PCDD/PCDF/PCB-DL	EN 16190	27	0.07	0.20	31	0.09	0.66	27	0.25	0.40	31	0.25	1.38
		∑ PAH	EN 16181	26	0.03	0.04	82	0.06	0.07	26	0.12	0.20	82	0.30	0.35
		∑ PCB	EN 16167	77	0.06	0.06	78	0.05	0.06	77	0.23	0.23	78	0.21	0.23
		∑ PCDD/PCDF	EN 16190				33	0.06	0.08				33	0.13	0.17
Waste solid samples	Method validation data	Elements	EN 12457-2	38	0.04	0.24	38	0.17	0.77				38	0.37	1.1
Reference material (liquid and solid)	Method validation data	EC_{50}	EN ISO 11348-3 EN ISO 8692 ISO 18187 ISO 17512-1				8 (1 test)	0.20	0.38	17 (3 tests)	0.25	0.39			

TABLE 2: Possible causes of reported high CVs in intra- and inter-laboratory measurements performed on laboratory samples or test portions, with identification of cases when the analysis should be improved, and cases when the sampling should be improved.

Type of Variability	Intra-laboratory - Repeatability			Inter-laboratory - Reproducibility	
Sample	"Homogeneous" samples (liquid or solid)	Prepared test portions from a laboratory sample	Set of identical laboratory samples	Prepared test portions from a laboratory sample	Set of identical laboratory samples
Analysis (no extraction)	CV > 0.10 (High)	CV < 0.10	CV < 0.10	-	-
Extraction and analysis	-	CV > 0.20 (High)	CV > 0.20 (High)	CV > 0.25 (High)	CV > 0.25 (High)
Causes and improvements	Improve the analysis methods in the laboratory	Improve the extraction methods in the laboratory	Check if the laboratory samples or test portions contain "enough" particles	Check and minimize the variations in the practical procedures allowed between laboratories by the technical standards	Check if the laboratory samples contain "enough" particles

from furniture and MSWI bottom ashes, the mean mass of particles was estimated respectively from data provided by CEDEN, the consulting company of Valdelia and Eco-Mobilier, and SVDU, this latter referring to unbound mixtures for roadwork platforms granulometry. For both samples of plastic shreds from SHA, it is estimated according original laboratory data (Wäger et al. 2011, CENELEC TS 50625-3-1, (2015)). The number of particles in the sample is given by the authors for WEEE Plastic scraps (Maris et al., 2015).

For wood coming from construction and demolition waste and furniture, the estimated corresponding number of particles in the laboratory sample using a mean particle mass is large, according to the authors of the study (i.e., 200,000 and 40,000 for the two considered lower size fractions). However, that number is calculated as insufficient (i.e., 33 for the 80-15 mm fraction) (Table 3).

For MSWI bottom ashes (Table 3), if fines occur in the sample (i.e., assuming low values for g), the calculated number of particles in the laboratory sample is large as well (greater than 100 million). Whether fines are not assumed present, that number is calculated as insufficient (165). Nevertheless, some (non-ferrous) metals are more concentrated in fractions of 1 to some millimetres, according to the literature (Chimenos et al 1999, Holm and Simon 2017) and to recovery practices that become widespread.

For plastics scraps of waste of electrical and electronic equipment (WEEE), a survey of RoHS regulated substances in WEEE plastic in Europe (Wäger et al. 2011) recommended a method for sampling, coming from LAGA (2001). The minimum volume and amount of single, mixed and laboratory sample for a total mixed plastics volume of maximally 30 m^3 (from about 20 tons in one day production) is between 2 and 5 kg, depending on size (Table 3). The corresponding n are probably too low and p are probably too high (between 0.09 and 0.20). This could mean that the rare "POP-concentrated" particles can be captured or not, randomly. Repeated samples will give (sometimes or not,indeed randomly...) different results, as observed by the authors (i.e., difference close to one order of magnitude for TBBPA, OctaDBE, and DecaBDE).

For plastic scraps of WEEE, according to technical specifications CENELEC TS 50625 3-1, (2015), the size of the laboratory sample is 7.5 to 25 litres for SHA, and 1 litre for fluorescent lamps. For SHA, the number of particles present in the laboratory samples of 7.5 to 25 litres (depending on the size of the plastic scraps) is calculated as 800-1 000, with corresponding p as 0.09 - 0.10. For shredded fluorescent lamp plastics, the values of p are calculated as 0.25 to 0.73. These p values must be verified for these plastics but are probably not unrealistic for the unsorted fraction. Plastics from SHA are largely brominated (Hennebert and Filella 2018) and plastic waste from fluorescent lamps are most often brominated (personal communication from the French organization of extended producer responsibility), indicating that most or all those wastes are brominated (i.e., p approaches 1).

At the contrary, for the sorted fractions of SHA for bromine in view of recycling (with as low as possible particles < 2,000 mg Br kg^{-1}), p can be estimated to 0.01 (Hennebert 2020), calculated n is 10,000, with corresponding masses of 20-80 kg and the corresponding volumes 60-240 litres, clearly larger than the recommendation of the standard.

Finally, aiming at the identification of polymers in plastics (Maris et al. 2015), from batch of 10 tons, a composite sample of 9.3 kg of scraps (from 10 increments) is taken, sieved > 20 mm for characterization, and the resulting fraction of 5.5 kg is "acceptable by all of the project partners" as laboratory sample mass. It is constituted of about 1,500 particles as mentioned by the authors. With samples of 1,500 particles, only the particles of interest with a frequency p ≥ 0.06 will be detected with a low variability. By

TABLE 3: Estimated number of particles (n) in laboratory waste samples collected according to published sampling plans (Eq. 10). The fraction of rare particles of interest (p) which can be assessed with a theoretical CV of 0.1 is calculated from Equation 7. S_{lot} = Assumed usual size of the lot of waste to be sampled. M_{sam} (kg) = mass of sample as indicated in the specific reference. For D_{95}, ρ_{solid}, g and f refer to Eq. 10. * = the number of particles n was provided directly in the reference without any hypothesis.

Sample	Reference	S_{lot}	D_{95} (m)	M_{sam} (kg)	$\frac{\pi}{6}(D_{95})^3 * \rho_{solid} * g * f$	n	$p\ (CV = 0.1)$
Waste wood from furnitures	Eco-Mobilier and Valdelia, 2018	100 - 1,000 tons	D_{95} <0.015	2	0.000010	200,000	0.0005
			0.015	2	0.000050	40,000	0.002
			0.080	2	6.0E-02	33	0.751
MSWI bottom ash (Un-maturated)	SVDU, 1995	2,000 - 20,000 tons	0.050, 1% < 63µm	2	2.00E-08	1.00E+08	0.0000010
			0.050, 1% < 63µm	8	2.00E-08	4.00E+08	0.0000002
MSWI bottom ash (Maturated)			0.050, 1% < 63µm	6.75	2.00E-08	3.38E+08	0.0000003
			0.050, No fines	6.75	4.1E-02	165	0.377
Plastic shreds from SHA	Wäger et al 2011	30 m^3	0.002 < D_{95} < 0.020	2	0.002	1,000	0.091
		30 m^3	0.020 < D_{95} < 0.050	2	0.005	400	0.200
		30 m^3	0.050 < D_{95} < 0.120	5	0.010	500	0.167
Plastic shreds from SHA	CENELEC TS 50625 3-1	Daily production	D_{95} <0.020	2.2	0.002	1,080	0.085
		Daily production	0.020 < D_{95} < 0.050	3.5	0.004	864	0.104
		Daily production	0.050 < D_{95} < 0.100	7.2	0.008	900	0.100
Waste from plastic lamps	EN 50625-3-2	Daily production	D_{95}<0.005	0.3	0.001	300	0.250
		Daily production	0.005< D_{95} <0.020	0.3	0.002	150	0.400
		Daily production	0.020< D_{95} <0.050	0.3	0.004	75	0.571
		Daily production	0.050< D_{95} <0.100	0.3	0.008	38	0.727
WEEE plastic scraps	Maris et al. 2015	10 tons	D_{95} > 0.020	5.5	*	1,500	0.063

repeating the sampling and the plastic identification, from another batch of 10 tons, repeatability was indeed good for ABS (29% mass fraction), HIPS (26%), PP (22%). But repeatability was not good for less represented plastics (CVs > 0.5 for PC-ABS 5% mass fraction, PMMA 3%, PC 3%, PA 1% and 14 others < 1%, total 21 polymers).

4.3.2 Test portions

Different cases are presented, from large to small test portions: laboratory percolation tests and leaching tests, aliquots for laboratory mineral digestion or organic extraction (Table 4). The maximum grain size and the mass of the test portions are given in the standards.

For test portions from laboratory sample, n is calculated with Equation 10, where the masses of the test portions are given in the standards, while the maximum grain size, as indicated in the standards, are multiplied by g (here set to 0.25) and a hypothetical solid density. For percolation and leaching tests, cases with the presence and non-presence of a fine fraction (i.e., 10% of particles characterized by a diameter < 1 mm) were calculated.

For percolation and leaching tests, the number of particles calculated assuming absence of fines never reaches satisfactory values and is even around 300 in the leaching test with the 10 mm grain size (EN 12547-4, (2002)). This number of particles is also always lower than the number calculated with a hypothesis of 10% of particles < 1 mm, which is a realistic assumption after the size reduction.

For analytical measurements (direct such as X-ray fluorimetry) or after digestion / extraction, the test portion calculated with Equation 10 is greater than or equal to 100,000, except for the PBDE analysis. As the size reduction occurs, it is likely that the real number of particles in the test portions will be higher.

5. CONCLUSIONS

The theoretical principles behind the EU technical standards for granular waste sampling are reviewed to ease their application and understanding in the waste community. In particular, the formula given to calculate the mass of a laboratory sample (or test portion, equivalently), is reviewed in terms of number of particles that should be present in the sample to be representative of the batch of waste to be characterized. Practical aspects aimed at ensuring the "probabilistic" performance of sampling are not addressed (i.e., the qualitative instructions on "how to" sample).

Granular wastes are assumed as a population of particles characterized by a fraction showing a property of interest, which is the object of the measurement. Sampling is conceptually modelled as repeated drawings of particles, with the binomial probability distribution describing the probability of picking up a fraction of particles of interest "reliably" similar to that occurring in the waste lot. Single particle concentrations of Br, determined in different samples of WEEE plastic scraps, are presented to discuss the distributions of properties of interest among particles in the waste field. When these are right-skewed by some rare

TABLE 4: Estimated number of particles (*n*) in waste test portions as indicated in different analytical standards (Equation 10). The fraction of rare particles of interest (*p*) which can be assessed with a theoretical CV of 0.1 is calculated from Eq.7. M_{sam} (kg) = mass of test portion as indicated in the specific reference. For D_{95}, psolid, g and f refer to Equation 10. [a] = Calculated assuming a percolation column characterized by an internal diameter of 0.1m and a bulk density and a solid density of the material of 1.6 kg L^{-1} and 2 kg L^{-1}, respectively. [b] = calculated assuming a percolation column characterized by an internal diameter of 0.05m and a bulk density and a solid density of the material of 1.6 kg L^{-1} and 2 kg L^{-1}, respectively. [c] = calculated assuming a solid density of the material of 1.1 kg L^{-1}. [d] = calculated assuming a solid density of the material of 1.1 kg L^{-1}.

Standard	Reference	D_{95} (m)	M_{sam} (kg)	$\frac{\pi}{6}(D_{95})^3 * \rho_{solid} * g * f$	n	$p\ (CV = 0.1)$
Percolation test	EN 14405	0.010, No fines	3.8 [a]	3.0E-04	14,400	0.007
		0.010, with 10% < 1 mm	3.8 [a]	5.2E-06	730,769	0.0001
		0.004, No fines	0.9 [b]	1.7E-05	56,250	0.002
		0.004, with 10% < 1 mm	0.9 [b]	4.6E-06	195,652	0.001
Leaching test	EN 12457-4	0.010, No fines	0.090 [c]	3.0E-04	344	0.225
		0.010, 10% < 1 mm	0.090 [c]	5.2E-06	17,308	0.006
	EN 12457-1 EN 12457-2	0.004, No fines	0.090 [c]	2.0E-05	5,371	0.018
		0.004, 10% < 1 mm	0.090 [c]	4.6E-06	19,565	0.005
	EN 12457-3	0.004	0.175 [c]	2.0E-05	10,445	0.009
Elements XRF analysis	EN 15309	0.00015	0.010 [c]	8.8E-10	11,317,685	0.000009
		0.00008	0.005 [c]	1.3E-10	33,571,746	0.000003
Elements Digestion	EN 13656	0.00025	0.0002 [c]	4.1E-09	48,892	0.002
		0.00025	0.0004 [c]	4.1E-09	97,785	0.001
PCB analysis	EN 15308	0.00050	0.010 [c]	3.3E-08	305,577	0.0003
		0.00050	0.025 [c]	3.3E-08	763,944	0.0001
PBDE products	EN 62321-6	0.00050	0.0001 [d]	1.8E-08	5,556	0.018
PBDE waste	EN 16377	0.00200	0.0030 [d]	1.2E-06	2,604	0.037

particles (i.e., the fraction of particles of interest is much lower than the unity value), their occurrence (or non-occurrence) in the sample can remarkably influence the reliability of the measurement.

By knowing or estimating the fraction of particles "of interest" and by assuming a controlled degree of variability, this paper shows that samples from waste characterization campaigns must simply contain 100 particles of interest in order to be representative and not very variable. From this requirement, mass of representative samples or subsamples can be calculated according to the particles sizes distribution and their physical features. With these results, the recommended mass of laboratory samples and test portions as laid down in published sampling plans or analytical standards are assessed. Here, samples containing less particles could lead to a higher uncertainty/variability associated with the measurement of the parameter of interest.

Finally, real data on observed analytical variability (inter- and intra-laboratory) are discussed to check the reliability of the assumptions made to derive the number of particles in a representative sample or subsample.

In summary, the calculation of the size of the representative sample must be based on the knowledge of the waste consistency. The sampling of particles according to possibly occurring size-concentration relationship is addressed in a second paper of this series.

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ASSESSMENT OF THE DEGREE AND SOURCE OF POLYOLEFIN RECYCLATES CONTAMINATION

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ABSTRACT

This study has the aim of analysing the degree of contamination of recycled polyolefin purchased from the market by focusing on the content of polycyclic aromatic hydrocarbons (PAHs). Additionally, the impact of the mechanical recycling process on the polyolefin chemical quality was investigated. Results indicated that recycled polyethylene (PE) had higher PAHs concentrations by 10 to 20 folds in comparison to the pristine PE. Similarly, recycled polypropylene (PP) indicated higher PAHs concentrations in comparison to the virgin polypropylene, yet with lower degree of difference. Analysing the 8 indicators assigned by the Regulation EU 1272/2013 amending REACH Annex XVII, all recycled specimens showed concentrations lower than the limit of 0.5 mg kg^{-1}, which indicates that there is no restriction in material's utilisation. This study functioned as a preliminary assessment to check the suitability of recycled plastics for their further utilisation. Additionally, the study indicates that polyolefin can experience quality deterioration when uncontrolled recycling conditions are applied.

1. INTRODUCTION

Due to the need for high quality of recycled plastics from the heterogeneous waste stream, deficiencies of the recyclates quality should be identified and avoided when possible, in particular with the assessment of the up-to-date regulations on substances, mixtures and products (Alassali et al., 2020a). Generally, the occurrence of unwanted substances that can migrate and accumulate in the plastic's cycle is a significant limitation and risk to its closed-loop recycling (Eriksen et al., 2019).

Contamination can occur throughout the whole plastic value chain. The main sources of plastic contamination are: degradation products generated during material ageing or exposure to different conditions (Alassali et al., 2018; Alassali et al., 2020c), addition of chemical substances in the form of additives to obtain a specific quality (Sanchez et al., 2020), or contamination by use or application (Hahladakis and Iacovidou, 2019).

The application of the circular economy concept on plastic waste requires the consideration of its recycling, where resources are maintained as long as possible and the maximum value is recovered after disposal. Plastic waste could be recycled mechanically, chemically or thermally. Yet, the mechanical recycling is the preferred option, due to the preservation of the material.

Many factors limit the mechanical recycling of plastic waste, especially the fact that plastics are organic components that are highly sensitive to elevated temperatures and mechanical stress (Al-Salem et al., 2009). Additionally, plastic waste contamination could be a significant challenge when considering plastic waste recycling. Hence, identifying contaminants and their possible sources in plastics will define the gaps in the plastic's value-chain. Consequently, the application of circular economy could be boosted on the plastic waste stream, while ensuring sustainability, high quality, and safety of products.

Compared with natural sediments, hydrophobic organic contaminants have greater affinity for a range of plastics like polyethylene (PE), polypropylene (PP), or polyvinylchlorid (PVC) (Teuten et al., 2007). Polycyclic aromatic hydrocarbons (PAHs) are among the contaminants of concern. They have toxic, carcinogenic and mutagenic characteristics. Most of the PAHs are categorised as persistent, bio-accumulative and toxic (PBT) substances. These substances do not degrade and can remain for extended periods in the environment (German Environment Agency, 2016). The presence of PAHs in plastics is mainly a result of the additives added during the production and the manufacturing stages (i.e. carbon black and extender oils) (Lassen et al., 2012). Additionally, plastics could accumulate PAHs from the surrounding environment as a result of their organic nature, which increases their affinity to a variety of

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organic pollutants (Rochman et al., 2013).

On December 6th, 2013, the European Commission published the Commission Regulation (EU) No. 1272/2013 amending Annex XVII to Regulation (EC) No 1907/2006 of the European Parliament and of the Council on the Registration, Evaluation, Authorization and Restriction of Chemicals (REACH). The regulation banns articles containing rubber or plastic fractions with certain levels of PAHs from being placed on the market for sale to the general public in the European Union. The regulation declares that defined articles cannot contain more than 1000 $\mu g\ kg^{-1}$ of the 8 selected PAHs. On the other hand, toys and children articles have the restriction limits of 500 $\mu g\ kg^{-1}$ (European Commission, 2006). Accordingly, the content of PAHs in recycled plastic should be controlled in order to be allowed on the European market.

The objective of this paper is to evaluate the chemical quality of the recycled polyolefin samples by studying the existence and the concentration of polycyclic aromatic hydrocarbons (PAHs) in comparison to virgin new samples. Furthermore, the impact of diluting recycled plastics with new plastics was studied to provide solutions for enhancing the recyclates quality in case of contamination. On the other hand, the study assessed if the mechanical recycling process is a source of plastics contamination with PAHs. In the context of this research, plastics extrusion was applied to simulate the effect of the mechanical recycling.

2. MATERIALS AND METHODS

2.1 Recycled polyolefin

The recycled plastics used in this study were obtained from recyclers. The samples used are representative since they are of a quality that is offered on the market and meeting the European standards. The samples were tested before and after undergoing further recycling cycles.

2.1.1 Recyclates without further processing

The quality of recycled plastics (available on market) in terms of contamination with PAHs was analysed. The aim was to test their application viability in consumer products and children's articles. For that reason, the recyclates shown in Table 1 were purchased.

PP1, PP2 and PE1 acquire a high level of purity. A selective recycling technology is applied, including degassing and filtration. PP1, PP2 and PE1 are products made from pre-sorted plastics (by colour and polymer type). On the other hand, the recycled polyethylene sample PE2 is a test set of recyclates originating from foils used in construction sites.

2.1.2 The impact of dilution on the chemical quality of recyclates

In the second part of the experiment, the chemical quality of the recycled material was studied in relation to the product's composition (i.e., the fraction of recycled plastic to virgin plastic: Recycled/Virgin (%)). The aim was to assess the effect of mixing the recycled plastic with virgin plastic on the total concentration of PAHs. Based on the decrease in the degree of contamination, an indication to the best dilution factor could be provided. To arrange the test sets (samples with different compositions (RE:VI)), five main mixtures were prepared as shown in Figure 1.

The extrusion was conducted using HAAKE™ Rheomex CTW 100 OS, a twin-screw extruder. The applied extrusion was done at a rotation speed of 25 rpm, with the heat profile of: 170-175-180-190 and 210°C at the die.

The produced filaments were separately shredded by Retsch SM 300 to the size of 4 mm x 4 mm. The shredded material of each mixture was separately collected for further testing.

2.2 Pristine polymers

In order to avoid the influence of additives on the chemical quality of plastics, pristine PE and PP samples were used in this section. In the context of this research, plastics extrusion was applied to simulate the effect of plastic's mechanical recycling. Three extrusion cycles were executed. The first one simulated the conditions plastics endure during the production process. The second extrusion cycle simulated the effects plastics undergo during the first recycling, and the third extrusion resembled a second recycling cycle. The pristine polymers used in this study were low-density polyethylene (LDPE) granules and PP pellets. The LDPE granules and PP pellets were purchased from INEOS Olefins and Polymers Europe.

The extrusion of plastics was performed using ZSE 27maxx (a twin-screw extruder from Leistritz), with a screw torque of 134 Nm $screw^{-1}$, total power of 46 kW and 12 heating zones (including the die). The applied rotational speed ranged between 100 and 150 rpm, with an extrusion speed of 3 kg h^{1}. The first extrusion cycle was applied on 5 kg of pristine granules. After each extrusion cycle, 1 kg of material was separated for testing purposes and the

TABLE 1: Recyclates purchased from the market.

PE1: Dark	PE2: Black	PP1: Black	PP2: Dark
			

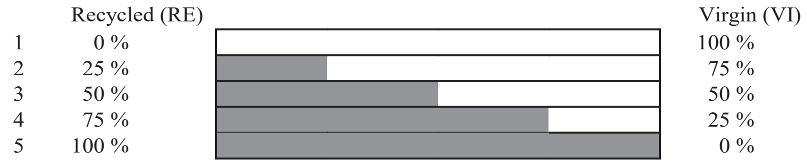

FIGURE 1: The composition of the 5 mixtures (study samples).

rest was dried overnight in BINDER ovens before shredding and further extrusion. This was repeated until the three extrusion cycles for each polymer were accomplished. The extrusion was achieved at a temperature range of 190 to 210°C for both polymers.

2.3 Extraction of PAHs from the plastic's matrix

Samples were extracted using a Randall extractor to be able to analyse the PAHs content. This method is simple, cost-effective, and time saving. Literature showed that this method can reach improved extraction efficiencies with higher reproducibility (Geiss et al., 2018).

The samples were weighed in duplicates in 33 x 60 cellulose extraction sleeves (thimbles) obtained from VWR. The weight of the test samples ranged between 0.1 and 0.5 g, weighed by Sartorius CP balance. The thimbles were manually fixed inside the metallic frames which attach to the magnetic height-adjustable holders (see Figure 2). The reaction vessel, in which the extract is collected, was filled with 70 mL of toluene, purchased from J.T. Baker®, and three to four boiling stones were added before connecting it to the condenser by screwing.

The upper part of the apparatus acts like a reflux cooler, which condensates the solvent's vapours to rinse the sample and bring the extract into the reaction vessel (see Figure 2).

The extractions were performed in duplicates. Randall hot extraction consists of three main steps: immersion, rinsing, and evaporation. The immersion step was conducted at 150°C for 120 min, where the sample is entirely in contact with the extraction solvent. Afterwards, the thimble was pulled out of the sump (reaction vessel) using the height-adjustable holder, while applying a temperature of 175°C to rinse the sample for 60 min. The evaporation was done at the same temperature (i.e. 175°C) for as long as needed to reach a solution's volume of ≤ 20 mL. The time of evaporation in this setup ranged between 20 and 40 min.

2.4 Extract preparation and clean-up

40 µL of an internal standard was added to the solution to calculate the recovery (concentration of 40 ng mL^{-1}). The internal standard was Phenanthrene-d$_{10}$ 98 atom % D, 98% (CP) from Sigma-Aldrich. The extract was then filtered to remove the plastic particles. Finally, the extract was evaporated by a 0.7 bar nitrogen (N$_2$) stream. Drying was applied until the solution reached a volume of ~500 µL. The clean-up was achieved using solid phase extraction (SPE). For that, silica gel Bakerbond™ disposable extraction columns were utilised.

2.5 PAHs analysis

The analysis of the samples was performed using a gas chromatograph HP 6890 coupled with a single ion monitoring mass selective detector. Before conducting the analysis, a calibration step preceded. The calibration was done prior to analysing each of the samples' sets. For the calibration, different established concentrations between 10 and 1000 ng mL^{-1} of an external standard containing the 16 US-EPA PAHs – naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-c,d)pyrene, dibenz(a,h)anthracene, and benzo(g,h,i)perylene – were analysed, and the respective responses were measured.

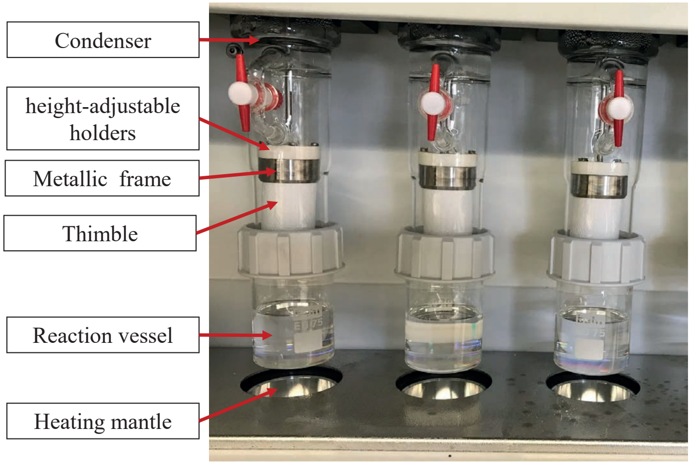

FIGURE 2: The setup of PAHs extraction using Randall extractor.

3. RESULTS AND DISCUSSION

3.1 PAHs in recycled polyolefin

3.1.1 Polyethylene

The content of the total 16-US-EPA PAHs in recycled HDPE was significantly higher in comparison to pristine (virgin) HDPE samples (Figure 3). The concentration of the total analysed PAHs in pristine samples was 155 ± 37.9 µg kg^{-1}. The highest PAHs concentration was observed in PE1 (3043 ± 837 µg kg^{-1}), a sample of a mixed source. A thorough analysis of the 16-US-EPA PAHs showed significant variances in the concentrations of phenanthrene and pyrene. Phenanthrene's concentration was 1200 µg kg^{-1} in PE1 in comparison to 310 µg kg^{-1} in PE2. Likewise, pyrene's concentration in PE1 was 2.7 times the concentration in PE2 (741 µg kg^{-1} in comparison to 271 µg kg^{-1}). Like most PAHs, phenanthrene is present in manufactured dyes and plastics. Hence, its high concentration is attributed to the contamination of the source material. Pyrene is found in high concentrations in crude oil and in extender oil. Accordingly, its presence is a result of the plastics manufacturing process. The difference between PE1 and PE2 is the source material. PE1 originates from a mixed source (post-consumer, commercial, or post-industrial waste), where PE2 originates from foils used at construction sites. Hence, the chemical quality of the two samples is different due to the additives in the source material. As was reported by Camacho and Karlsson (2000), the concentration of aromatic hydrocarbons in the recycled resin is approximately five times higher in comparison to virgin polyolefin. The results of this experiment indicated that the total content of the 16-US-EPA PAHs is 20 times and 10 times higher in PE1 and PE2, respectively, when compared to pristine resins, depending on the materials' source and the efficiency of the applied sorting.

Among the 16 US-EPA PAHs, 6 belong to the REACH 8 priority PAHs (i.e. benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, and dibenz(a,h)anthracene). The concentrations of the 6 priority PAHs in PE1 and PE2 were ranging between 300 and 400 µg kg^{-1} (see Figure 4). The threshold limits for the 8 priority PAHs are 500 µg kg^{-1} for children articles, and 1000 µg kg^{-1} for all other consumer products (Geiss et al., 2018). Hence, samples PE1 and PE2 might show risks if applied in children articles (Alassali, 2020). Nonetheless, their application in consumer products shows limited risks.

3.1.2 Polypropylene

The two tested recycled PP samples are of undefined sources. The concentration of the 16-US-EPA PAHs in the purchased PP recyclates showed an increase by 173% for PP1 and by 264% for PP2, in comparison to the pristine PP samples (see Figure 5). The black sample showed lower concentrations of the 16-US-EPA PAHs in comparison to the dark grey sample. However, considering the 6 out of the 8 priority PAHs, PP1 had higher concentration of ben-

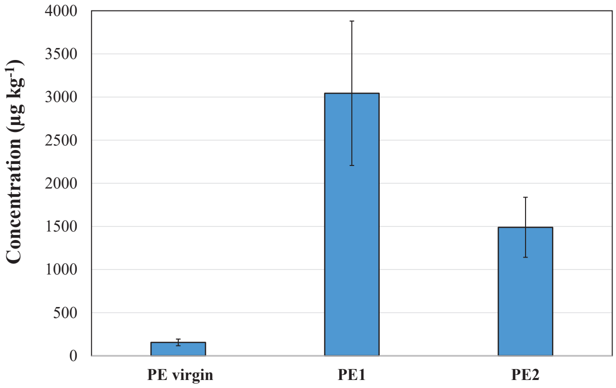

FIGURE 3: The concentration of the 16-US-EPA PAHs in different HDPE samples.

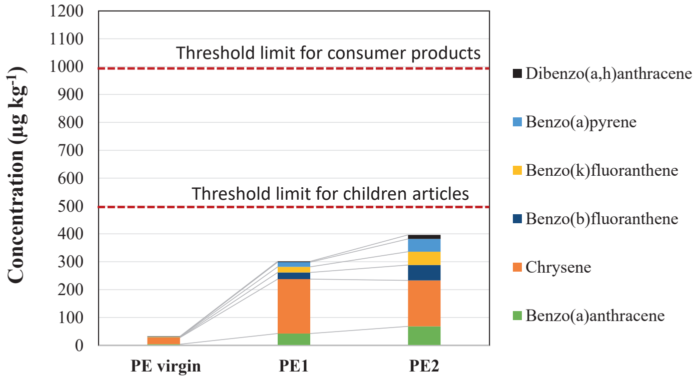

FIGURE 4: The content of 6 out of 8 priority PAHs in the recycled and virgin HDPE samples.

zo(a)pyrene. Additionally, PP1 (black in colour) contained dibenzo(a,h)anthracene, which was missing in PE2. Dibenzo(a,h)anthracene is mainly found in crude oil, which is an indication of the presence of crude oil residues, probably through the plastic manufacturing process. All in all, the concentrations of the 6 priority PAHs were always below the REACH-indicated threshold limits, for both children articles and consumer products. Hence, and due to the low contamination risk, the recycled PP samples indicate suitability for application without restriction (see Figure 6).

The concentration of the priority PAHs in recycled PP ranges between 0.3 to 0.5 of the concentration in recycled PE. This could be explained by the higher degradability of PE in comparison to PP under the recycling conditions, or by the higher affinity of PAHs to the polymer PE.

3.2 Does the mechanical processing per se generate PAHs in the plastic matrix?

In this section, the impact of plastic recycling was simulated in the lab on new and pure polymers (LDPE and PP). The content of PAHs was then compared between new plastic samples and 3-times extruded samples (as the worst case).

For PE 3x-extruded sample, the 16-US-EPA PAHs concentrations increased by 185% (from 155 ± 37.9 μg kg^{-1} to 442 ± 133 μg kg^{-1}). A similar factor of increase was obtained for the 6-priority PAHs, showing that there is a general trend of increase (see Figure 7). The increase of the concentrations of naphthalene, phenanthrene, fluoranthene, pyrene, and chrysene were most significant in comparison to the rest of analysed PAHs (increasing by 200 to 300%) (Alassali, 2020; Alassali et al., 2020b). This proves that exposing polyethylene to the heat and stress involved in the mechanical recycling process may result in polymer degradation, oxidation and the formation of new chemical groups. As was reported by Alassali et al., 2018, the degradation of LDPE can be detected by one or more of the following evidences: increase in the crystallinity, decrease in the molecular weight, increased chain scissoring, oxidation (i.e., formation of C-O, C=O, ether, aldehyde, ketone and/or carboxylic acid products) and a minor decrease in the tensile strength. Another reason of contamination could be the high affinity of the PAHs to the PE and PP polymers (Teuten et al., 2007), which could be absorbed from the surrounding environment during the extrusion process.

The same trend was observed for PP. After extruding the pristine PP, a minor increase in the total concentration of PAHs was observed. However, the percentage of increase was lower by a factor of 43.6% than that for the LDPE polymer. Even a lesser percentage of increase was obtained by the 6-priority PAHs (29.5%) (see Figure 8). Nonetheless, the PAHs content was tangibly below the threshold limits for children articles as well as consumer products for PE

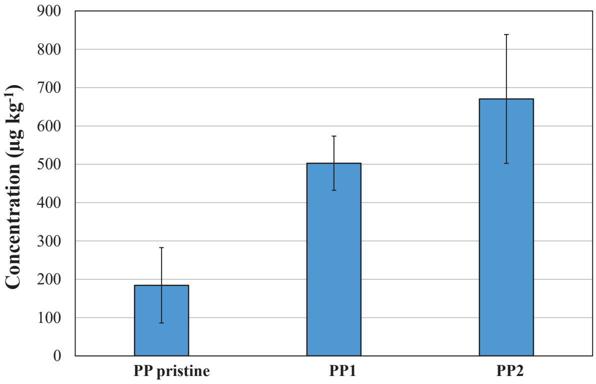

FIGURE 5: The concentration of the 16-US-EPA PAHs in different PP sample.

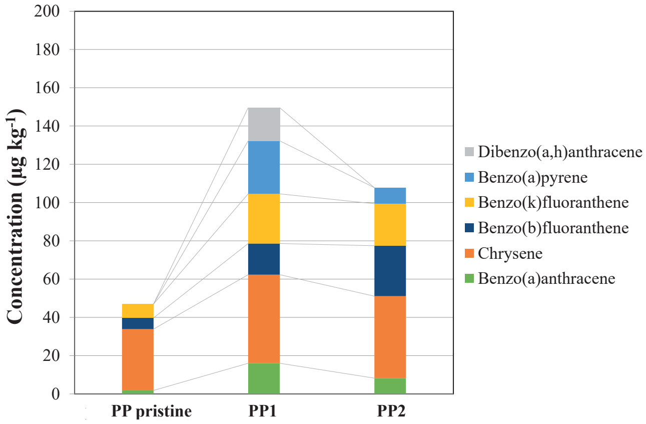

FIGURE 6: The content of 6 out of the 8 priority PAHs in the recycled and pristine PP samples.

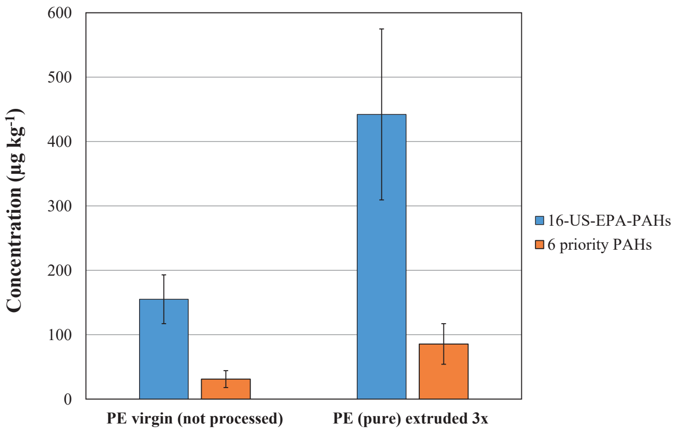

FIGURE 7: A comparison in the PAHs content between pristine PE and 3-cycles extruded pure PE.

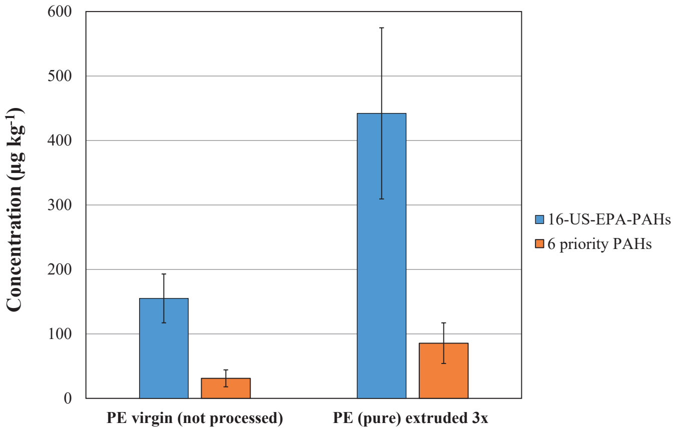

FIGURE 8: A comparison in the PAHs content between pristine PP and 3-cycles extruded pure PP.

and PP samples that are recycled without the presence of additives (Alassali et al., 2020b).

3.3 The impact of mixing recycled plastics with pristine polymers (dilution) on the PAHs content

Generally, recyclates dilution with pristine polymers resulted in a decrease in the total concentration of the 16-US-EPA PAHs. It was observed that the decrease was 16% for the 50%-RE sample and improved by almost the double (decrease by 30%) for the 25%-RE (see Figure 9).

Phenanthrene was lost in both diluted samples (i.e. 50%-RE and 25%-RE). This could be attributed to the low melting point of phenanthrene (99°C) (National Center for Biotechnology Information), resulting in its evaporation during the extrusion process. Additionally, the dilution of the material resulted in further decrease in its concentration to be undetectable.

Analysing the 6-priority PAHs showed an insignificant decrease in their concentration when the PE2 was diluted by a 50%-factor. When the 6-priority PAHs were separately evaluated, a tangible increase in the chrysene concentration and a minor increase in the acenaphthene concentration were observed in the 50%-RE sample. This is explained by the additional extrusion step the 50%-RE sample has undergone, in comparison to the 100%-RE sample (original sample, which was not further extruded in the lab). The same trend was not observed in the 25%-RE sample, because of the additional dilution of the sample with pure and new material, resulting in a substantial dilution in the PAHs content (Alassali et al., 2020b).

4. CONCLUSIONS

The aim of this study was to analyse the impact of the mechanical recycling of plastics on the degree of their contamination by polycyclic aromatic hydrocarbons (PAHs). Firstly, recyclates purchased from recyclers were tested to assess for the quality of recycled plastic put on the market. Results showed that HDPE and PP recyclates had higher concentrations of PAHs in comparison to pristine samples. HDPE recyclates originating from mixed sources had higher concentrations of the 16-US-EPA PAHs than those recyclates originating from one defined source. This indicates the importance of controlling the plastic waste streams put for recycling. Similarly, recycled polypropylene (PP) indicated higher PAHs concentrations in comparison to pristine material, yet with lower degree of contamination than that for HDPE, which could be explained by the less affinity it has to PAHs in comparison to the PE polymer. Considering 6 out of the 8 priority PAHs indicators (assigned by the Reg-

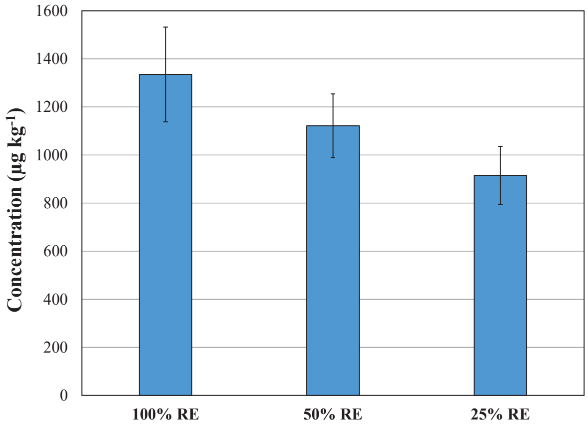

FIGURE 9: The concentration of the 16-US-EPA PAHs in PE recyclates, before and after dilution (by a 50% and 75% factor).

ulation EU 1272/2013 amending REACH Annex XVII), recyclates were most of the times complying with the threshold limits for consumer products.

Taking everything into account, the recycling process contributes to the formation and accumulation of PAHs in plastics, yet the increase is insignificant in pure plastics, due to the absence of organic additives and dyes. The PAHs content can be intensified in recycled plastics when the source material comes with higher degrees of contamination. As a result, the quality and source of plastic waste define the quality of produced recyclate. Adding pristine resin to the recycled plastic can enhance the chemical quality of the end product by obtaining less contamination risks.

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HAZARDOUS PROPERTIES OF BROMINATED, PHOSPHORUS, CHLORINATED, NITROGEN AND MINERAL FLAME RETARDANTS IN PLASTICS WHICH MAY HINDER THEIR RECYCLING

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ABSTRACT

Flame retardants are numerous and some of them are (re)classified with time as hazardous for the mankind and the environment. A list of 69 flame retardants used in EU was set from three sources and their chemical properties were searched in their registration dossier at ECHA. Substance self-classifications (hazard statement assignment by the registrant) frequently indicate no hazard or data not available, while for the same substances a re-evaluation by ECHA is underway as persistent, bioaccumulative, toxic or endocrine disruptor. When the substance has hazard statement(s), the concentration that triggers the classification of a plastic as hazardous when it is a waste can be compared to the functional concentration, when available. Registration dossiers should be completed for the many "non-available" information. Of these 69 substances, 12 (= 17%) are used at concentrations greater than those making plastic waste hazardous and 13 (= 19%) are under re-evaluation by ECHA. These 12 or 13 substances should not become "legacy" substances which hinder the recycling of plastics. The sorting (mainly by density) and management options of these flame-retarded plastics are discussed. The technical concentration limit of 2000 mg total Br/kg for sorting should not be modified as it includes all organobromine substances currently reassessed by ECHA. A two-step sorting process is necessary to avoid the loss of non-hazardous dense plastics.

1. INTRODUCTION

The flame retardants (FR) protect people and property from fire, by their retarding or intumescent properties. They are useful additives in plastics of electrical circuits, furniture, upholstery, thermal insulation of electrical and electronic equipment, vehicles, construction products, textile and non-food packaging (Drage et al. 2018, review in Hennebert 2020). Their use is generalised (Alaee et al. 2003) and they are present in household products (Chen S.J. et al. 2010). The toxic ones are subject of active research for their substitution, as halogen-free combination of phosphorus and silicon (Cui et al. 2021, Gibertini et al. 2021), use of alumina in battery (Delaporte et al. 2021), development of eco-friendly NP substances (Liao et al. 2021) or polyols substances (Chen M-J et al 2018), or more physical approach for polyester (Zhang et al. 2021) or polypropylene (Zhao et al. 2021). The use of plastics in Europe in the sectors using FR is important: 19.8% for building and construction, 16.7% for medical equipment, plastic furniture and furniture equipment, technical parts used for mechanical engineering or machine-building, and 4.1% for household, leisure and sport (PlasticsEurope 2018), totalling so about 40% of the plastics used in EU or 20Mt per year, as much as packaging (food and non-food) plastics (calculated from PlasticsEurope 2018).

Some plastic additives are banned over time by the Persistent Organic Pollutants (POPs) recommendations of the United Nations Stockholm Convention or other regulations (EU 2016, 2019). Prohibited substances are gradually replaced by other substances (Santillo and Johnston 2003, AFP 2015). What are the substitutes or the used substances and their eventual hazard properties? Are they used in concentration(s) that make(s) the plastic hazardous when it becomes a waste?

To set a list of flame retardants, three sources of information were used: (i) the Plastic Additives Initiative (PAI), a collaboration between the ECHA and the plastics industries, which in 2019 delivered a list of 418 additives currently used in products in the EU (it is not known if it is EU26 or EU27), along with their function(s), the polymer(s) they improve, and their functional concentration(s) (ECHA 2021a); (ii) the catalogs of three large producers of brominated flame retardants (Hennebert, 2021), and (iii) the

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catalog of the Phosphorus, Inorganic and Nitrogen Flame Retardants Association (PINFA) site (PINFA 2021b).

The additives are first detailed by function, by polymer and by functional concentration mentioned in the PAI file. Their hazardous properties of human toxicity and ecotoxicity from the ECHA registration site of chemicals in the EU (ECHA 2021b, open access chemical portal https://echa.europa.eu/information-on-chemicals) are then presented by families based on main elements (bromine, phosphorus and phosphorus-chlorine, chlorine, nitrogen, antimony, boron and boron-zinc, magnesium, aluminium). When their functional concentration is documented, it is compared for every hazard statement with the concentration that makes a waste hazardous (EU 2014, 2017). A synthesis of the chemical classification of all the flame retardants of plastics officially used in the EU is presented.

The sorting and management options of these flame-retarded plastics are then discussed.

2. MATERIAL AND METHODS

2.1 The list of flame retardants used in the EU

A common list of used additives in plastics is available on the so-named "Mapping exercise – Plastic additives initiative" (https://echa.europa.eu/fr/plastic-additives-initiative). This joint project by the ECHA and plastics industries since 2016 resulted in a list of 418 functional additives used in plastics, including information on the polymers they are most found in and the typical concentration ranges. The mapping considered substances registered under REACH at above 100 tonnes per year, and focused on plasticisers, flame retardants, pigments, antioxidants, antistatic agents, nucleating agents and various types of stabilisers. An excel file has been delivered in 2019. The polymers' names are abbreviated: ABS: acrylonitrile butadiene styrene; PA: polyamide ; PC: polycarbonate ; PET: polyethylene terephthalate; PMMA: polymethyl methacrylate; Polyolefin-I: polyethylene group; Polyolefin-II: polypropylene; EPS: (expanded) polystyrene; PUR: polyurethane; PVC (rigid): polyvinylchloride (without plasticisers); PVC (soft): polyvinylchloride (with plasticisers).

The catalogs of the three large brominated flame retardants producers (Albemarle, ICL, Lanxess) were compiled and the 34 substances (some polymers that do not have to be registered, some are not for sale in EU) are presented in details in Hennebert (2021). The significant production in China (> 50% of all BFRs) has not been documented.

The Phosphorus, Inorganic and Nitrogen Flame Retardants Association (PINFA 2021a) presents a summary of its stakeholders flame retardants (PINFA 2021b), which has been used here.

2.2 Properties of substances and hazard classification of waste

The self-reported chemical properties of substances on human health and the environment are found in their European ECHA registration dossier (https://echa.europa.eu/information-on-chemicals). The "Brief Profiles" are a practical summary of the dossier. The most frequently reported hazard statement codes have been used here. Some hazards are graduated from level 1 (high) to level 4 (low). For some substances, the ECHA mentions its own classification, or indicates that a re-assessment is in progress.

The hazard classification of the additivated plastics as waste is done according to the EU regulations (EU 2014, EU 2018). A synthesis is presented in Hennebert (2019a). In the tables, the concentration of hazard statements classifying a waste as hazardous is indicated if it is ≤ 20%.

3. RESULTS AND DISCUSSION

3.1 Additives per function category and per polymer type

The number of additives per function is presented in Figure 1 in decreasing order: Pigment agents (979 occur-

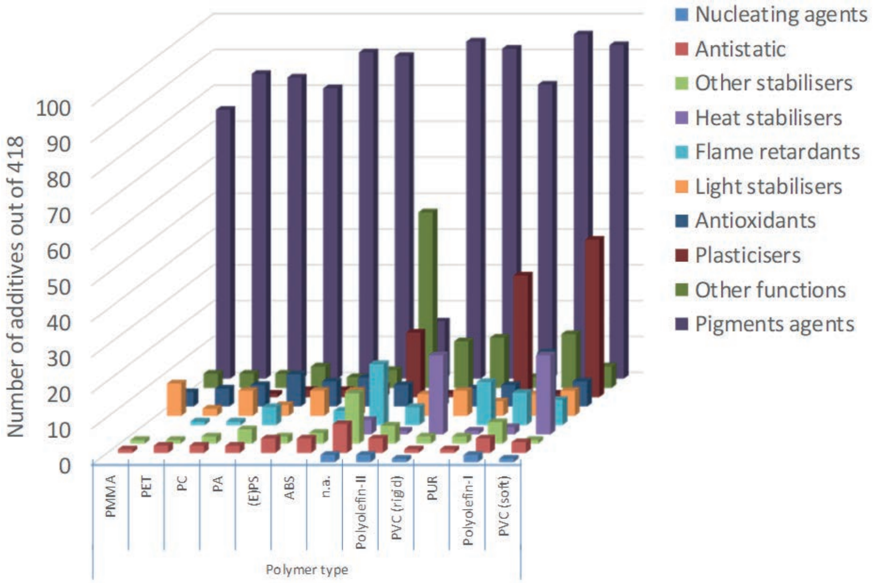

FIGURE 1: The number of additives in the Plastic Additives Initiative per function category and per polymer type.

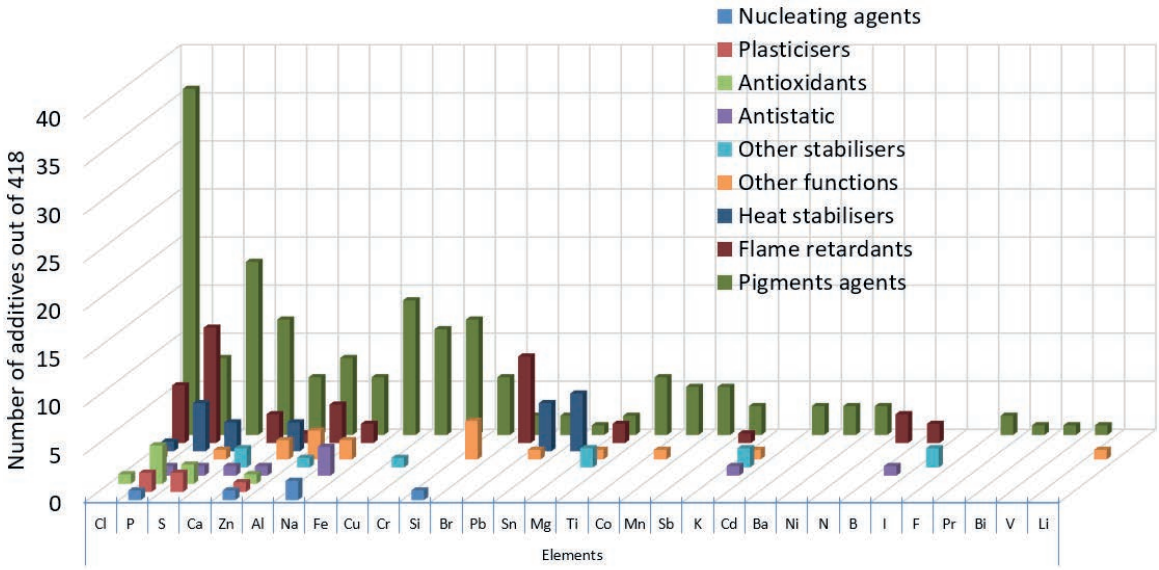

FIGURE 2: The number of additives in the Plastic Additives Initiative per function category and per element.

rences) > Other functions (126) > Plasticisers (106) > Antioxidants (91) > Light stabilisers (65) > Flame retardants (61) > Heat stabilisers (52) > Other stabilisers (43) > Antistatic (36) > Nucleating agents (8). A total of 1567 occurrences for 418 substances, indicating that a substance may have more than one function.

3.2 Additives per function category and per element

The decreasing number of elements in additives is presented in Figure 2: Cl (45) > P (33) > S (27) > Ca (18) > Al, Zn (16) > Na (15) > Fe (14) > Cr, Cu (12) > Br, Si (11), Pb (8) > Mg, Sn (7) > Co, Ti (6) > Mn (5) > K, Sb (4) > B, Ba, Cd, N, Ni (3) > F, I (2) > Bi, Li, Pr, V (1). Total 300. The elements C, O and H are not accounted for, as well as N when it is in substituting groups and is not the skeleton of the substances. Some additives have two elements, for instance the 3 additives (P- and Cl-).

3.3 Additives per functional concentration

The concentration of additives recommended in the mixtures before moulding or injection of parts or plastic material is given for a part in the listing of the PAI. The available concentrations are summarized in Table 1 and Figure 3. The substances with the highest concentrations are shown in the last row of the table. Plasticisers and flame retardants are used at higher average concentrations than other additives. The three flame retardants that are

TABLE 1: The functional concentrations of additives by function category, with the additives with highest concentrations (sorted by decreasing mean concentration – yellow row) (in case of range, the highest concentration is used).

Functional concentration (%)	Plasticisers	Flame retardants	Antistatic	Pigments agents	Other functions	Heat stabilisers	Light stabilisers	Other stabilisers	Antioxidants	Nucleating agents	Total
N data	40	19	4	102	16	23	13	7	17	2	243
(including concentration ranges)	33	7		5	4		8	2	12		71
Min	0.5	0.3	1.0	0.1	0.1	1.5	0.0	0.2	0.0	0.2	0.0
Mean	20.4	13.7	5.3	3.4	2.3	2.2	1.4	0.7	0.7	0.2	6.4
Max	35.0	50.0	10.0	50.0	20.0	4.0	6.0	1.0	3.0	0.2	50.0
Substances with high concentrations (%)	Dodecanoic acid, subtituted phtalates and other organics (33 substances used at 35%)	Aluminium hydroxide (50%); 1,1'-(ethane-1,2-diyl) bis[pentabromobenzene] (35%); Phenol, isopropylated, phosphate (3:1) (35%)	Multi-Walled Carbon Nanotubes (MWCNT) (10%)	Barium sulfate (50%); Carbon black (40%)	Kaolin (20% - filler)	2-ethylhexyl 10-ethyl-4,4-dimethyl-7-oxo-8-oxa-3,5-dithia-4-stannatetradecanoate (4%)	2,2'-methylenebis (6-(2H-benzotriazol-2-yl) -4-(1,1,3,3-tetramethylbutyl) phenol) (6%)	Calcium oxide (1%); Magnesium carbonate (1%)	Ethylenebis(oxyethylene) bis[3-(5-tert-butyl-4-hydroxy-m-tolyl) propionate] (3%); 2 others (3%)	2,2'-methylene bis-(4,6-di-tert. butylphenyl) sodium phosphate (0.2%); Sodium benzoate (0.2%)	

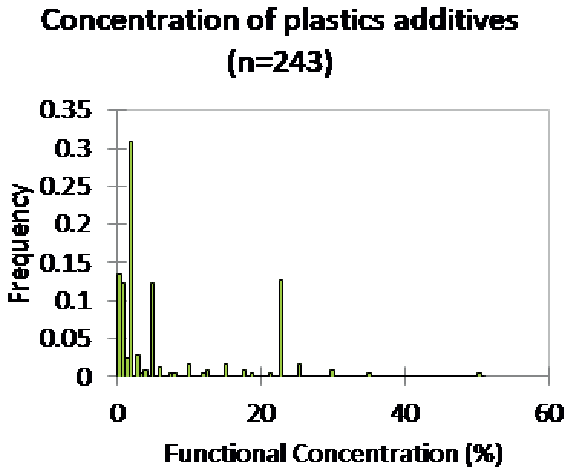

FIGURE 3: The functional concentrations of some additives in the Plastic Additives Initiative (when a range is documented, the mean concentration is presented).

used in the highest concentration are bromine, phosphorus and aluminum groups.

3.4 Organo-brominated flame retardants

Nine Brominated flame retardants (among a total of 35 FR in that list) are declared in the list of 418 plastic additives actually used in the EU (Table 2). Their situation is worrying. There are 2 substances classified as Persistent Organic Pollutants (POPs) and banned, and the 7 others are currently under re-assessment by the ECHA as persistent, bioaccumulative and toxic (PBT), endocrine disruptor (ED) or both.

A detailed table with additional brominated flame retardants from three large producer's catalogs can be found in (Hennebert 2021). In that list of 34 substances, some are not sold in the EU, and others are polymers, that have not been declared in the REACh system of ECHA. In total, there are 34 substances, among which 3 with functional concentrations making the additivated plastic hazardous, and 5 under re-assessment. Of these 5, 4 are listed in the PAI and are presented in Table 2, and the fifth one is 2,4,6-tribromophenol (CAS 118-79-6) and is reassessed in the PBT list. These substances are considered in the synthesis Table 7.

3.5 Phosphorus and phosphorus-chlorine flame retardants

Twelve substances are listed in the Plastic Additives Initiative, and 2 additional substances are found in the Phosphorus, Inorganic and Nitrogen Flame Retardants Association (PINFA) catalog, being in total 14 substances (Table 3). Four out of 14 substances have functional concentration greater than the concentration making plastic hazardous when it becomes a waste (EU waste classification). One substance is under assessment by the ECHA.

3.6 Organo-chlorinated flame retardants (without P)

Three substances are listed in the Plastic Additives Initiative (Table 4). One out of 3 substances has a functional concentration greater than the concentration making plastic hazardous when it becomes a waste (EU waste classification) (according to reclassification by the ECHA of that substance). Two substances of 3 are under re-assessment by the ECHA.

TABLE 2: The chemical properties of the brominated flame retardants of the Plastic Additives Initiative (in red: the functional concentration is higher than the concentration that makes a waste hazardous; in yellow: re-assessment by the ECHA in progress).

Name	Formula	CAS	FC%	Polymer type	Self-classification		Note	ECHA	BP
Hexabromocyclododecane – HBCD or HBCDD	$C_{12}H_{18}Br_6$	25637-99-4	n.a.	n.a.			NU	POP+others	+
Bis(pentabromophenyl) ether - DecaBDE	$C_{12}Br_{10}O$	1163-19-5	n.a.	n.a.			NU	POP+others	+
2,4,6-tris(2,4,6-tribromophenoxy)-1,3,5-triazine	$C_{21}H_6Br_9N_3O_3$	426-040-2*	n.a.	n.a.	Not classified		PAI+PC	PBT	+
1,1'-(ethane-1,2-diyl)bis[pentabromobenzene]	$C_{14}H_4Br_{10}$	84852-53-9	15.0 - 35.0	PUR; PVC (soft)	Not classified		PAI+PC	PBT	+
N,N'-ethylenebis(3,4,5,6-tetrabromophthalimide)	$C_{18}H_4Br_8N_2O_4$	32588-76-4	n.a.	n.a.	Not classified		PAI+PC	PBT	+
1,1'-(isopropylidene)bis[3,5-dibromo-4-(2,3-dibromopropoxy)benzene]	$C_{21}H_{20}Br_8O_2$	21850-44-2	15	n.a.	Not classified		PAI+PC	PBT, ED	+
1,1'-(isopropylidene)bis[3,5-dibromo-4-(2,3-dibromo-2-methylpropoxy)benzene]	$C_{23}H_{24}Br_8O_2$	97416-84-7	n.a. supposed 15% by similarity	PUR; PVC (soft)	Not classified		PAI	ED	+
2,2-bis(bromomethyl)propane-1,3-diol	$C_{23}H_{24}Br_8O_2$	3296-90-0	n.a.	n.a.	Not classified		PAI	ED	+
2,2',,6'-tetrabromo-',4'-isopropylidenediphenol	$C_{15}H_{12}Br_4O_2$	79-94-7	5.0 - 10.0	Polyolefin-I; Polyolefin-II; ABS	H400	H410 0.25%	PAI	PBT, ED	+

*n.a.= not available; * = No CAS number in the file; NU: not used, banned; PAI+PC = data from the Plastic Additives Initiative and in the Producer's catalogs; PAI = data from the Plastic Additives Initiative; POP = persistent organic pollutant; PBT = persistent, bioaccumulative and toxic (PBT); ED = endocrine disruptor; H410 = Ecotoxic chronic level 1. BP = brief profile (summary report) in the ECHA*

TABLE 3: The chemical properties of the phosphorous and phosphorous-chlorine flame retardants of the Plastic Additives Initiative (in red: the functional concentration is higher than the concentration that makes a waste hazardous; in yellow: re-assessment by the ECHA in progress.

Name	Formula	CAS	FC%	Function	Polymer	Self-classification						ECHA	BP
Reaction mass of tris(2-chloropropyl) phosphate and tris(2-chloro-1-methylethyl) phosphate and Phosphoric acid, bis(2-chloro-1-methylethyl) 2-chloropropyl ester and Phosphoric acid, 2-chloro-1-methylethyl bis(2-chloropropyl) ester		EC 911-815-4 No CAS number	15	Flame retardants; plasticiser	PUR; PVC (soft)	Not classified							+
Reaction mass of p-t-butylphenyldiphenyl phosphate and bis(p-t-butylphenyl) phenyl phosphate and triphenyl phosphate		EC 700-990-0 No CAS number	n.a.	Flame retardants	n.a.	H400	H410 0.25%	H411 2.5%					+
Phenol, isopropylated, phosphate (3:1)	$C_{90}H_{96}O_{16}P_4$	68937-41-7	15.0 - 35.0	Flame retardants; plasticiser	PUR; PVC (soft)	H361 3%	H373 10%	H317	H411 2.5%	H410 0.25%	H413	PBT	+
Polyphosphoric acids, ammonium salts	$H_{48}N_{11}O_{25}P_7$	68333-79-9	30	Flame retardants	Polyolefin-I	Not classified	H302	H319 20%					+
1,3,5-triazine-2,4,6-triamine phosphate	$C_3H_9N_6O_4P$	41583-09-9	n.a.	Flame retardants	n.a.	Not classified							+
2,2-bis(chloromethyl)trimethylene bis(bis(2-chloroethyl) phosphate)	$C_{13}H_{24}Cl_6O_8P_2$	38051-10-4	12	Flame retardants	PUR	Not classified							+
6H-dibenz[c,e][1,2]oxaphosphorin 6-oxide	$C_{12}H_9O_2P$	35948-25-5	n.a.	Flame retardants	n.a.	Not classified	H317					Ss	+
Dimethyl propylphosphonate	$C_5H_{13}O_3P$	18755-43-6	15	Flame retardants	PUR	H360 1B 0.3%	H319 20%						+
Tris[2-chloro-1-(chloromethyl)ethyl] phosphate	$C_9H_{15}Cl_6O_4P$	13674-87-8	n.a.	Flame retardants	n.a.	H351 : 1%	H410 0.25%	H411 2.5%	H315 20%	H302	H373 H332	H 351 1%	+
Calcium phosphinate	CaO_4P_2 = $Ca(PO_2)_2$	7789-79-9	1	Flame retardants	Polyolefin-I	H228 1	H302	H228 2	H319 20%	H318 10%			+
Ammonium dihydrogenorthophosphate	H_6NO_4P = $(NH_4)\ H_2PO_4$	7722-76-1	n.a.	Flame retardants	n.a.	Not classified	H319 20%	H315 20%	H335	H412			+
Triethyl phosphate	$C_6H_{15}O_4P$ = $(C_2H_5)_3\ PO_4$	78-40-0	10	Flame retardants	PUR	H302	H319 20%	H336				H302 25%	+
Fyroflex SOL-DP = Hydroquinone bis-phosphate (= benzene-1,4-diol) (PINFA)	n.a.	EC 479-310-7		Flame retardants		Not classified							+
red phosphorus (PINFA)	P	EC 918-594-3		Flame retardants		H228 flammable solid	H412						+

PBT = persistent, bioaccumulative and toxic (PBT); Ss = skin sensitising; H302 Acute Toxic 4 (oral); H351 Carcinogenic 2; H360 1B Reprotoxic 1A and 1B; H361 Reprotoxic 2; H410 = Ecotoxic chronic 1; H411 = Ecotoxic chronic 2. BP = brief profile (summary report) in the ECHA site

TABLE 4: The chemical properties of the chlorinated flame retardants of the Plastic Additives Initiative (in red: the functional concentration is higher than the concentration that makes a waste hazardous; in yellow: re-assessment by ECHA in progress).

Name	Formula	CAS	FC%	Function	Polymer	Self-classification	ECHA	BP
Alkanes, C14-17, chloro	-	85535-85-9	15	Flame retardants; plasticiser	PUR; PVC (soft)	Not classified	PBT H400 H410 0.25% H362 Assessment	+
Paraffin waxes and Hydrocarbon waxes, chloro	-	63449-39-8		Flame retardants; plasticiser	PUR; PVC (soft)	Not classified, H319, H400, H362		+
Dechlorane plus	$C_{18}H_{12}Cl_{12}$	13560-89-9	3	Flame retardants	Polyolefin-I	Not classified	PBT, POP	+

PBT = persistent, bioaccumulative and toxic; POP = persistent organic pollutant; H363 = Reprotoxic 3; H400 = Ecotoxic acute 1; H410 = Ecotoxic chronic 1. BP = brief profile (summary report) in the ECHA site

3.7 Nitrogenous flame retardants

Many substances incorporate nitrogen. Here are only considered the substances where nitrogen is part of the molecular skeleton and has a large mass fraction (> 50%) of the molecule.

Three substances are listed in the Plastic Additives Initiative, and 2 additional substances are found in the Phosphorus, Inorganic and Nitrogen Flame Retardants Association (PINFA) catalog, for a total of 5 substances (Table 5). Melam is a condensation product made of 2 molecules of melamine. On heating, melam first loses ammonia to form melem (with three triazine rings), and then melon (a condensation product of melem). Melon is finding only experimental use at this stage (PINFA 2021).

Two out of 5 substances have functional concentrations above the concentration making plastic hazardous when it becomes a waste (EU waste classification). One substance is under reassessment by the ECHA.

3.8 Mineral flame retardants

The carcinogenic antimony oxide is placed first (Table 6), followed by 9 flame retardants ordered by group of the periodic table of elements: boron group (B, Al) and alkaline earth metals (Mg, Ca).

Diantimony trioxide is used as a synergist of brominated flame retardants, with a functional concentration of 8%. That substance is H351 Carcinogenic level 2 (low level), with a concentration limit of 1% Sb_2O_3 (= 0.83% Sb) in waste, which makes it hazardous. As the speciation of total Sb cannot be done routinely, and as it is a generic classification ("antimony compounds") (Hennebert 2019), a plastic with a total concentration of 0.83% of Sb is classified as hazardous.

Aluminum hydroxide can be used as flame retardant up to 50%. This substance may classify a waste as HP 4 "Irritant" if its concentration is ≥ 20%, due to its hazard statement H319 "Eye irritant 2" (low level). It is probably not irritating to the eyes when incorporated into a polymer, such as polypropylene for outdoor furniture. As in this case eye exposure is unlikely, the risk is low, and it is not considered here as triggering a classification of hazard in plastic waste.

3.9 Synthesis of classification of flame retardants for hazardous concentrations and for re-assessment by the ECHA

The number of FRs, the (minimum) number of FRs with a functional concentration greater than the hazardous concentration, and the number of FRs under reassessment by the ECHA are presented in Table 7. The total number of 69 FRs is consistent with the number 75 recently published (Haarman et al. 2020).

In the PAI alone, 35 flame retardants are used in the EU. Nine of them (= 26%) are used at concentrations greater than those making plastic waste with these additives hazardous (when this concentration is documented), and 12 of them (= 34%) are under re-assessment by the ECHA and may be restricted or prohibited in the future.

In the PAI and the manufacturer's catalogs, 69 flame retardants are used in the EU. Twelve of them (= 17%) are used at concentrations greater than those making plastic waste dangerous with these additives (when this concentration is documented): 4 bromines, 4 phosphorus, 1 chlorine, 2 nitrogen and 1 mineral (antimony trioxide). Of these 69 substances, 13 of them (= 19%) are under re-assessed by the ECHA and may be restricted or banned in the future.

3.10 Management of these plastics

These plastics should be separated from the plastic stream during recycling. The sorting can be done by product origin (if well characterised beforehand), by density (FR make plastics denser), or by the presence of substances or elements by optical methods. Density sorting is obtained by flotation in a bath or by X-ray transmission. Some plastics of specific items can be closed loop recycled if disassembled and processed separately (Tange et al. 2012).

For the sorting of a plastic fraction without FR, the additional density created by the FR unfortunately overlaps with the density ranges of some non-additivated polymers (soft PVC, PC+ABS, PC, some PP, some PS, Polybutylene terephthalate - PBT, hard PVC, PET according to Haarman et al. 2020). Today, this results in a loss of "pure" or potentially recyclable polymer when only density is used. This loss was estimated to be 30% in number of parts in one batch of WEEE plastics (Hennebert 2019b) (Figure 4). In this figure, the distribution of total bromine of 350 individual particles in the dense fraction (> 1.18 kg/l) of plastic scraps of screens, mainly cathode ray tubes (CRT), is presented. A first group < 1000 mg/kg of about 30% of particle numbers are the dense unbrominated plastics, or plastics with non-brominated additives. An intermediate group of 15 000 - 45 000 mg Br/kg has insufficient concentration for fire protection, probably due to improper recycling of brominated plastics. A third group of 50 000 - 150 000 mg Br/kg is protected against fire by brominated flame retardants.

A second step pre- or post-density sorting could avoid the loss of dense polymers or polymers with additives other than unwanted in the dense fraction. This requires the identification or measurement of substances or elements. Today, two methods are available:

by X-Ray fluorescence (XRF) with a handheld device or sorting machine. The measurable elements of FR are Mg, Al, P, Cl, Ca, Br, Sb. The elements B, N and F are too light to be measured, but are present only in some FRs (Figure 2). Ratio of element concentrations can be calculated and improve the specificity of the measurement and the sorting;

by short-wave infrared hyperspectral imaging (1 000 – 2 500 nm) calibrated for polymer type, Br and Sb recognition (Bonifazzi et al. 2021). The technology is ready in the laboratory stage but not suitable for black plastics, as they do not reflect infrared waves.

For the FR fraction, the simplest management of these plastics would be their reuse as flame retardant plastics. Due to the heterogeneous and variable composition, to date and to our knowledge, no article producer reuses these plastics, at least the brominated ones. One possible solution is chemical dissolution or decomposition, separation of additives and reconditioning of the purified polymer or building blocks for the chemical industry. For the specific case of hexabromocyclododecane in EPS insulation, this technology is currently in the pilot phase (PolystyreneLoop

TABLE 5: The chemical properties of the nitrogenous flame retardants of the Plastic Additives Initiative and PINFA catalog (in red: the functional concentration is higher than the concentration that makes a waste hazardous).

Name	Formula	CAS	FC%	Polymer type	Self-classification						ECHA	BP
Melamine = 1,3,5-triazine-2,4,6-triamine	$C_3H_6N_6$	108-78-1	25	PUR	Not classified	H361 3%						+
Cyanuric acid = 1,3,5-triazine-2,4,6-trio	$C_3H_3N_3O_3$	108-80-5	n.a.	Polyolefin-I; Polyolefin-II	H319	Not classified	H335	H315 10%	H302	H332		+
1,3,5-triazine-2,4,6(1H,3H,5H)-trione, compound with 1,3,5-triazine-2,4,6-triamine (1:1)	$C_6H_9N_9O_3$	37640-57-6	5.0 - 30.0	PUR; PA	H373 10%	Not classified						+
Melamine homologues such as melam, melem and melon (PINFA)												No
Melam = 1,3,5-triazine-2,4,6-triamine-N-[4,6-diamino-1,3,5-triazine-2-y]	$C_6H_9N_{11}$	3576-88-3				Not classified						+
Melon = 1,3,5-Triazine-2,4,6-triamine, deammoniated (PINFA)	$(C_6H_3N_9)1-3H_3N$	68649-66-1			Not classified							+

H361 = Reprotoxic 2; H373 = Single target organ toxicity, Respiratory 2. BP = brief profile (summary report) in the ECHA site

TABLE 6: The chemical properties of the mineral flame retardants of the Plastic Additives Initiative (in red: the functional concentration is higher than the concentration that makes a waste hazardous).

Elements	Name	Formula	CAS	FC%	Polymer type	Self-classification						ECHA	BP
Sb	Diantimony trioxide	Sb_2O_3	1309-64-4	8	Polyolefin-I; Polyolefin-II; PVC (soft); ABS; PA	H351 1%	H373	H411 2.5%	H412	H372	H360	H351 1%	+
B, P	Boron orthophosphate	BO_4P	13308-51-5	n.a.	n.a.	H319 20%	H315 20%	H335	H360	H302			+
B, Zn	Hexaboron dizinc undecaoxide	$B_6O_{11}Zn_2$	12767-90-7	0.3 - 0.4	Polyolefin-I; Polyolefin-II; PA	H400	H319 20%	H361	H411 2.5%	H410 0.25%	H335		+
Al	Aluminium hydroxide	AlH_3O_3	21645-51-2	0.25 - 50.0	Polyolefin-I; PUR; PA	NC	H319 20%	H335	H315 Skin irrit. 2 20%				+
Al	Boehmite (Al(OH)O)	$AlHO_2$	1318-23-6	5	PA	NC							+
Al, Na	Aluminium sodium dioxide	$AlO_2.Na$	1302-42-7	n.a.	n.a.	H318 10%	H314 1A 1%	H314 1B	H271				+
Al, Na	Aluminium sodium tetrahydroxide	AlH_4NaO_4	12251-53-5	n.a.	n.a.	H314	H318 10%						+
Mg	Magnesium hydroxide	MgH_2O_2	1309-42-8	4.0 - 8.0	Polyolefin-I; Polyolefin-II; ABS	NC	H319 20%	H315 20%	H335				+
Ca	Calcium dihydroxide	CaH_2O_2	1305-62-0	n.a.	n.a.	H318 10%	H315 20%	H335					+
Ca, Mg	Calcium magnesium dihydroxide oxide	CaH_2MgO_3	58398-71-3	n.a.	n.a.	H318 10%	H315 20%	H335					+

H351 = Carcinogenic 2. BP = brief profile (summary report) in the ECHA site

https://polystyreneloop.eu/). POP substances present in plastics must in all cases be destroyed or irreversibly modified. The most common method today is the incineration in an industrial waste incinerator, or in small proportions in a municipal solid waste incinerator or in cement kilns, with quality control of the fumes and the ashes.

The proposal of the bromine industry (Haarman et al. 2020) recommending moving the plastic sorting limit from

TABLE 7: Synthesis of the chemical properties of the flame retardants of the Plastic Additives Initiative and the Producer’s catalog.

Flame retardants	Data	n	n with functional concentration > hazardous concentration (Minimal n)	n under assessment by ECHA
Br	Plastic Additive Initiative (PAI)	7	1	7
	Among which: Plastic Additive Initiati–e - other than produ’er's catalogs	3	1	3
	3 main Producer’s catalogs (Hennebert 2021)	34	3	5
P and P-Cl	PAI (12) + PINFA (2)	14	4	3
Cl	PAI	3	1 (ECHA)	2
N	PAI (3) + PINFA (2)	5	2	0
Sb	PAI	1	1	0
B (P, Zn), Al (Na), Mg, Ca	PAI	9	0	0
Total (PAI only)		35	9 (26% of 35)	12 (34% of 35)
Total (PAI + Produ’er's Catalogs)		69	12 (17% of 69)	13 (19% of 69)

2 000 mg Br/kg total (EN 50625-3-1) to 6 000 mg Br/kg, since regulated BFRs are no longer used, is not valid, since all substitutes are being reassessed by the ECHA as persistent, bioaccumulative and toxic (PBT), endocrine disrupting (ED) or both (Table 2). This results from very incomplete classification files: the toxicity and ecotoxicity data for humans are simply entered as not available ... A great advantage of this 2000 mg of total bromine kg of plastic is that it includes all substitutive brominated substances. It is not too conservative because all these substitutes (with the exception of additive and polymers) are currently re-evaluated by ECHA and may be prohibited at the protective fire concentration in recycled plastics.

4. CONCLUSIONS

This study is focused on flame retardants only. Many ECHA dossiers for the registration of substances are uncompleted. Twelve flame retardants with Br, P, Cl, N and Sb are used in concentration that makes the plastic hazardous when it becomes a waste. This could hamper the acceptance of these plastics when recycled in the circular economy. Thirteen flame retardants with Br, P and Cl are reassessed by the ECHA as PBT (persistent, bioaccumulative, toxic), ED (endocrine disruptor), PBT + ED, or Ss (skin sensitising). These 13 substances must not become future “legacy” substances, hindering or prohibiting the recycling of these plastics.

Density sorting is effective, but dense polymers without FR or with harmless additives are lost. A second sorting step is necessary to sort these plastics into the dense fraction. Financial incentives and the participation of the producers are now necessary to promote this second sorting stage.

The technical concentration limit of 2000 mg total Br/kg for sorting includes all organobromine substances and is not too conservative since these substances are all currently reassessed by the ECHA.

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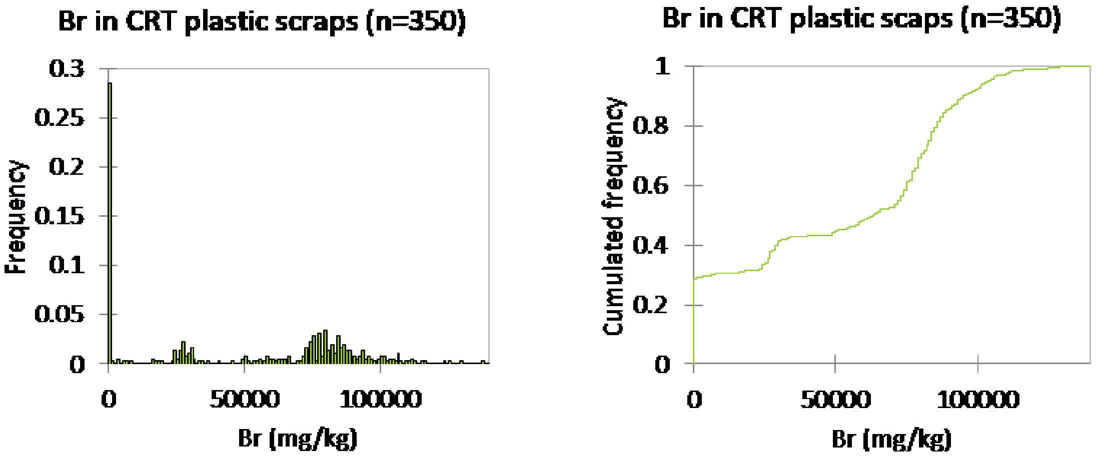

FIGURE 4: Distribution of total bromine in the dense fraction of plastic scraps of screens, mainly cathode ray tubes (CRT) (Hennebert 2019b).

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MICROPLASTICS IN LANDFILL LEACHATES IN THREE NORDIC COUNTRIES

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ABSTRACT

We investigated the occurrence of microplastics (size range 5,000-50 μm) in leachates at 11 landfills of different age and operational status in Finland, Iceland and Norway. Collective sampling was carried out by pumping leachate with a stainless-steel submergible pump through a custom-made, stainless-steel filter unit containing filter plates with decreasing pore sizes (5,000, 417 and 47 μm, respectively). Samples were pre-treated and split into particles size classes above 500 μm and above 50 μm, and screened for occurrence of microplastics made of PE, PP, PVC, PS, PET, PA, PU, PC, PMMA, POM, SBR (rubber) or PMB (polymer modified bitumen). Samples were analysed by FT-IR spectroscopy, both to identify and to count microplastic particles (SBR and PMB were merely identified). Most samples tested positive for multiple microplastics. Three leachates, including drinking water (blank), tested positive for SBR particles and/or PMB only. Treated leachate samples exhibited lower total microplastic's counts than untreated, up to several orders of magnitude. National waste management practices over time, landfill age or operational status do not seem to explain differences in microplastic abundance or counts between leachates. Particle count and calculated loads of microplastic emissions through leachates differed several orders of magnitude between landfills. Results indicate that landfill leachates might be a relatively small source of microplastics (>50 μm) to surface waters compared to untreated and treated sewage or road runoff. Continued data acquisition, improved sample preparation and understanding of variability of microplastics in landfill leachate are necessary, including particles smaller than 50 μm.

1. INTRODUCTION

Although discovered in the oceans more than 40 years ago (Carpenter et al., 1972), microplastics have recently attracted growing public and scientific attention. Global plastics production is increasing, and expected to increase exponentially (Crawford and Quinn, 2017). Both macroplastics (>5 mm) and microplastics (1μm < x < 5 mm) are of great concern, as they can spread and be ingested by organisms. Microplastics have, amongst other, been detected in deep sea organisms (Pereira et al., 2020), in remote mountainous areas (Ambrosini et al., 2019), fish (Sequeira et al., 2020), bottled water for human consumption (Welle and Franz, 2018), and human stool (Schwabl et al., 2019). Plastics are considered a ubiquitous pollutant in the oceans (Eriksen et al., 2014). Some studies have shown that microplastics can have negative effects on aquatic and terrestrial organisms (Teuten et al., 2009; Deng et al., 2017). Microplastics have been suggested to act as vectors for antibiotic resistance genes (Su et al, 2021). Few studies, however, have indicated potential effects on freshwater ecosystems at microplastic concentrations currently observed in the environment (Triebskorn et al., 2019). The potential risks of adverse effects of particles as small as 1 μm, and of nanoparticles, on organisms are not well understood, though (Triebskorn et al., 2019, Sana et al., 2020). Waste management, especially landfilling of waste, has been pinpointed as a potentially significant source of microplastics (Sundt et al., 2014, Magnusson et al., 2016, Lestari and Trihadiningrum, 2019, Prata et al., 2020), in particular through the emission of landfill leachates, the liquid effluents from landfilled waste to surface waters. Leaching of various contaminants from landfills, including plastic additives, is well known and documented (Kjeldsen et al., 2002; Haglund et al., 2015; van Praagh et al., 2011 and 2013). However, comprehensive information on microplastic content in landfill leachates and on the potential impact of landfill leachate treatment on microplastic has only recently come into research focus (Kokalj et al., 2019; He et al., 2019).

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In order to address the questions of landfill leachates as potential sources of microplastics and of efficacy of prevailing leachate treatment processes at landfills, the two working groups "Nordic Waste Group" and "Marine Group" under the Nordic Council of Ministers commissioned the design and completion of a study on the occurrence of microplastics in landfill leachates. (The Nordic Council is the official body for formal inter-parliamentary co-operation, formed in 1952 with members from Denmark, Finland, Iceland, Norway, Sweden, the Faroe Islands, Greenland and Åland). This study aimed at acquiring quantitative data on counts of microplastics, and at estimating their concentrations in leachates from landfills in Finland, Iceland and Norway (van Praagh et al., 2018). Furthermore, the aim was to acquire information on the impact of different leachate treatment methods on microplastic emissions, and to put potential microplastic emissions by landfill leachate into context with other potential sources of microplastics to surface water.

2. METHODS AND MATERIAL

2.1 Sampling locations

Leachate sampling took place during May 2018 (Iceland, then Finland, then Norway). After the sampling campaign in Finland, a stormwater pond receiving runoff from local highways in Stockholm, Sweden, was sampled. Loaded filter plates were removed from the filtering unit with a stainless-steel knife, placed in stainless steel boxes, sealed, packed, and delivered by courier to the laboratory at the Environment Agency Austria (Umweltbundesamt), Vienna, immediately at the end of each sampling campaign.

2.1.1 Landfills

Table 1 shows the type of landfill, location and information on operational status and leachate treatment at those landfills covered by this study. Landfills have been selected in order to reflect different levels of leachate treatment and operational status, type and estimated age of the landfilled wastes. Additionally, different landfilled classes (hazardous and non-hazardous) were to be included. In total, samples were taken at 11 different landfill sites in three different countries. At some locations, leachate could not be sampled separately from other potential microplastic sources such as storm water, service road runoff or recycling activities, as is common at waste management facilities in the Nordic countries. The ratio of landfill leachate in the effluents sampled varied, and was estimated to be between 70 and 100%.

2.1.2 Storm water pond

A storm water pond in the municipality of Huddinge south of Stockholm, Sweden's capital, was selected for a reference sample. The pond has a surface area of approximately 670 m^2 and a maximum depth of ca. 2.5 m. The pond receives runoff from adjacent local roads, a 880 m stretch of a 2-by-2 lane regional inner state highway, as well as from non-paved areas. Approximately 7.5 ha drainage area are connected to the pond. In the Stockholm area, the nominal annual precipitation is 600 mm.

2.2 Definition of microplastics

For this study, microplastic particles were defined as particles within the size range of 5 mm and 50 µm, consisting of manufactured polymers derived from petroleum or petroleum by-products. Landfill leachates were targeted for the following polymers:

- Polyethylene (PE)
- Polypropylene (PP)
- Polyvinylchloride (PVC)
- Polystyrene (PS)
- Polyethylene terephthalate (PET)
- Polyamide (PA)
- Polyurethane (PU)
- Polycarbonate (PC)
- Polymethylmethacrylate (PMMA)
- Polyoxymethylene (POM)

TABLE 1: Type and location of landfills covered in this study (type of waste disposed of: MSW = municipal solid waste, IW = industrial waste; landfill class: Non-haz = non-hazardous waste, Haz = hazardous waste; landfills with years of operation, "-date" still in use at the time of sampling; effluents at sampling point: L = landfill leachate, RR = road runoff; S = storm water, W = other waste processing; minor contribution in brackets).

Country	No.	Landfill class	Type of waste	Leachate treatment type	Main effluents to sampling point	Years of operation
Finland	1	Non-haz	MSW	None	L	1971-1989
	2	Non-haz	MSW, IW	None	L (S)	1989-date
	3	Haz	IW	Filtration and active carbon	L	1989-date
	4	Non-haz	MSW, IW	Artificial soil filtration	L, (S)	1980-2001
	5	Non-haz	MSW	None	L, W	1959-2007
Norway	6	Non-haz	MSW, IW	Sequencing batch reactor	L	1989-date
	7	Non-haz	Mixed	None	L	2009-date
	8	Non-haz	MSW, IW	None	L, (RR, S)	NN-1987
Iceland	9	Non-haz	MSW, IW	Sand bed filtration	L, (S?)	2012-date
	10	Non-haz	MSW, IW	None	L	2004-2012
	11	Non-haz	MSW, IW	None	L, (S?)	1989-date

- Styrene-Butadiene-Rubber (SBR, essentially the main component in tyre rubber)
- Polymer-Modified Bitumen (PMB, an admixture in asphalt paving, e.g., see Zhu et al., 2014)

According to PlasticsEurope, 2018, the first 10 polymers in the list above represent the major share of plastics produced globally.

2.3 Sampling and analysis

2.3.1 Collective sampling

Sampling was carried out by means of pumping leachate through three custom-made stainless-steel filter plates with decreasing mesh sizes, incorporated in a stainless-steel unit. Filter mesh width were 5000, 411, and 47 µm, respectively (filter unit designed and provided by Resource International, Iceland). A submersible, stainless steel pump (Proril X-SMART, 400A, 2", 0.4kW/230V/50 Hz) was connected via a reinforced PVC-hose attached to brass hose nipples on the stainless-steel filter housing. The filter unit was equipped with a flow meter and a pressure release valve. Flow meter readings were annotated prior and after each sampling occasion. At two sampling campaigns, in Finland and Iceland, flow meter readings were cross-refenced by means of timing filling containers with known volumes.

In some cases, leachate was collected in a bucket (PE) and subsequently pumped through the filter unit as described above (see Annex 1). Reasons for this approach were either extremely low water levels after a dry spring, or lack of accessibility at the sampling location.

In order to evaluate potential cross-contamination of leachate samples due to a) occupational safety gear of the staff; b) the PVC hose and power cable connected to the pump; and c) the use of plastic buckets, a blank sample with drinking water was collected at landfill 3 and included in the study as a control, or "blank". The presence of plastic materials used during sampling was documented (photographed and labels identified). Sampling locations and sampling volumes collected are described in Annex 1. Pumping and filtration took place until pressure built-up stalled further sampling, and flow was negligible or came to a total standstill. This was checked visually by observing that flow meter needles remained idle. The pressure release valve did not open during sampling on any occasion, which means that pressure was always below 1 bar.

An exception from this rule occurred when sampling storm water. The sample was collected by means of hauling a stainless-steel bucket attached to a stainless-steel wire repeatedly but at different lengths into the water pond (maximum 10 meters from the shore). The individual grab samples were then administered to the filtration apparatus directly, without using the stainless-steel pump. Sampling continued until no flow or dripping could be observed from the filter unit anymore.

2.3.2 Sample pre-treatment

Filter plates and containers were back-flushed with ultrapure water (Milli-Q, particle filter 0.22 µm) and treated with hydrogen peroxide (15% H_2O_2) for at least five days to remove non-plastic organic matter (see for example Claessen et al., 2013; Cole et al., 2014; Nuelle et al., 2014; Imhof et al., 2012). Some samples were additionally treated with small amounts of hydrochloric acid (10% HCl, see for example Eriksen et al., 2013). The solid matter remaining after the chemical pre-treatment was wet-sieved through 500 and 50 µm metal sieves, and thus separated into two size fractions: (1) particles larger than 500 µm and (2) particles of size 50-500 µm (Hohenblum et al., 2015; Robertson et al., 2015). Either size fraction (>500 µm and 50-500 µm) was removed from the metal sieves into ultrapure water. This particle-water suspension was homogenized, and a representative aliquot was transferred onto an inorganic filter membrane (Whatman Anodisc, 47 mm diameter, 0.2 µm pore size) via vacuum filtration, and subsequently dried at maximum 60°C, as residual humidity can interfere the IR-signal. The total mass of solid residue was calculated by the weight differences before and after chemical treatment.

Intermittently, all lab equipment was rinsed several times with ultrapure water that was pre-filtered through a 50 µm stainless steel sieve. In addition, a blank sample, undergoing the whole sample preparation procedure was analysed: No micro plastic was found in the blank sample.

2.3.3 Analysis

Sample preparation for the qualitative and quantitative analysis included representative subsampling and loading of particles onto an inorganic filter membrane (aluminium oxide), which were then analysed by µ-FT-IR (Fourier transform infrared)-spectroscopy and imaging (Spotlight 400, PerkinElmer Inc., USA). Subsampling was performed by suspending the samples' particles in water in a beaker. Numerous subsamples were subtracted while stirring the suspension. These subsamples were then combined and analyzed. Each subsample represented at least 20% of the respective total sample. In screening mode, samples were checked for occurrence of PE, PP, PVC, PS, PET, PA, PU, PC, PMMA, and POM (result of screening: present yes/no).

For each sample, a total area of 12.5 cm² was then scanned via imaging for acquisition of transmission infrared spectra. Via software assisted comparison (based on correlation, SpectrumIMAGE, Version R1.8.2 0413, PerkinElmer Inc., USA) with reference materials from a spectra database, the "chemical image" of the filter (2D map plus IR spectra) was evaluated for the polymers (see above), with an exemption for rubber (SBR) and polymer modified bitumen (PMB). Microplastic particle occurrence was estimated with the help of the counts of unambiguously identified particles.

Samples of three different SBR from two different Swedish producers as well as three different types of car tyres (PMB) were scanned and added to the laboratory's IR reference material database. Samples of SBR were collected by removing ca. 3x3 cm^2 large parts from disposed tyres at a workshop. For screening of SBR and PMB particles, a different measurement technique was applied; rather than scanning from a distance in the so-called transmission mode, the ATR (attenuated total reflection)-FT-IR micro-spectroscopy established contact between a Germanium crystal and the suspected particles for reflection measurements. The crystal was positioned onto 5 different spots on the filter, each of which exhibited an area of 0.16 mm², where SBR/PMB particles were preliminary identified visually. The total sample area that was screened for the presence of SBR/PMB particles resulted in 0.8 mm². As this is only a tiny fraction of the total sample area, SBR and PMB particles were neither counted nor their numbers estimated. The ATR-measurements were combined with imaging.

2.4 Mass calculations

Microplastic counts per litre were used to calculate mass concentration with the following assumptions.

- Uniform density of particles of the same polymer
- Density (kg/l or Mg/m^3) PA: 1.05, PE: 0.965, PET: 1.45, PMMA: 1.20, PP: 0.91, PS: 1.1, PU: 1.2, PVC: 1.58 (maximum values in GESAMP, 2015, or Hidalgo-Ruz et al., 2012)
- Uniform shape (globe)
- Radius r = 50 µm (exception storm water sample >500 µm: r = 250 µm)

No mass calculations for SBR and PMB have been undertaken, as these were only identified as part of the screening.

3. RESULTS AND DISCUSSION

3.1 Screening results

Results from screening to elucidate the occurrence of microplastic particles in samples after pre-treatment and re-filtering are shown in Annex 2 alongside the mass loading on the filters. No microplastics were found on 5000 µm filter meshes. Microplastics initial count and total amount of particulate matter remaining in the sample after chemical pre-treatment are depicted.

The mass of the remaining particles after chemical treatment can be used as an indicator of total microplastics' amounts in samples. The chemical treatment prior to the analysis described above does, however, not completely remove non-target matter. The 50 µm sample from landfill 8 reacted heavily upon contact with pre-treatment chemicals, producing precipitation residues. Large amounts of remaining insoluble inorganic residues impaired the screening for microplastics. An additional investigation into the nature of reaction products revealed prevailing minerals containing iron and silica. Double-checking with the landfill operator did not reveal any chemical anomalies in the sample which might suggest what caused the reaction with pre-treatment agents. The leachate from the sample point is normally rich in iron, but this is not uncommon for MSW-landfill leachates.

Generally, negligible numbers of microplastic particles of the size 5000-500 µm were detected, with an exception for the storm water sample. Rather, particles much smaller than 500 µm, and approximately closer to 50 µm were detected on the 411 µm screens. Consequently, a partition in particle size fractions was not considered meaningful, and results are displayed as sum of particles > 50 µm subsequently. Microplastics (including SBR and PMB) where detected in all samples. In three samples, a single polymer was detected: SBR residue was found in treated leachate from landfill no 6, leachate from no 10, as well as in the blank sample.

Abundance of identified plastics in leachate samples is shown in Figure 1. Except for PE, it differs from polymer production figures for EES/EU27. Historical data indicates that few changes in ranking of abundance have occurred since production started (Roland et al., 2017).

The lack of larger particles might be explained by the fact that landfill leachate quality is likely to be dominated by the lowest waste layer deposited, or rather the lowest layer of waste contributing to leachate drainage. The porosity of this layer i likely to be relatively low due to degradation of organic material and compression (Bleiker et al., 1995; Muaaz-Us-Salam et al., 2019). It can be assumed that small pore size restricts larger particles being drained.

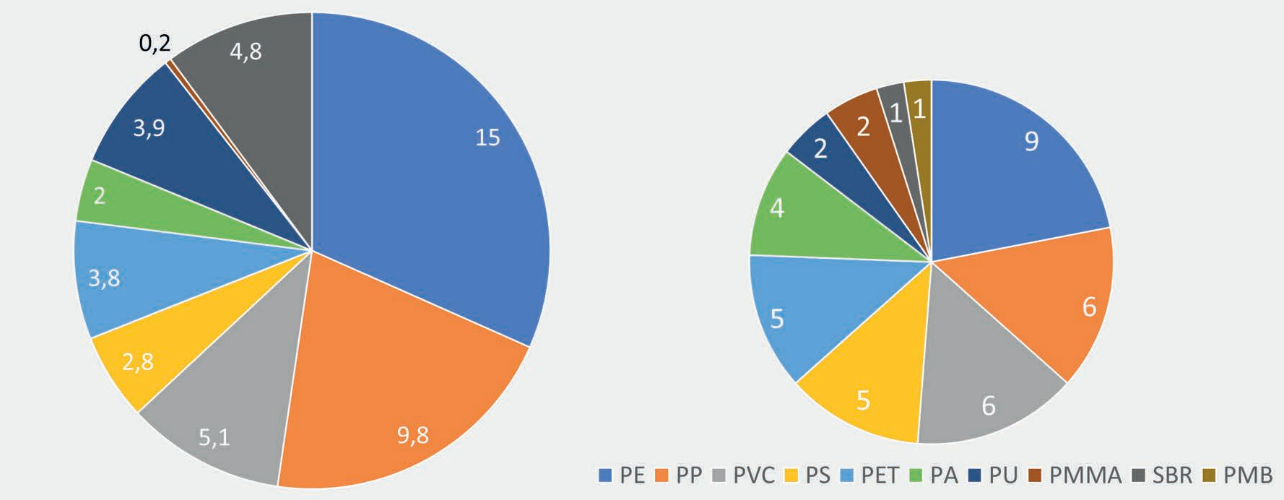

FIGURE 1: Production of polymers in Mtons (left, polymers for extrusion in EES-countries, year 2017, PlasticsEurope, 2018; SBR = tire production EU27, Echa, 2017), and abundance of polymers identified in leachate sample screening (right, total counts for all samples, PC = n.d.).

The presence of SBR in the blank sample indicates that cross-contamination has occurred. At first, residues from the rubber seals between sections of the filter unit were suspected.

However, the rubber seal material is significantly different from SBR-samples used for IR-imaging control spectra, and mixing up spectra is highly unlikely. The tap water for the blank sample was collected through a 5-meter-long reinforced PVC hose and pumped from the same bucket (PE) used at locations were submerging the stainless-steel pump was not possible. Staff was wearing personal protection equipment (PPE) comprising of PVC-gloves and PET-clothing. Consequently, contamination with these polymers might be expected, but was not detected. As the PE-bucket was open to the atmosphere at landfill site No. 3, where the blank sample was taken, air-born particles might have entered the sample. Although the sampling equipment was rinsed, filter plates renewed after each sampling occasion and the filter unit swapped with paper towels between sampling occasions, cross-contamination from prior sampling occasion cannot be ruled out. At this point, sources of sample contamination can neither be unambiguously identified nor ruled out.

3.2 Results from microplastic quantification

In Table 2, the microplastic counts and concentration as counts per sampling volume are displayed (observe that PMB and SBR were only screened for but could not be quantified, see the discussing section).

As can be derived from the results displayed in Table 2, polymer particles were quantified in all samples, except for the control sample (No. 0), and leachate samples Nos. 5, 6-treated and 10. The restrictions of the analytical method for black particles (see chapter 2), let to SBR- and PMB-particles not being accounted for, although they were identified in the previous “screening”.

The number of different identified polymers varies from 0 to 7 between samples, with PE being the most abundant polymer, found in 11 of 15 leachate samples with a total of 301 counts. Overall, counts in treated samples are ca 1 or even 2 orders of magnitude lower than in untreated samples, except for landfill no 3.

PE was found to be the dominant polymer in other studies on both leachate and other sources, as well (see Table 3, and even Silva et al., 2021, for a compilation of microplastic counts in landfill leachates).

Although differences between landfills/waste treatment facilities appear in the first three studies depicted in Table 3, the order of magnitude of observed maximum microplastics’ counts per liter in leachates appears to be comparable. Su et al., 2021, and Xu et al., 2020, reported concentrations almost three orders of magnitude higher.

3.3 National differences and years of landfill operation

Little is known about the main factors influencing microplastic particle release from landfills (Silva et al., 2021). Still, the amount and kind of plastic waste entering the landfill is likely to play a role, together with other potential sources of microplastics, such as recycling operations and service road runoff on site, atmospheric deposition, as well as materials used in leachate or landfill gas collection and treatment systems. Economic growth (Gardiner and Hajek, 2020), laws and regulations (van Praagh and

TABLE 2: Results from microplastic quantification (counts >50μm, blank cells = non detect).

No.	PE	PP	PVC	PS	PET	PA	PU	PMMA	Total count	Count/l
0 control										0
1	13	6							19	0.16
2	19		15	17	25	4	8	4	88	1.10
3 untreated					9		9		18	0.30
3 treated	25			35					60	0.32
4 untreated	41			16	8		73		138	1.97
4 treated	4			2					6	0.03
5										0
6 untreated	22				4				26	1.3
6 treated										0
7	6				51			26	57	1.40
8	10								10	1.00
9 untreated	14			2	4		40		60	0.20
9 treated	15								15	0.06
10										0
11	132	25		17			25		199	4.51
Storm water 50 μm [a]	8	23		10	109				150	4.17
Storm water 500 μm [a]	8	6		16	51				81	2.25

[a] *particles of PVC, PMMA, PA and PU were not quantified (fewer than 5 particles detected in screening-mode)*

TABLE 3: Compilation of results from studies on microplastics in leachates.

Study	No samples	Size range [µm]	Analytical technique	Count/l	No of polymers included/ identified (most abundant)	Comment	Reference
This study	15	50-5,000	FT-IR	0-4.5	11/11 (PE)		Van Praagh et al., 2018
Treated leachates in Sweden	7	≥ 100	Micro-scope	0-2.7	-	Waste facilities with landfill	Swedish Waste Association, 2018
Sorting facility Sweden	1	≥ 100	Micro-scope	2.3-4.2	-	Waste facility without landfill	Swedish Waste association, 2018
Chinese landfills	12	25-500	FT-IR	0.4-2.6	17/17 (PE)		He et al., 2019
Chinese landfill	18	10-150	µ-Raman	ø235	12/27 (PE)	[a]	Su et al., 2021
Chinese landfills	1[b]	20-100	FT-IR	291	4/? (PP)		Xu et al., 2020

[a] *raw leachate, study covered different parts of leachate collection and treatment system;* [b] *duplicate*

Persson, 2006), consumption habits (Kagawa et al., 2007), cultural aspects in economic sectors (Ajayi et al., 2016), type of waste management strategy and organisation (Lestari and Trihadiningrum, 2019); all these factors impact on amounts and types of waste going to landfill. Landfilling of (micro)plastics and microplastic emissions through leachates might be dependent on those factors, as well.

Plastics have been and are still target of direct or indirect waste management policy efforts in the Nordic Countries (Norden, 2017; Papineschi et al., 2019). Differences in recycling performance occur (Behzad et al., 2020; Zaman and Swapan, 2016). Performance figures for MSW management in the Nordic countries and EU average are displayed in Figures 2, 3 and 4 (data from Norden, 2020, where available; the term "Nordic countries" is used to discuss the data and figures, although not all Nordic Countries are included in the data).

Figure 2 indicates that most Nordic countries have a per capita MSW production comparable to the EU-average. Exceptions are Denmark with a continuously higher per capita production, and Norway. The apparent steep decrease in waste production year 2001, as well as the apparent steep increase in 2016 are suspected to reflect different input data or different definitions of "MSW", rather than real developments in MSW per capita.

Over time, percentages of collected MSW going to landfills have differed considerably between the Nordic countries (Figure 3). Although following the EU-average until year 2001, a much larger proportion of MSW ended up in landfills in Norway compared to Sweden, Denmark and Greenland. The same is true for Finland until 2016, and it appears to be true for Iceland year 2018. Residual waste, i.e. non-source separated waste is likely to contain plastic waste (Papineschi et al., 2019).

Only three active landfills covered in this study started operation in the time frame covered in the data behind Figures 2 to 4: two in Iceland (triangles in Figure 2) and one in Finland (dot in Figure 3).

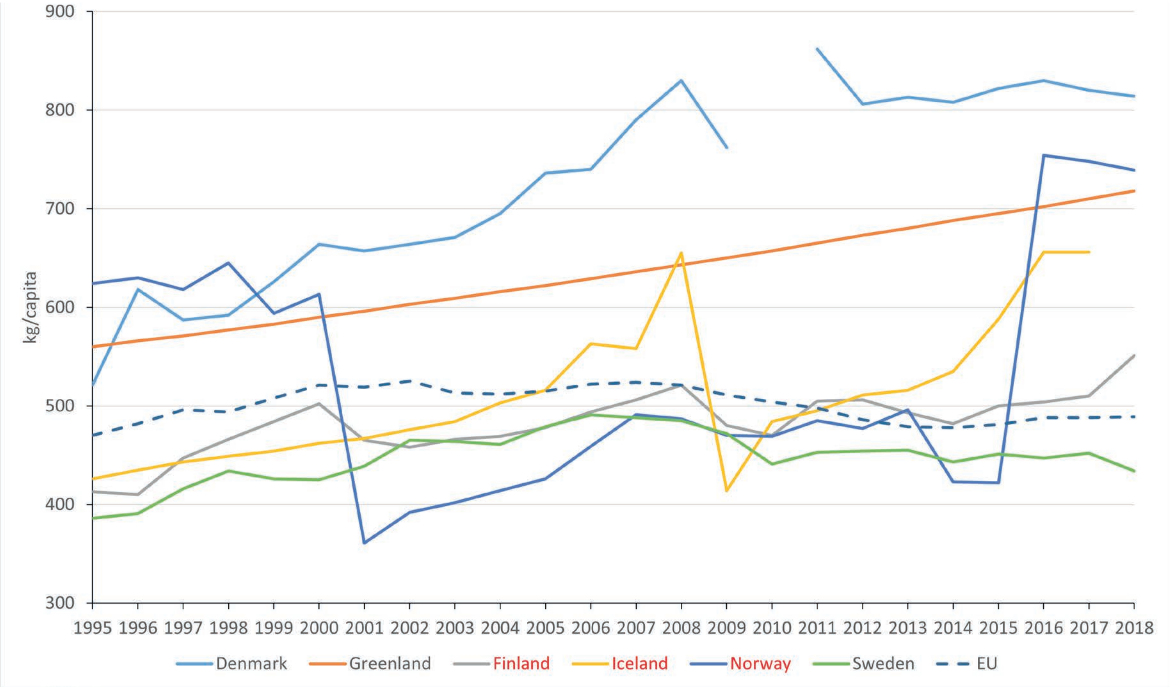

FIGURE 2: Municipal solid waste produced per capita in some Nordic countries (in Kg/capita; countries covered in this study in red text, EU depicts average of member countries, cut lines = missing data; different number of countries apply through timeline; Norden, 2020. Different definitions of "household waste" might apply, see e.g., Papineschi et al., 2019).

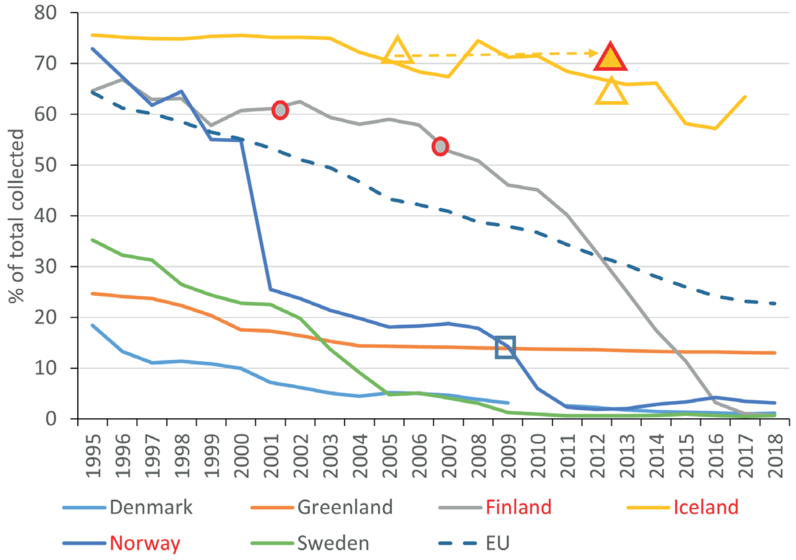

FIGURE 3: Municipal solid waste landfilled (deposited onto or into land) in Nordic countries (in %; countries covered in this study in red text, EU depicts average of member countries, cut lines = missing data, symbols depict year of start (blank symbols) or closure (solid symbols with red outline) for Iceland (triangel), Norway (box) and Finland (dot) in the indicated time period; Norden, 2020).

Generally, resource efficiency regarding plastics have increased in Nordic countries over time (see Figure 4, and, e.g., Robaina et al., 2020). As can be derived from Figure 4, material recycling rates in Finland and Norway were considerably higher than the EU-average up until around 2007/2008. Recently, recycling rates have moved closer to the EU-average, which in turn has steadily increased since 1995. The data behind Figure 4 covers a wide range of materials such as metal, paper, cardboard and plastic, and plastic material recovery lags (Robaina et al., 2020; Milios et al., 2018). Consequently, it can be assumed that between 95 and 70% of plastics in MSW have not been subject to material recycling in the Nordic countries between 1995 and 2018; either they ended up in waste incineration, were exported, became litter, or – to a smaller extent – were disposed of at landfills prior to landfill bans on combustible waste (observe that this observation is true for plastic packaging only for items not subject to deposit-refund-schemes). Diversion of plastics from landfills started not least in the wake of the EU landfill directive and related waste acceptance criteria (EC, 1999 and EC, 2002).

Although Norway and Iceland remain outside the union, Norway's landfill regulations are similar to the EU's, such prohibiting landfilling of organic waste, and separate collection of plastic packaging waste is available in more than 80% of municipalities (Papineschi et al., 2019). Still, even without a detailed look at particular waste acceptance data from the landfills included in this study, it is safe to assume that plastic materials have been disposed of at the landfills,

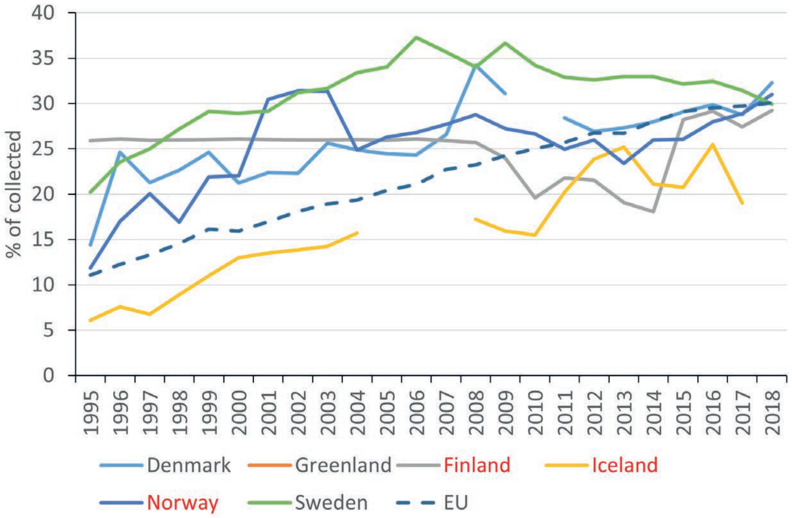

FIGURE 4: Municipal solid waste recycled (material recycling) in some Nordic countries (in %, countries covered in this study in red text, EU depicts average of member countries, cut lines = missing data; Norden, 2020).

albeit in different amounts and with declining rates since turn of the last century.

(Micro)plastics are relatively recalcitrant to degradation (Barnes et al., 2009). Plastics are found in abundance in waste from landfill excavation (Canopoli et al., 2018). Still, biodegradation has been shown to occur, even under anaerobic conditions, and by microbes isolated from landfills (Ganesh Kumar et al., 2020; Giacomucci et al., 2020, Park and Kim, 2019). Aging, alteration and degradation might occur over time in the waste body (Hou et al., 2021; Su et al., 2021). However, landfill conditions are unlikely to be favourable for microbial degradation of plastics, not least due to the abundance of other, more readily available microbial substrates and mass-transfer limitations (Shah et al., 2009; Canopoli et al., 2020; Tansel, 2019, Ishigaki et al., 2004). Still, differences in microplastic emissions might be expected between landfills of different age due to the factors stated above.

Figure 5 depicts the number of microplastic counts per litre leachate in untreated leachates against the number of years since start of landfill operation, with the additional information of country of origin and mode of operation for each landfill.

Leachate samples from landfills in Iceland exhibit both non-detect and the highest microplastic counts per litre. Microplastic counts in leachate samples from Norway show relatively little variation (average count per litre for all untreated leachate samples is 0.995 l^{-1}). As the active Finnish landfills started operating round about the same time (1987 to 1989, blue dots in Figure 5), similar age, operational procedures and/or similarities in waste disposed of might lead to comparable microplastic concentrations in counts per litre. With the data at hand, this cannot, however, be verified statistically.

Considering the limited data on microplastic counts in leachate samples, and the lack of detailed information about amounts and types of plastic waste actually landfilled at the sampling locations, no link can be drawn between the two.

3.4 Landfill leachates as sources of microplastics

In Table 4, the summarized analytical results of microplastics in landfill leachate are put into perspective to results from other published studies, both on different microplastics sources and pathways. Scope, sampling methods and analytical techniques differ widely between studies. Particle size cut-offs differ considerably between studies. Therefore, results have not been recalculated to mass-concentrations. Consequently, the loads emitted by different sources should be regarded preliminary indications.

3.5 Limitations and potential sources of error

Not least due to the lack of standardization regarding sampling and analysis of microplastics, certain sources of error cannot be ruled out. No duplicate or triplicate samples have been analysed, and the sampling method has not been verified with spiked samples with known microplastic contamination. As a result, error margins and detection limits are not verifiable, which warrants caution when interpreting results. Optical analytical methods such as FT-IR are susceptible to influence from non-plastic material in samples, and pre-treatment to remove non-target material has been shown to impact analytical results (Masura et al., 2015, Simon et al., 2018, Collard et al., 2015). Thus, an initial follow-up trial on a number of samples taken in this study has been conducted at Lund University. Samples on aluminium oxide filter plates from the initial FT-IR analysis have been re-examined.

Initial results indicate that increasing the H_2O_2 concentration from 15 to 30% (reaction time 6 days) enables previously unidentified plastic particles to become "visible" in

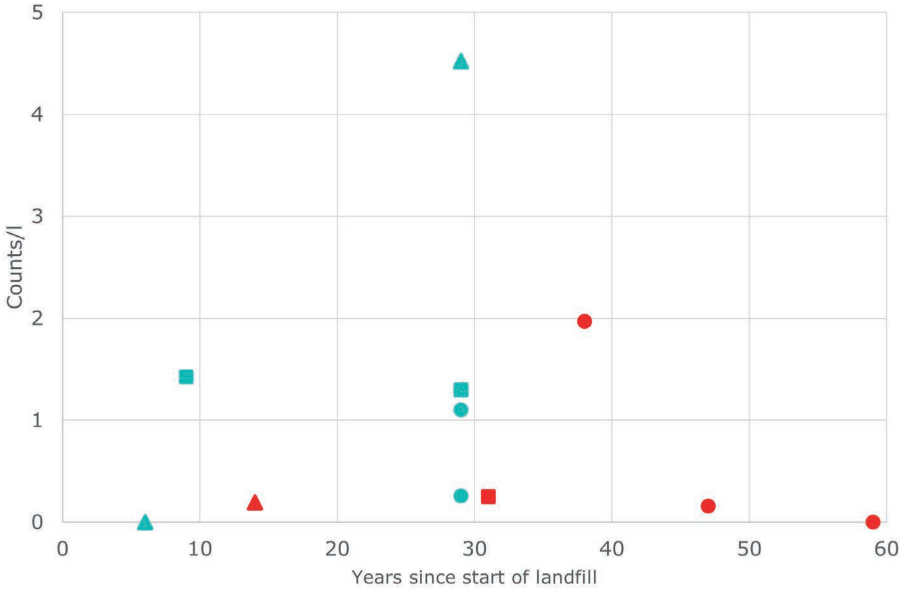

FIGURE 5: Years since start of landfill operation vs. microplastic count per litre in untreated leachates with country indicated (triangle=Iceland, box=Norway, dot=Finland; closed landfills are represented in red).

TABLE 4: Approximated microplastic concentrations and estimated loads from different potential sources/pathways.

Source/ pathway	Particle size range µm	Count/L (µg/L)	Annual Load	Comment	Reference
Landfills	50-5,000	0-4.5[a] (0-2.4)	15 g - 25 kg[b]	on average	This study; van Praagh et al. 2018
Landfills in Sweden	≥ 100	0-2.7	0-170 kg	treated leachate	Swedish Waste Association, 2017
Incoming Sewage to WWTP, Sweden	>20	20-80	$2.6 \cdot 10^{12}$ particles		Magnusson and Wahlberg, 2014
Effluent WWTP, Sweden	>20	10-100	$2.6 \cdot 10^{11}$ particles		Magnusson and Wahlberg, 2014
Traffic in Sweden	>100	n.d.	7,670 tons		Magnusson et al., 2016
Storm water pond inner-city highway	5000-50	6.4 (195)	[c]		This study
Air deposition in Paris	100-5,000		3-10 tons fibres		Dris et al., 2016
Artificial turfs in Sweden	>100	n.d.	1,640-2,460 tons		Magnusson et al., 2016
Players on artificial turfs in Norway		2 ml	65 tons	2 ml per game and player	Sintef, 2018

[a] calculated with the assumption in chapter 2.5; [b] calculated with annual leachate production volume for the last year available, provided by the respective landfill operator (see van Praagh et al., 2018 for details); [c] as the sample was not taken in the outflow but from the water body of a pond, emissions cannot be calculated

the filter residues (Simongini, 2021), putting into question whether microplastic counts might actually be higher than depicted above.

As a result of the sampling method, variations in particle content of the leachates caused different sampling volumes, as sampling prevailed until the smallest filter got clogged. Sampling a fixed amount of leachate at one occasion with subsequent filtration in the laboratory would most likely have given different results. In that case, the chance of "catching" microplastics would have been much lower. If microplastic particle concentrations were, in fact, correlated to particle concentrations of non-plastic matter in leachates, the sampling method chosen for this study should have enabled representative sampling.

Sampling pre-treatment might have removed or altered microplastic particles (Karami et al. 2017).

Although similarities of different SBR-materials and different polymer-modified bitumen are likely to create similar and coherent FT-IR patterns, it cannot be ruled out that microplastic particles of significantly different blends of both materials than those used as references might go undetected in leachate samples: According to a producer of polymer modified bitumen, there is an almost unlimited number of blends that can be used with different fractions of added polymers.

The polymers included in the screening represent the main plastics used in the Technosphere (>80%). Still, it cannot be ruled out that microplastics of non-targeted polymers were present in the samples.

The filter equipment was cleaned between samples, and treated samples were taken before untreated samples. Still, cross-contamination cannot be ruled out, which is indicated by SBR particles in the blank sample.

The choice of lower size limit of 50 µm (47 µm during sampling) is likely to exclude numerous smaller particles. Particularly regarding microplastic particles from PE and PVC, but also others, it cannot be ruled out that these at least partly stem from landfill drainage and leachate treatment and collection systems rather than from the landfilled waste itself. This could, for example, explain the occurrence of PE and PS particles in the treated leachate at landfill 3 (although an investigation into the material used in the on-site treatment facility was inconclusive).

The variation of (micro)particles in landfill leachates over time, and factors influencing the emission of these have, to the knowledge of the authors, not been subject of comprehensive studies before. Silva et al. (2021) pointed out this knowledge gap, as well. Consequently, variations of microplastic concentration in leachate, e.g., seasonal variations or the influence of heavy rainfall events, are not accounted for in this study (what is more, the northern hemisphere experienced unusual weather conditions year 2018, with large, but relatively early, spring floods, and extremely dry and warm weather during the sampling campaign). Although landfill leachate treatment methods appeared to be effective for the sum of microplastic particles (5000-50 µm) with reduction ratios of between 3 and 100%, the sources of error mentioned above restrict comprehensive conclusions regarding treatment efficacy.

Although the landfills covered in this study, with the exception of the hazardous waste landfill no. 3 in Finland, were chosen as "typical landfills" in their respective countries, it is unknown how representative they actually are when it comes to the emission of microplastic particles in the Nordic countries as a whole.

4. CONCLUSIONS

Microplastic counts and the abundance of different microplastic polymers vary largely in leachates sampled at landfills in Finland, Norway and Iceland. Counts and calculated annual loads from leachate emissions appear to be small compared to other sources or pathways such as untreated and treated sewage and road runoff. Based on the results from this study, the underlying hypothesis of landfills generally being a relatively large source of microplastics is put in doubt. As this study neither covered time-series nor duplicate samples, and weather conditions were extraordinary at most locations, further studies are needed to determine the range of microplastics concentrations in treated and untreated leachates.

In 3 out of 4 studied cases, landfill leachate treatment seems to significantly reduce the counts of microplastics larger than 50 µm. Future work on microplastics should focus on standardization of leachate sampling and finetuning analytical techniques, in order to comprehensively elucidate the variability of microplastic concentrations in landfill leachates and of treatment efficacy, despite the challenging chemical matrix landfill leachates often present. Quantification methods for tyre rubber and polymer-modified bitumen microplastics should be developed, and future sampling and analysis of landfill leachates should include microplastic particles smaller than 50 µm, preferably even nanoparticles.

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ANNEX 1

TABLE: Sampling locations for blank sample, stormwater, untreated and, if available, treated leachates and respective sample volumes (in L, blank cells = no leachate treatment).

Landfill	Untreated leachate	Sample volume	Treated leachate	Sample volume
No.	Location	L	Location	L
0	Tap water (PE-bucket)	105		
1	Pumping station	120		
2	Pumping station	80		
3	Pumping station (PE-bucket)	70	Pumping station (PE-bucket)	190
4	Pond	70	Pipe (PE-bucket)	210
5	Pond	10		
6	Pumping station	20	Pumping station	5
7	Pumping station	40		
8	Well	40		
9	Bore hole	295	Pipe (PE-bucket)	255
10	Pipe	307		
11	Pond	44		
Storm water	Pond + steel bucket	36		

ANNEX 2

TABLE 2: Microplastic polymers identified by screening and total mass on sample filters after pre-treatment (neg = negative, n.d. = non detect, limit <0,001 mg).

No.	Polymers detected	Total mass 50 µm filter	Total mass[a] 500 µm filter
Unit		mg	mg
0 control	SBR	8	11
1	PE, PP, PMB	64	93
2	PE, PVC, PS, PET, PA, PU, PMMA	11	n.d.

No.	Polymers detected	Total mass 50 µm filter	Total mass[a] 500 µm filter
3 untreated	PET, PU	2	23
3 treated	PE, PS, PMB	5	2
4 untreated	PE, PS, PET, PU	27	n.d.
4 treated	PE, PS	12	n.d.
5	SBR, PMB	60	11
6 untreated	PE, PET, SBR	9	10
6 treated	SBR	29	122
7	PET, PMMA	23	9
8	Negative[b], PE	483[b]	15
9 untreated	PE, PS, PET, PU	4	5
9 treated	PE, SBR	21	12
10	SBR	11	1
11	PE, PP, PS, PU, PMB, SBR	16	46
Storm water	50 µm : PE, PP, PVC, PS, PET, PA, PU, PMMA, PMB, SBR, 500 µm : PE, PP, PVC, PS, PET, SBR	<1	<1

[a] Total mass includes recalcitrant inorganic or non-plastic organic material, which was not removed by the chemical pre-treatment; [b] chemical reaction and precipitation occurred, see discussion.

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PLASTIC WASTE AND ITS ARTISTIC CONTEXT

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ABSTRACT

The prevalence use and handling of plastics have become a global menace to the environment. This menace has even led to a national discourse on banning plastics in Ghana. The plastic waste situation seems to be an oblivious less concerned by some Ghanaian sculptors, engineers and scientists on its artistic exploration and contribution to the quota of environmental sanitation in Ghana. However, having identified the artistic qualities of plastics, this article seeks to transform plastic waste into art by exploring and analysing non-biodegradable polyethylene as a viable and unconventional material for sculpture. The focus of this studio-based research employed the Praxis with arts-based recycling approach as technique and procedures to create a bust from plastic waste as a means of establishing its viability as an unconventional material for sculpture. It was established from the outcome of the research that plastics as non-biodegradable material should not be seen as an environmental menace, but a viable and unconventional material for sculptors and other professionals like engineers and scientists beyond Ghana must also expand on this research further.

1. INTRODUCTION

Plastics have benefited the world in various ways, and Ghana has become a beneficiary of the commercial use of plastics. Historically, biodegradable materials such as leaves were used to pack food in Ghana. However, the advent of technology introduced plastics for packaging and transporting goods like food from the market to homes. Plastic's importance as a non-biodegradable material has inspired innovation in recycling and makes life better, healthier and safer every day. Recycling innovation of plastics comes in various forms of making cell phones cases, bicycle helmets, child safety seats, airbags in automobiles, televisions, computers and other electronic equipment that makes modern life possible (Clutz, 2018).

Plastic packaging helps to keep food healthy and fresh. It has provided sustainable design and construction in houses, buildings and infrastructure such as bridges. Plastics are more efficacious in recycling. Polyethylene or poly (methylene) is the most common type of plastic seen. It is mainly used in packaging (plastic bags, plastic films, geo-membranes and containers, including bottles). A plastic bag or poly bag as popularly called in Ghana is a type of container made of thin, flexible, plastic film used as packaging for containing and transporting goods such as foods, powders, ice, magazines, chemicals and waste (Wikipedia contributors, 2020).

In Ghana, the plastic bag is one of the most widely used non-biodegradable materials, but at present, improper handling of plastic bags has caused more harm than good. Plastic bags adversely affect the environment by posing a threat and hazards for its inhabitants as waste. Greentumble (2018) hints that plastic waste affects all types of biomes and organisms. These consequences are manifested throughout the world and constitute a multinational global problem that must be addressed. Plastic bags continuously harm the natural environment from the beginning to the end of its lifecycle. Plastic shopping bags also account for a significant amount of plastic pollution on land. Plastic bags are easily windblown and transported over long distances. These plastics are mainly caught in trees or storm sewers. Improper handling of plastic bags is found in storm sewers, offshore or contributes to pollution. Blocked storm sewers can lead to flooding during heavy rains and create large areas of standing water, which are breeding grounds for disease-bearing insects such as mosquitoes.

Greentumble continued to stress that at landfill sites, plastics use a lot of space and can take 400 years to break down. This enormous period of biodegradation is causing more and more plastic bags to accumulate in our landfill sites. There is plastic pollution in the ocean and in our rivers as well. One of the biomes that is increasingly impacted by plastic waste is the ocean. Every year, about 13 million tons of plastic are thrown into the ocean. Certain plastics release chemicals into the water causing cancer and other health problems, but the most common problem is the consumption of plastic by animals. Fish, turtles and seabirds

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are the populations most affected by plastic debris. Almost 100 million marine animals per year die directly from the consumption of plastic waste. These animals often eat plastic that is not digestible in their bodies. It blocks their digestive tract, causing them to die. Even plants are not protected from plastic waste. When plastic decomposes in the soil, it releases harmful chemicals, such as bisphenol A (BPA), which can harm the natural microorganisms on which plants depend for their survival (Greentumble, 2018).

Musah (2019) stresses that plastic has been used for commercial and household purposes. Large quantities of plastic waste in Ghana appeared to lack the economic environment for recycling and the artistic use of art. This has made an enormous contribution to environmental degradation and pollution of the environment. As a nation, the mismanagement of plastic waste has become very critical and therefore needs to be addressed.

Ministry of Health, Ghana (2014) confirms that Ghana's cholera epidemic reached a record 17,000 cases with 150 deaths. The last time Ghana experienced such an alarming number of cases of cholera was in 1982. Figure 1 shows the heavy rains after exposing the dirt of the plastics which had engulfed the capital. Plastic bags can get stuck on plants, depriving them of the nutrients they need. Delicate natural cycles that equilibrate ecosystems are threatened. Other countries are attempting to prohibit the use of plastics because of their negative impact. Countries such as Rwanda, New Zealand, China, Israel, South Africa, the Netherlands, Morocco, Kenya, Mauritania, Sri Lanka and even Ghana are attempting to ban the production and importation of plastics.

Plastic waste in Ghana is mainly found in landfill sites, beaches, streets, sewers, households and in all parts of the environment. Environmental concerns about plastic waste have become less of a concern for some Ghanaian sculptors, engineers and scientists. This requires rethinking, handling and controlling plastic waste and seeing how this waste could also be artistically analyzed to serve a beautiful purpose in the environment. In line with Musah (2019), Greentumble (2018) and Ministry of Health, Ghana (2014), this global menace of plastic waste, as shown in Figure 1 and 2, has resulted in environmental challenges where, on the other hand, these waste materials could widen the scope of sculpture in terms new approaches to materials. Consequently, the article aims to transform plastic waste into art by exploring and analyzing non-biodegradable polyethylene as a viable and unconventional material for sculpture.

1.1 Plastic as a non-biodegradable material for art

The idea of plastic as a non-biodegradable material for art suggests that the plastic material would not deteriorate over time. Thomlinson (2019) is of the view that there are more sustainable plastic alternatives that exist; but they cannot be a sustainable solution without the infrastructure required to manufacture, collect and recycle them on a large scale. Mustalish (2004) adds that the development of plastics from the middle of the 19th century to the present has dramatically changed the materials of the physical world. Plastic has become a general term for synthetic materials which, as the name suggests, can be folded, molded or formed in any shape, be it rigid or flexible. In the 19th century, the world of synthetic chemistry started to expand, giving rise to new technologies in the chemical industry, dyeing, paper and textiles.

Visual-Arts-Cork (2019, para.1) describes plastic art as the term is derived from the word "plasticize", meaning to “mould". This describes any art form which involves modeling or moulding in three dimensions”. Based on the assertions of Thomlinson (2019), Mustalish (2004) and Visual-Arts-cork (2019), it is believed that non-biodegradable plastics can be used as a durable, non-conventional material for the artist.

1.2 Some plastics artists

1.2.1 Serge Attukwei Clottey

Clottey is a Ghanaian multimedia artist who practices Afrogallonism as a concept he has worked with for approximately 17 years. He uses yellow plastic gallon containers to investigate migration and interactions between Ghana and the West. The containers were originally used to store cooking oil that was imported into Ghana, and once discarded, they are typically transformed into plastic art. Plastic waste is problematic because Ghana does not have many recycling facilities. Using gallons of plastic as an artistic material, Clottey cuts, pierces and overlaps them for his sculptures. Plastic gallons migrate through his practice

FIGURE 1: Accra engulfed with plastic waste (Source: Boadu, 2017).

FIGURE 2: Environmental challenges with plastic waste (Source: Field Study, 2021).

FIGURE 3: Gallon works of Serge Attukwei Clottey (Source: Geyser, 2020).

FIGURE 4: Serge Attukwei Clottey with gallon mask (Source: Geyser, 2020).

of reselling them to the West as artwork (Brito, 2018). This statement from Brito (2018) highlights the artist's techniques as an installation in reusing discarded materials such as gallons to the community. Figures 3 and 4 show a few artworks by Serge Attukwei Clottey.

1.2.2 Mbongeni Buthelezi

Buthelezi was born in 1966 in Johannesburg, South Africa. Mbongeni Buthelezi is an artist who became renowned for his plastic "painting". He studied at the African Institute of Art in Johannesburg from 1986 to 1992 and at the University of Witwatersrand from 1997 to 1998. The material Mbongeni Buthelezi uses for his "paints" is always plastic waste. He cuts it into small pieces and glues them to the canvas, creating surfaces and structures in subtle and changing colours and tones. The use of such material shows Buthelezi's awareness of environmental problems and the physical decay of the townships as well as the references to general social and political impoverishment and flaw of opportunities and unconventional that he observes in South Africa (Artnet, 2020).

In view of this, the artist has developed a technique of painting with collage form of heating plastics on a canvas. The artist has been working on developing a unique style of art making by using discarded plastic of a certain quality in melting process. He paints in impastos solid forms burnt with a heat gun. His unique paintings are often larger than life. He is able to work realistically and abstractly with the technique being extremely detailed as shown in the Figures 5, 6, 7 and 8.

1.2.3 Angela Haseltine Pozzi

Pozzi is also a female sculptor who works with plastics. She was born in Portland, Oregon to a family of artists. Pozzi's evolution as an artist shifted when she noticed immense amounts of plastic pollution on pristine southern Oregon beaches. As she learned more about ocean pollution from plastics and marine debris, she became motivated to do something about it. Thus, the Washed Ashore Project was born. Pozzi decided to enlist the help of hundreds of local volunteers to clean up the beaches, and use all the debris to construct massive sculptures of the sea animals most affected by the pollution. Pozzi is intrigued with textures, patterns, and colours in the world around her. She sees the designs of sea creatures in familiar human made objects, and creates additional elements out of anything that works. Her childhood of wading in the Pacific Ocean and digging in the dirt of Puget Sound has greatly influenced her work. Being raised by relatives who were artists and naturalists also gave Pozzi a sense of direction. These sculptures now tour as the "Washed Ashore Project" traveling exhibit, educating and inspiring countless people from diverse backgrounds to take action in their own lives to prevent contributing to this global problem. She works as a Lead Artist, designing and creating a multitude of marine creatures from continuous tonnes of marine debris with the aim of having a global impact. As the leader of a team of dedicated employees and hundreds of volunteers, Pozzi has vowed that this effort is her calling and "until we run out of plastic on the beach, we will keep doing our work" (Exploratorium, 2020).

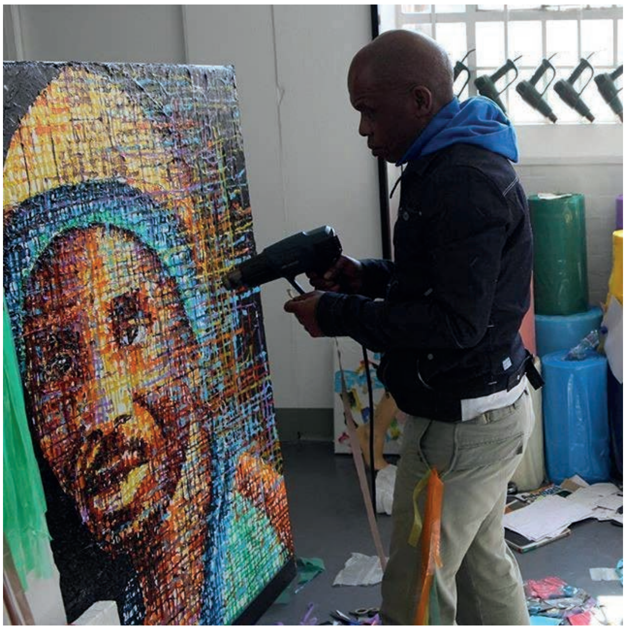

FIGURE 5: Artist working (Source: Pinterest, 2019).

FIGURE 6: Mbongeni Buthelezi and his works (Source: Pinterest, 2019).

FIGURE 7: Work by Mbongeni Buthelezi (Source: Pinterest, 2019).

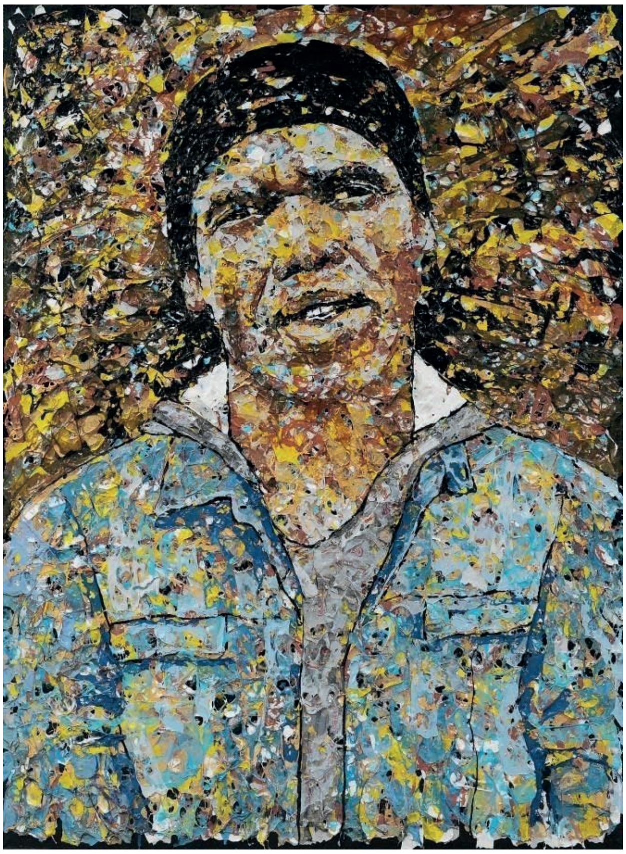

FIGURE 8: Self-portrait by artist Mbongeni Buthelezi (Source: Alchetron, 2019).

Pozzi's style and technique of work are ascribed to her construction of textures, patterns and coloured plastics for massive sculptures as shown in Figures 9 and 10.

2. MATERIALS AND METHODS

This studio-based research focused on Praxis with arts-based recycling approach as technique and procedures employed for the execution of the sculptural work. Marshall (2010, p.1) points out that, "studio-based research is rich with possibilities for contributing to the body of knowledge concerning creative processes". This research design focused on the connections between the Praxis and the assumption that the plastic wastes which contribute to environmental challenges by polluting the environment could be also transformed into sculptural works by artistically beautifying the environment. The purpose of the interpretive analysis was to explain the techniques and procedures for sculpting busts from plastic waste.

2.1 Theory and technique

For the practitioners to produce a bust within the studio or artistic context, a theoretical framework has to be established through several ideas and processes regarding the materials and methods for production of the artwork. The arts-based recycling approach as technique and procedures was used to create a piece of sculpture with

FIGURE 9: Washed ashore (Source: Muldoon, 2010).

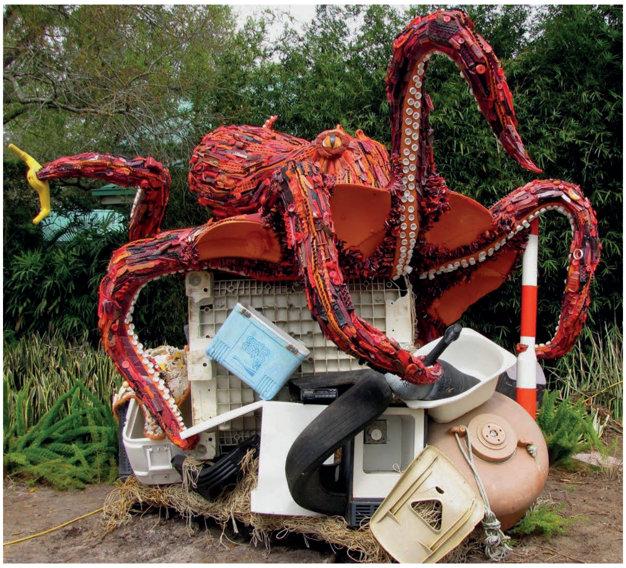

FIGURE 10: Washed ashore (Source: Washed ashore, 2020).

plastic waste as a means of establishing its viability as an unconventional material for sculpture. With this approach, a greater portion of the plastic wastes that frequently ends up in landfill, dumpsites can be sourced, retrieved efficiently for free or at low cost for production of art. The use of modelling and gluing techniques in the production of the bust served as the basis for the research. In line with the statement of Ward (2008), using techniques to transform materials into objects that have the ability to stir emotions and defy the intellect with created art. This basic technique was used to recycle ideas and styles so that the bust could be created.

2.2 Tools, materials and equipment

This section provided a detailed account on tools, materials and equipment for producing the bust that practically included hacksaw, hammer, blade, scissors, buttons, toothbrushes, tape measure, plier, drilling and arc welding machines. The tools and equipment were tools used for the realization of the bust. Materials, however, were non-biodegradable substances used for production processes. Kuhtz (2017) argues that any material that can be three-dimensional can be sculpted. Some materials, due to their structural and aesthetic properties and availability, have been shown to be particularly suitable. The following materials were used for execution of the work; polythene bags (non-biodegradable), wooden board (Red wood), iron metal rod, galvanized round metal pipe, chicken wire mesh, foam, buttons and adhesive (Contact glue).

2.3 Quantities of materials and analysis of the costs for the bust production

Prior to the execution of the work, a detailed report on the quantities of materials and the cost analysis is provided for the production of the bust. This helped the research to identify the specific and exact materials available as set out in Table 1 for the bust production.

2.4 Procedures about the production processes for the bust

In this studio practice, the production processes conducted in the production of the bust were practically oriented and intellectual commitment. In the production of sculptures, the exploration of different materials, notably

TABLE 1: Quantities of materials and analysis of the costs.

S/N	Item	Description	Total Quantity	Unit Price	Total Price
1.	Plastic wastes (Polyethylene/Polythene bags - all kinds were collected from the environment)	Large = 16 pcs Small = 20 pcs	36 pcs	*	*
2.	Iron rods	7.5 mm (3/8) 12 mm	2 pieces 2 pieces	8.00 x 2 26.00 x 2	₵16.00 ₵52.00
3.	Galvanized metal pipe	2” round metal pipe	1 bar	85.00 x 1	₵85.00
4.	Wooden board	hard wood (Red wood)	1 board	70.00 x 1	₵70.00
5.	Chicken wire mesh	Stainless steel hexagonal mesh	1 (full) roll	175.00 x 1	₵175.00
6.	Foam	Polyurethane foam – low density	2” sheet	110.00 x 1	₵110.00
7.	Buttons	Plastic buttons (Fancy)	5 pieces	1.00 x 5	₵5.00
8.	Adhesives (Contact glue)	Type 99-glue	6 cans (Small)	18.00 x 6	₵108.00
	Grand total				₵621.00

** pcs= Pieces, ” = Inches, x = Multiply, mm = Millimetres, ₵ = Ghana currency (cedi sign)* unconventional materials such as plastic waste, is accompanied by new approaches and new styles. This gave practitioners the chance to explore polyethylene as a material for the bust. In addition, plastic waste as the main material of the research was stretched to test its flexibility, strength, toughness and retention properties (Rosato et al., 1991). This allowed the study to use plastic waste of various kinds for sculpture work. In this production process, practitioners effectively used five procedural steps in a sequential approach to achieve the goals of studio research.

2.4.1 Procedure 1: Idea development

The development of ideas was the planning stage when practitioners redefined the concept of production of Prof. Victor Kweku Bondzie Micah (1974-), who is a practising sculptor and the Pro Vice Chancellor of Takoradi Technical University (2018-). Micah was born on 9th October 1974 in Winneba, Ghana and married with three (3) children. He is also the "Okyeame of Ekumfi Akosti Anona Okusubenstir Ebusua". The motivation of this research was based on Micah's practical skills in the fraternity of art and his higher heights in academia. The development of ideas took the form of images, as illustrated in Figures 11 to 14. These images were taken from various angles to produce the work.

2.4.2 Procedure 2: Securing materials for the bust

The following materials (polythene bags, contact glue, round metal pole, red wood, foam, buttons, wire mesh, and metal rod) were acquired for the execution of the work. Figure 15 shows a redwood panel. This redwood panel

FIGURES 11-14: Side view, back view, three-quarter view, front view.

FIGURE 15: Wooden board (Redwood) with galvanized round metal pipe.

FIGURE 16: Chicken wire mesh.

FIGURE 17: Iron metal rod.

FIGURE 18: Polythene bags.

FIGURE 19: Foam cuts into stripes.

FIGURE 20: Contact glue (type 99-glue).

was used as a support for the base of the work. Figure 16 shows a chicken wire mesh used to strengthen the work. It was used as a substrate on the armature for modelling and gluing of the polyethylene bag. As shown in Figure 17, Iron metal rod made of three-quarter and half-inched sizes were used for the work. Figure 18 also shows the acquisition of various types of polyethylene bags as the main material of the artwork. Polyethylene bags collected from the waste were cleaned and used for artwork. Figures 19 and 20 show the foam and contact glue of the structure.

2.4.3 Procedure 3: Producing the armature for the bust

The angle grinder with sandpaper was used to polish the surface of the wooden base for neatness and precision of the wooden base. A hole was drilled in the middle of the wooden base. The hole served as a passage and support for the round metallic pipe to be placed firmly into the wooden base. This helped to build the armature. The armature with iron metal rods and round galvanized metallic round pipe were welded together to fix the head to the shoulder level of the artwork (Figures 21-24).

2.4.4 Procedure 4: Constructing the bust with Polyethylene bags

At this point, the wrapping of chicken wire mesh on the armature as shown in Figures 25 to 28 was done. Tools like scissors and plier were used to cut the chicken wire mesh and wrap it around the armature. After wrapping process, the foam (flat foam) was cut into pieces, then applied onto the armature bit by bit to achieve the shape of the head. After establishing the armature with the chicken wire mesh, polyethylene bags were cut and wrapped

FIGURE 21: Sanding the wooden base.

FIGURE 22: Drilling a hole on the wooden base.

FIGURE 23: Welding the metal rods together.

FIGURE 24: Completion of the armature.

around the armature using contact glue. Foam and polyethylene bags were used to minimize the heaviness of the work. The modelling technique was used to get a round-shaped on the head and box-shaped of the bust. After obtaining the shape of the head with foam, polyethylene bags were sliced with scissors. It was then folded over the foam. Time was taken to ensure that the modelling of the face and suit on the bust with polythene bags was carefully done to achieve resemblance of the Pro Vice Chancellor (Prof. Victor K. B. Micah). The modelling technique was used throughout this step to obtain the resemblance indicated in Figures 25 to 48.

FIGURE 25: Cutting the wire mesh.

FIGURE 26: Wrapping the wire mesh around the armature.

FIGURE 27: Wrapping process of the wire mesh.

FIGURE 28: Completion of wrapping process.

FIGURE 29: Polythene bag and blade.

FIGURE 30: Cutting the polythene bag into pieces.

FIGURE 31: Applying the glue on the polythene bag.

FIGURE 32: Wrapping the polythene bag around the armature.

FIGURE 33: Wrapping process with polythene bag.

FIGURE 34: Completion of the wrapping process.

FIGURE 35: Building the head with foam.

FIGURE 36: Covering the foam with polythene bag.

FIGURE 37: Completion of the foam process.

FIGURE 38: Covering the foam with polythene bag.

FIGURE 39: Building the suit with foam.

FIGURE 40: Completion of the wrapping process with polythene bag.

FIGURE 41: Folding of polythene bag.

FIGURE 42: Modelling with polythene bag.

FIGURE 43: Modelling process (a).

FIGURE 44: Modelling process (b).

FIGURE 45: Modelling process (c).

FIGURE 46: Modelling process (d).

FIGURE 47: Modelling process (e).

FIGURE 48: Modelling process (f).

2.4.5 Procedure 5: Finishing the bust

Adding the final touch to the constructed work, colourful polyethylene bags were cut into square pieces with a blade. The square pieces of polyethylene bags were glued to the face to create the skin tones. Plastic buttons were attached to the work jacket to increase realism. The final steps are shown in Figures 49-57. The resemblance was assessed by juxtaposing the development of the image idea (front view) taken with the final work done in figure 57.

3. CONCLUSIONS

This studio-based research focused on transforming

FIGURE 49: Coloured polythene bags and blade.

FIGURE 50: Cutting of coloured polythene bags into square pieces.

FIGURE 51: Creating the skin tones.

FIGURE 52: Skin tones created.

FIGURE 53: Fixing the buttons on the suit.

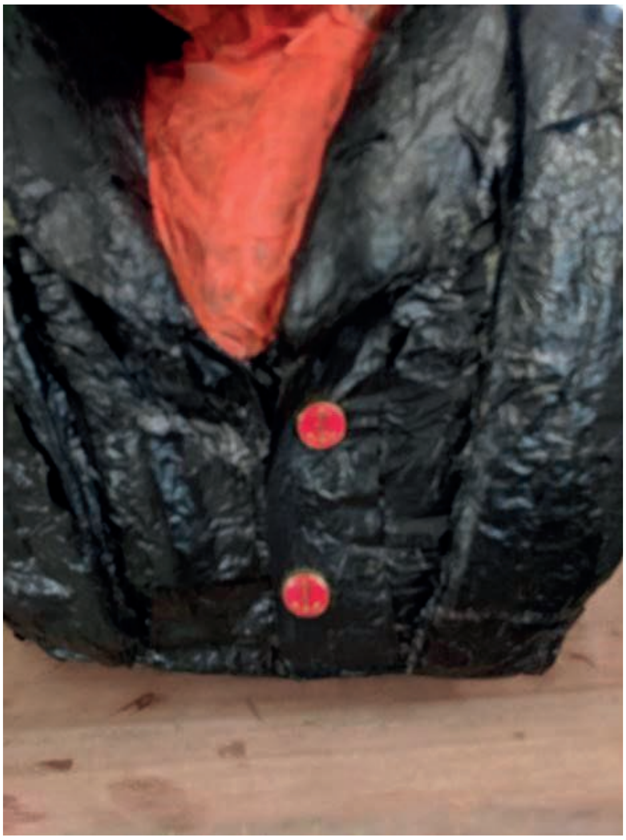

FIGURE 54: The fixed buttons.

FIGURE 55: Finishing process.

FIGURE 56: Completion of the bust.

FIGURE 57: The finished work.

plastic waste (polyethylene bags) into a bust of Prof. Victor Kweku Bondzie Micah (Professional sculptor and Pro Vice Chancellor of Takoradi Technical University- (2018-). The research was premised on plastic waste which threatened and saddled the environmental situations in Ghana, thereby exploring and analyzing the artistic context of plastic waste as having the potentials to serve as sustainable and alternative raw materials for the artist.

Through this exploration on plastic wastes, it was established from the outcome of the research that the plastic sculpture (bust) produced from polythene bags has a great benefit of building a better Ghana and its sustainable development plan on environmental issues. It is therefore recommended that plastic waste as non-biodegradable material should not be seen as an environmental menace, but a viable and unconventional material for sculptors and other professionals like engineers and scientists beyond Ghana must also expand on this research further. It is also recommended that the policy makers on environmental development, such as Environmental Protection Agencies and other responsible entities in Ghana and beyond should develop collective responsibilities of using plastic waste. This helps as a potential and alternative purposes whereby giving artists, engineers, and scientists the platform to ensure that environmental issues with plastic waste can be valued by using them more responsible for the production of plastic artworks and other plastic products.

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CISA

PREVALENCE OF INJURIES AMONG WASTE PICKERS. A CASE STUDY IN NIGERIA

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ABSTRACT

Waste picking might provide, in low-income countries, a livelihood for many individuals representing an important survival strategy. However, during their activities, waste pickers are at risk of encountering harmful waste, which could cause injuries and other infectious diseases. This paper investigates the occurrences of injury among waste pickers and the methods they use to treat the injuries in Bauchi city, Northeastern Nigeria. A total of 322 waste pickers were randomly selected across 80 waste pickers' middlemen shops. Data was obtained through questionnaire and interview. Based on the data presented, 1474 frequencies of injuries were reported among 247 waste pickers. Age, education and working experience are significant parameters to the prevalence of injuries among waste pickers, and the incidence of injuries increased with the decrease in those parameters. The study shows that most of the waste pickers experienced injuries, most of whom do not attend clinic when injury occurs; instead, they used salt, ash, sand, hydraulic, kerosene, battery acid, among others, to treat their wounds. Cuts and pierces are good entry points for bacteria and viruses, which can eventually spread to the general public infectious diseases, such as Hepatitis, Cholera and Lassa fever. Provision of Personal Protection Equipment (PPE), a labor rights policy, immunization and the launch of an awareness campaign are among the recommendations made by this study.

1. INTRODUCTION

Solid waste management (SWM) has become a serious problem in most cities of the world, and a topic of growing concern especially in Low-Income countries, (Lavagnolo and Grossule, 2018; Ali et al., 2017). In the view of United Nations Sustainable Development Goals (SDGs) 12, the global goals will be met effectively only once waste management is recognized as a powerful driver of sustainable development (SDG, 2019). This can be realized through the substantial reduction of waste generation, prevention, recycling and reuse (Nurfaiza et al., 2019), considering some fundamental factors which underpin the operation and the enhancement of SWM in developing countries (Mukhtar et al., 2018).

Several authors encouraged the act of waste picking as part of waste management and resource recovery to ensure environmental sustainability (Gutberlet et al., 2020; Nzeadibe, 2019; Steuer et al., 2018; Nabegu et al., 2017; Adama, 2012) as this helps meet the growing demands of raw materials and the reduction of significant amounts of waste. For instance, Ogwueleka (2009) revealed that 40% of artisans and small-scale industries in Onitsha, Nigeria, receive 48% of their raw materials from waste pickers. It also provides job opportunities for many people through the recovery of recyclable materials across the Low-Income Countries (Bonini-Rocha, 2021). For example, about 86% of waste pickers generate more than ₦20,000 per month in Warri, Nigeria, which equates to more than the minimum wage scale in the country (Irabor and Oghenekohwiroro, 2017).

According to Lambu (2016), the process of waste picking involves the collection, purchase, and recovery of materials for economic benefits. Reno (2019) stated that waste picking is portrayed as something done out of necessity and that the people doing it suffer from abject poverty. These informal workers represent a significant proportion of the world's working poor, with over 15 million people undertaking such work, primarily in Low-Income countries (Medina, 2009) and about 1 million across Nigerian cities (Nzeadibe, 2019). Waste picking is a physically demanding work, as it involves carrying heavy loads of recyclable materials and walking for hours without adequate rest (Mathema et al., 2017). This could lead to the development of musculoskeletal problems, such as back, shoulder and neck pain, among others (Singh and Chokhandre, 2015). As a result of the environment in which they work, waste pick-

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ers are also prone to other physical injuries, including cuts from sharp objects, such as pieces of glass, razor blades, scrap metal and pricks from piercing items like needles and nails. This eventually becomes the entry points for infection and exposure to bacteria (Yusuf et al., 2021).

Despite their vuluneráblility to injury, a number of studies narrated how waste pickers attributed injuries and diseases to God's will and supernatural phenomena, rather than to work-related causes; for example Nzeadibe et al. (2012) reported that most of the waste pickers in Aba do not believe that the health and safety problems they face are related to their occupation, but rather they are related to the influence of witchcraft from their communities. Chimere et al. (2017) found a similar result across Ibadan, Lagos, and also Aba (however, on e-waste informal workers).

Chukwunonye et al. (2009) revealed that the waste pickers in Nigeria are not aware of the dangers of their occupation and are concerned only with the economic benefits of the occupation; Uthman et al. (2017) confirmed a similar finding in Illorin. The consequence of such negative beliefs makes it difficult for waste pickers to comply with health and safety rules. For example, some waste pickers often walk in a heap of waste without shoes and use their bare hands to search for recyclables through clinical and other hazardous wastes without gloves. Moreover, their health status must be considered a public health issue as well, as they could be potential spreaders of communicable diseases to the populace (Chukwunonye et al. 2009).

It is of great concern to know that very little research has been conducted in the northern part of Nigeria in regard to waste picking, despite the presence of prejudice socio-economic and cultural conditions in the region which lead to the growth of the informal sector (Adama, 2014). The few available research were, however, focused primarily on the socio-economic wellbeing of waste pickers, e.g., Nzeadibe (2019), Lambu (2016); Adama (2014) and Nzeadibe et al. (2012 & 2013), and the risk-awareness of waste scavengers, e.g., Uthman et al. (2017). Eventhough, Ohajinwa et al., 2018 studied prevalence and injury patterns among electronic waste workers in Nigeria, this study has concentrated, largely, on waste pickers. . The study also examined the various methods used by the waste pickers in treating injuries, with the view of proffering solutions regarding their health and safety, as well as halting or minimizing the possible spread of infectious diseases to the general public as essential components of sustainable development goals (SDG 3). Taking into consideration that most of those waste pickers are Internally Displaced Persons (IDPs) and Almajiri children, who rely considerably on waste picking as a means of livelihood. Almajiri refers to under-aged children that leave their hometowns and travel to other towns or cities in the pursuit of Islamic education particularly in northern Nigeria and some parts of West Africa (Yusuf et al., 2021).

The study was conducted in Bauchi city, in the North-eastern region of Nigeria. The city, which has a population of almost 800,000 inh., was chosen because it serves as a refugee safe zone for the residents of the neighboring states of Borno, Yobe, and Adamawa due to the recent Boko Haram insurgency and the security instability of Plateau state. This led to increased dependency on informal activities (including waste picking). Another important factor is the high number of Almajiri children in the city. Similarly, the state has about 1,080,150 out-of-school children, which is the second highest in Nigeria after Kano State (UNICEF, 2019).

The problem of waste management systems in Bauchi city is similar to that seen in other cities, e.g., Chukwunonye & Clive (2012) in Abuja; Nzeadibe & Anyadike (2012) in Aba; Kofoworola (2007) in Lagos; and Maigari (2014) in Kano. The system reflects low levels of public awareness of, and poor institutional/regulatory framework for, sustainable solid waste management (Chukwunonye & Clive, 2012). According to Bogoro et al. (2013), Bauchi city has 89 recognized dumpsites that are managed by Bauchi State Environmental Protection Agency (BASEPA). Some of the dumpsites designated by the agency include a Railway playground, a Games village playground, Kofar Idi, Karofi, and Yelwantudu, among others. Surprisingly, illegal dumpsites almost tripled the recognized dumpsites by the BASEPA, which has recorded 205 sites around the city streets, drainages, and uncompleted buildings. Nonetheless, both the recognized and illegal dumpsites serve as source of recyclables to the waste pickers.

2. MATERIALS AND METHODS

Mixed-method approach was adopted for this study due to the flexibility needed to accommodate the whole nature of the research objectives. This approach uses a mix of quantitative and qualitative data in the collection and analysis stages of a single study (Croswell and Plano, 2011). The results of the qualitative data support the quantitative data and reflect the voice of the waste pickers and their masters (i.e., middlemen) where necessary.

2.1 Sampling procedure

Researchers find it difficult to reach waste-pickers, as they cannot be pinned down to a specific dumpsite at a specific time. The best place to find waste pickers is where they sell the recyclables they have collected (Schenck and Blaauw, 2011). This reason, coupled with a fear of collecting data more than once from a particular group or individual waste pickers in a dumpsite, warranted the need to reach the respondents (waste pickers) in the middlemen shops (i.e., where the waste pickers sell the collected waste items). Middlemen are agents who sit next to the waste pickers in the recycling chain (Adama, 2014). Middleman operate as buyers who store and might process waste recyclables before transferring them to final recycling (Steuer et al., 2018).

Using stratified and simple random sampling, 88 middlemen shops were selected from 121 registered middlemen from their union. In order to ensure proper representation of the population of the study, the middlemen shops were selected based on the type of recyclables they purchase; i.e., from those who buy plastic bottles ("robobi"), rubber ("danƙo"), aluminium and metal ("dalma da ƙarfe") bottles and cables ("kwalba da waya"), and carton boxes ("kwali"). Three hundred and twenty-two waste pickers were sampled across the 80 middlemen shops; the selection was based on the numbers of waste pickers per middlemen shop. The sampled locations were visited mostly between 4pm and 6pm, when the waste pickers typically arrive at the Middlemen shops to sell their recyclable items. Questionnaires were used to capture data from the waste pickers, and interviews were conducted in the local language (Hausa) to complement the responses. The interview comprised two sections: one for the waste pickers, and one for the middlemen. This helped obtain sufficient information required for the study, and also elicited the co-operation of the middlemen in the sense that they felt involved and comfortable with the data gatherings. Field observation was also underken where pictures of injuries were taken, alongside other vital information related to waste picking activities. Subsequently, GPS was used to capture the coordinates of the 80 sampled middlemen shops' locations. Figure 1 illustrates the locations of 77 out of the 80 sampled middlemen shops using Gamin GPS. Most of the middlemen shops are concentrated around Muda-lawan market, IBB Square, Sabon-kasuwa, Wunti, Makera, and Gwallaga. Although there are few outlying areas that have more than four middlemen shops, such as Gombe Road, Tirwun, Yelwa, and Inkil. Based on the survey, the concentration of the middlemen shops correlates with densely populated areas and proximity to markets. But nevertheless, the use of tools such as GPS and GIS could be important for mapping and tracking informal waste management activities and related impacts (Villa et al., 2020; Golder and Alamgir, 2018). The survey was conducted from December 2019 to March 2020. Four men team participated in the survey. Ethical approval was granted by Bauchi state Government before the commencement of the research work.

3. RESULTS AND DISCUSSION

3.1 The socio-demographic characteristics of the respondents

Table 1 indicates that all the respondents were male. This is because scavenging activity in the northern part of Nigeria is a male-dominated occupation (Nzeadibe, 2009). This factor could be attributed to the culture of the study area, which restricts women from participating in some occupations, especially in the informal sector. The age structure in the study shows that more than half of the respondents (52%) were 18 years and below; 38% are between 19 and 29 years old; 9% are between 30 to 39 while the remaining 1% are aged 40 years and above. Obviously, children and teenagers formed the majority of the waste picking occupation. Educationally, 35% of the waste pickers did not attend any formal education; while 41% attended primary school, and 24% attended secondary school. According to the result none of the respondents is educated beyond secondary school. Moreover, about 28% of the waste pickers engaged in the occupation for 1 year and below; while those in the occupation for 2-5 years stand at 38%, and between 6-10 represent 19%, while those that have worked for 11 years above are 15%. About 1 in 5 of the respondents worked in dry season only, while the remaining almost 80% worked all year round.

3.2 Work-related injuries among waste pickers

The results reveal (Table 2) that 246 out of 313 respondents reported cases of injury, while the remaining 66 claimed never to have sustained any injury. A total of one thousand four hundred and seventy-four (1474) multiple injuries had been reported amongst the waste pickers since they engaged in the job. Among the injured respondents, about 37.8% suffered from cuts by sharp objects, which include metal, glass/broken bottles and razor blades, followed by 23.7% cases of musculoskeletal injury, which includes joint, shoulder, neck and back pains. Irritations/rashes ranked as the third most reported case, which accounts for 14% of the total. 13.5% suffered from animal/insect bites, while 10.6% reported being pierced or punctured by needles and nails, whereas 8.3% suffered from waste heap fire burns.

According to the result, cuts represent the highest score. This may be due to the presence of clinical and industrial sharp waste items in the dumpsites and could also be linked to the poor waste management in the city by the responsible government agency (BASEPA). The agency does not enforce a policy for the segregation of industrial and medical wastes from domestic waste, thus further exposing waste pickers to a wide array of risks. Moreover, according to Bogoro et al. (2012), BASEPA is responsible for managing waste at city level. The resultant poor management also causes perforation/piercing of the feet and hands of the waste pickers by pandemic needles, nails, animal bones, sharp metals, among others, when searching for recyclables in heaps of waste. A similar assertion was made by Rushton (2003), who stated that the risks associated with waste remain prevalent in Low-Income nations because the regulatory framework and enforcement system to separate hazardous wastes are largely absent.

Based on the result, musculoskeletal injury ranks second, which could be due to lifting heavy loads, and alternate bending and trekking. This is in accordance with Jerie's (2016) findings, which revealed that the activity of solid waste pickers exposed them to considerable risk of developing ergonomic disorders, such as lower back pain and neck pain, and may also affect their shoulders and arms. Similarly, Leton and Nweke (2013) reported that bending and carrying heavy loads of scavenged items caused backache, pains in the arms and legs, and joint stiffness. Burns to the feet and hands of waste pickers was found to be the least prevalent injury (13.6%). This may be due to fires set by residents living around the dumpsites for volume reduction, which further endangers waste pickers while searching for recyclables.

Despite the reported cases of injury featured in the study, some waste pickers claimed that they had never experienced any injury or even that they were naturally made immune by God. For example, one waste picker narrated that "many people think that we are getting closer to our grave by doing this job without knowing that God protects us more than anyone." The responses to religious faith among the waste pickers comes back on a regular basis, as some believe that Personal Protective Equipment (PPE) will never protect them from sustaining injuries or contract-

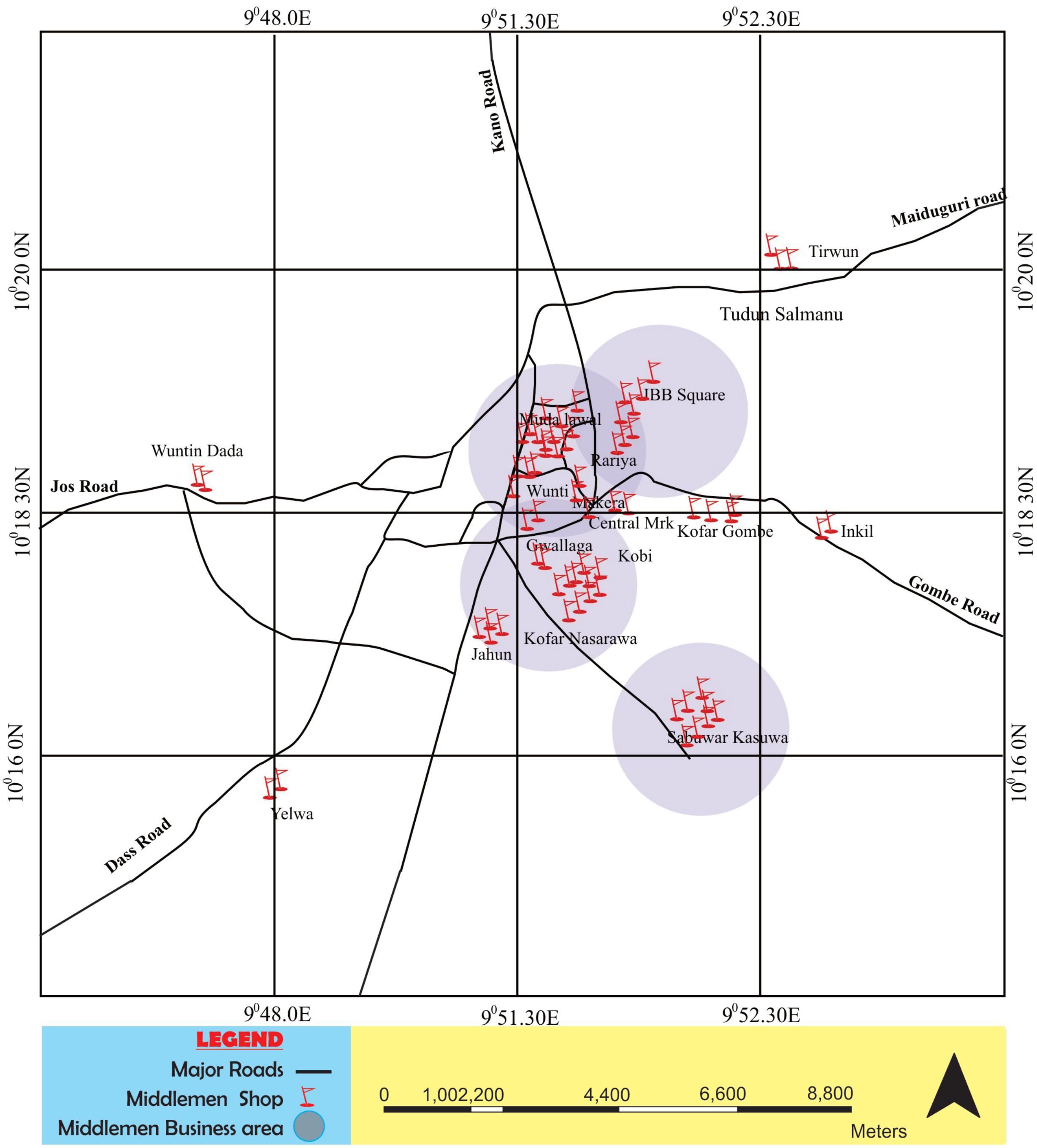

FIGURE 1: Locations of Middlemen shops.

ing diseases. This is similar to the findings of Nzeadibe et al.'s (2012) in Aba. The waste pickers defend the fact that no one can run away from injuries even when they wear protective clothes. They seem to accept their fate as a decision of God, and rely on Him for protection.

3.3 Influence of socio-demographic characteristics on work related injuries

It is important to note that age is an important parameter associated with the prevalence of injuries among the waste pickers. However, a chi-square test was performed to demonstrate the association between occupational characteristics and the occurrence of work-related injuries. The Chi-square result (Table 3) shows a significant relation between age (p=0.000), educational qualification (p=0.011) and working experiences (p=0.005) with the prevalence of injuries. Meanwhile, no relation was found between working hours (p=0.098), working days (p=0.078) and working season (p=0.059) with the prevalence of injuries. Based on the result, one can conclude that injuries are more prevalent among the lower age group than the higher age group and are also higher among non-formal literate waste pickers than those who attended formal education. This is apparent as child waste pickers reported more cas-

TABLE 1: Waste pickers' socio-demographic and occupational characteristics.

Characteristic	Frequency	%
Sex		
Male	313	100
Female	00	00
Total	313	100
Age		
18 and below	161	52
19-29	121	38
30-39	26	09
40 and above	04	01
Total	313	100
Educational Level		
None	111	35
Primary	127	41
Secondary	74	24
Tertiary	00	00
Total	313	100
Working Experience		
1year below	86	28
2-5years	120	38
6-10 years	60	19
11 and above	47	15
Total	313	100
Working Season		
All Seasons	248	79
Dry season	62	21
Rainy Season	00	00
Total	313	100
Working Hours		
1-3 Hours	38	12
4-7 Hours	135	44
8-10 hours	134	43
11 and above Hours	03	01

es of injuries than adults. This goes along with) findings which revealed that the number of injuries decreased with the increase in age (Ivens et al., 1998).

Similarly, most Almajiri children and IDPs who did not attend formal school reported more incidents of injury than those who attended primary or secondary schools. Perhaps those who attended school are more aware of the potential risks of the occupation than those with non-formal school qualification. Subsequently, years of experience and working hours, days and seasons do not determine the high incidence of injury among the waste pickers.

3.4 3.4. Methods of treating injury by the waste pickers

TABLE 2: Prevalence of Injuries among waste pickers.

Injuries		Frequency	%
Cuts	Sharp metal	249	18.67
	Broken-glass	174	13.04
	Razor blade	81	6.07
	Total	**504**	**37.78**
Punch	Clinical needle pierce	93	6.97
	Nail puncture	48	3.60
	Total	**141**	**10.57**
Burns	Foot burns	88	6.60
	Hand burns	23	1.72
	Total	**111**	**8.32**
Animal /Rodents bites	Dog	2	0.15
	Rat/Mice	24	1.80
	Scorpion	29	2.17
	Insect/flies	144	9.7
	Total	**196**	**13.86**
Musculoskeletal	Back pain	45	3.37
	Neck pain	48	3.60
	Chest pain	31	2.32
	Shoulder pain	108	8.10
	Joint pains	84	6.30
	Total	**316**	**23.69**
Irritations/ rashes	Nasal irritation	3	0.22
	Eye irritation	9	0.67
	Skin irritation	141	10.57
	Swelling limps	43	3.22
	Total	**196**	**14.16**
	Others	**11**	**0.82**
Grand Total		**1474**	**100%**

The study discovered only 17% of the waste pickers visit the clinic when injury occurs. Another 29% go to a nearby pharmacy for treatment, while the remaining 54% had their own methods of treatment, from the dumpsite (the point where injuries occur) to the healing stage. These methods (Table 4) include the use of procaine powder and herbal medicinal leaf; other mixtures sound unbelievable, for example, ash, sand, salt, grass fluid, hydraulic, kerosene, and car battery acid. All these are used by the waste pickers as healing remedies for their wounds and bruises.

During the interview session, when one of the middlemen was asked about the treatment of injuries, he affirmed that the waste pickers do not buy medicine with their money. Moreover, even if they were given money to go to the nearest chemist or clinic, they do not; instead, they spend the money. While the other middleman narrated that they save some money out of their earnings and take waste pickers to the clinic or chemist when injuries occur; if not, they will not pay for their treatment, because their health condition is not their concern.

The interviewer also asked, "Why can't you provide PPE to them to minimize injuries and save your money?" He responded: "It is not our responsibility, because we pay them

TABLE 3: Summary of Chi-Square test for association of occupational characteristics and prevalence of injuries among waste pickers @ 0.05significance level.

Variables	X^2	d.f	p value
Age	112.62	3	0.000
Educational qualification	129.71	2	0.011
Working Experiences	165.14	2	0.005
Working Hours	417.81	2	0.098
Working Days	561.02	1	0.076
Working Season	688.13	2	0.059

TABLE 4: Treatment remedies for wounds, pricks and bruise by waste pickers.

Treatment remedy	NO.	%
Procaine Powder	36	22.5
Ash	26	15.5
Sand	11	6.5
Salt	28	16.6
Grass Fluid	12	7.1
Hydraulic	11	6.5
Kerosene	15	9.0
Car Battery Acid	11	6.5
Herbal Medicinal Leaf	12	7.1
Others	06	3.6
Total	**168**	**100**

for their hard labor; besides, even if we provide some PPE to them, they sell it".

As a matter of fact, there is lack of support from some middlemen regarding the health and safety of waste pickers, despite benefitting more from the recycling chain (Nzeadibe, 2019), while most of the waste pickers confirmed the unaffordability of PPE due to their low earnings. This is why some people relate the low incomes of waste pickers directly to the low pay by middlemen (Adama, 2014), which has a direct correlation with poor health and safety compliance. Moreover, waste picking in northern Nigeria is considered among the worst forms of child labor (International Labor Organization [ILO], 2004). This contradicts with SDG 8, which aims to protect labor rights and promote safe and secure working environments for all workers.

A similar method of curing needle piercing or cuts from broken bottle was reported by a picker, who said that, at times, they came across a broken needle in an injection bottle while washing the bottles and sometimes, before they noticed it, the needle would perforate their hand. The interviewer asked him, "What first aid measure do you take immediately?" He replied: "The water in which we wash the bottles contains leftovers of different injection medicines; and once we soaked our hand inside the bucket of water for some seconds the bleeding stops and gradually heals."

Regarding musculoskeletal injury, 86% of the respondents use different types of balm as a remedy, such as Adabarakur, Aboniki, Confo, and Tiger. Similarly, most of the respondents use the same medicinal balm to cure skin rashes/irritations.

4. CONCLUSIONS

Waste pickers do not perceive injury at work as serious enough to worry about. Hence, they do not go to the clinic when injury occurs; instead, they drip salt, ash, sand, battery acid, among others, into the pricks or wounds. The use of such remedies may kill body cells and gradually cause tissue damage. Cuts and piercing are the entry points for infection or pathogens following exposure to bacteria and viruses, which eventually spread infectious diseases to the general public. Regular medical check-ups and immunization against tetanus and other viral infections should be provided by the government to prevent waste pickers from contracting diseases.

The middlemen should provide PPE to the waste pickers and monitor them to ensure its effective use. This will help realize the maximum safety compliance by the waste pickers and, thus, reduce the potential risks and hazards present in the waste picking activities. Moreover, periodic sensitization gatherings should be carried out in each middlemen shop on issues concerning health and safety for the both middlemen and the waste pickers regarding the importance of PPE utilization.

There is a need for BASEPA to proffer arrangements for waste segregation from the source, as well as designating disposal sites for clinical and other hazardous waste, in order to minimize the occurrence of injuries and other environmental problems. It was observed that the waste scavengers' union only exist at the top level (i.e., middlemen) in Bauchi city. Therefore, there is a need for the waste pickers to form a union in order to protect their labour rights and have a fair relationship with the Middlemen. By so doing, it will be easier to organize and educate the members of the union on health and safety issues. Moreover, Nigerian Labour Congress (NLC) and International Labour Organisation (ILO) should intervene to ensure the employer and employee rights are maintained by law, between Waste pickers and Middlemen.

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Extra contents

COLUMNS AND SPECIAL CONTENTS

This section comprises columns and special contents not subjected to peer-review

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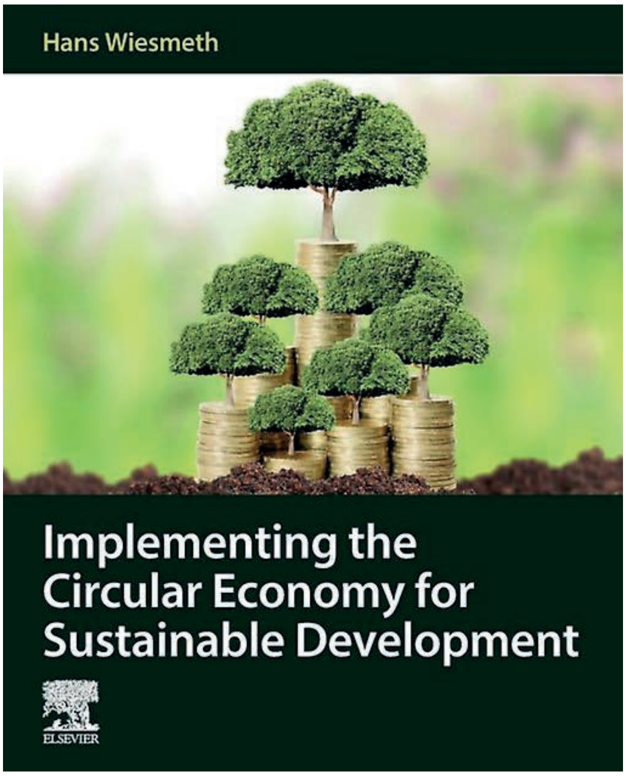

IMPLEMENTING THE CIRCULAR ECONOMY FOR SUSTAINABLE DEVELOPMENT

Author: Hans Wiesmeth

Circular economy (CE) is a mainstream concept, yet a quick glance is enough to understand that its definition and application is heterogenous, and highly context dependent. What is the difference between the economy as we know it and the circular economy? And what are its boundaries? The book “Implementing the circular economy for sustainable development” addresses these questions and beyond, giving a comprehensive and detailed overview both on the theory and on practical applications of CE, thus supporting those who approach the topic for the first time and those wishing to acquire in-depth knowledge.

Section one of the book starts from definitions and meaning attributed to “circular economy” (chapter 1), by analyzing different policy frameworks (chapter 2), then showing how the concept is represented in the scientific literature (chapter 3) and detecting the leaders and the followers countries in the adoption of CE agendas. Is there a unique definition of circular economy in practice or in scientific literature? [spoiler alert: no, there is not!]. And what about business models? Are they profitable and scalable? These are some of the questions addressed in the first three chapters. Chapter 4 describes the possible drivers that lead a country to undertake a rigorous policy strategy towards a circular economy. According to the author, the country characteristics influencing such path are a) Endowment with natural resources b) Density of the population, respectively land available for landfilling c) Level of environmental awareness d) Motivation for strategic behavior. Some countries have been analyzed as early adopters (leaders), such as Germany with its advanced legislation about waste; and China with its pioneering development strategy implemented already in 2002. Late adopters (followers) have been identified in Georgia and Russia, while USA have been described as laying “in between”. Chapter 5 presents environmental laws, directives and ordinances from different countries targeting crucial topics of a circular economy, such as waste management and climate change regulations in the European Union (EU), or the case of the “California’s bottle bill”.

In the second section of the book, the nexus between the economy and the environment is explored. The concept of environmental commodity is presented (Chapter 6), and basic concepts as perceived scarcity and perceived feedback from environmentally friendly actions are illustrated. Chapter 7 focuses on the allocation of environmental commodities. According to the author, the Tragedy of the Commons and the Prisoners’ Dilemma are two mechanisms able to explain the failure or success of developing an environmental strategy; indeed, the case study of an involuntary policy failure is shown through the example of the German refillable quota issue, explained through the prisoners’ dilemma. Chapter 8 presents an introduction to behavioral economics, bringing to the forefront some principles of possible relevance for environmental economics and for the implementation of circular economy initiatives. Prospect theory, limited information, the role of social norms and finally, the environmental awareness and perceived feedback, all play a role in the possible success of the CE implementation. Once again, a case study clarifies the issue, but it’s in paragraph 8.5 where we find the ultimate answer to the question: how useful are behavioral economics to implement a circular economy?

Section three of the book analyzes the role of technology in boosting the CE implementation. Innovative technologies are crucial in enabling the development of CE in practice, but their adoption also entails some drawbacks. Yet, where are the roots of the idea that technology can help achieve a circular economy? Chapter 10 conceptualizes the link between CE and the technological endeavor re-

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lying on the industrial ecology theory. After that, it provides a frame about the environmental technologies, their economy and role in the global markets, as well as their interconnectedness with policy. Chapter 11 enquires into the role of information (and its asymmetries), its links with governmental policies to favor the adoption of CE measures and it brings a case study of (partial) success: the promotion of renewable energy sources in Germany. Chapter 14 explains the rebound effects and path dependencies (technological, societal) and illustrates their possible impact on the implementation of a circular economy. Chapter 15 examines how the digital economy and the circular economy boost each other and sometimes "impede each other in a variety of ways": the most practical case of half success is represented by smart cities (13.1.1), while some challenges are illustrated by the case of e-commerce and online shopping.

Section four addresses the issues of policies to implement environmental measures. It starts from the description of some policy regimes (chapter 14) such as laissez-faire, technology-guidance, command-and-control policies, augmented market system and it ends with the importance of engaging stakeholders through appropriate framework conditions. Chapter 15 examines environmental standards and the mechanism through they are changed. The case study reports on the emission standards for vehicles. Chapter 16 deals with market-oriented policy tools, explaining the main set of measures commonly applied: pollution tax- with a focus on the polluter pays principle; tradable emission certificates and related markets; last, a brief examination of the Coase Theorem and some behavioral aspects relating to voluntary contributions and flexible information-based policies are illustrated. Eventually, chapter 17 considers holistic policy approaches with their origins, their economic background, and practical experiences gained. The holistic approach takes into account a large set of stakeholders, information issues and need for inter-disciplinary target-setting. Two practical cases are carefully illustrated: the Integrated Waste Management policies and the Extended Producer Responsibility. Chapter 18 analyses the economics of waste hierarchy, highlighting the failure of the waste prevention (defined as "the forgotten child" of the waste management) due to societal path dependencies. The issue of recycling and its path dependencies is illustrated as well.

Section five offers a guidance to implement holistic policies, defined as "integrated Environmental Policies (IEP)". In chapter 19, the constitutive elements of an IEP are analyzed with reference to the question "where are we on the road to a circular economy?". Germany's case about the state of the art of the CE implementation is reported. Chapter 20 is focused on packaging waste, while chapter 21 is about Waste Electrical and Electronic Equipment (WWEE) and End-of-life vehicles (ELV). Chapter 22 faces the topic of climate change mitigation with special attention paid to the emissions, from the Kyoto protocol to Copenhagen, Paris and Madrid. An explanation about the Emission Trading System (ETS) and its application at national and global level follows. Chapter 23 is about plastics and its potential reduction thanks to an IEP for plastic waste; the chapter illustrates the different type of plastics, the critical issues about recycling, the international market and China's ban and it ends with the constitutive elements of an IEP on plastic. Chapter 24 is about textiles waste, and it follows a similar structure of the previous chapter. The last chapter (25) presents conclusive remarks about a real possibility for the system to change, along with a summary of the issues presented in the book, connected to the potential development of specific IEPs. Some reflections on the impact of the lockdown on the system and the potentialities shown to change it are offered.

Overall, this book examines all the aspects that can determine the success or failure of the CE application; the theoretical discussion is complemented with the analysis of both specific IEP pillars and single case studies.

Anybody who wants to learn about circular economy in theory and practice may benefit from it, as the content is highly technical, but the language is easy-going. The book is recommended for professionals, consultants, policy makers and researchers. Master students may benefit from it as well.

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Environmental Forensic

TOTAL PETROLEUM HYDROCARBON: A CONTROVERSIAL MACRO-PARAMETER IN ENVIRONMENTAL FORENSIC

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In environmental forensic practice, values measured for chemical parameters, such as chemical concentration in a specific matrix (soil, wastewater, air, waste), are crucial for the assessment of possibly occurred pollution. If these values exceed regulatory limits and if it can be demonstrated that they are the result of a deliberate release from anthropic activities, an environmental crime can be supposed.

"Macro-parameters" are widely used in many environmental fields; examples are Total Organic Carbon (TOC) in wastewater; Particulate Matter (PM) in atmospheric air andTotal Petroleum Hydrocarbons (TPH) in soil. In these cases, the parameter does not refer to a specific compound but it quantifies the presence of a larger class of chemicals characterized by a common property.

In a forensic investigation, the aim is to identify the potential cause of the presence of the chemicals. Due to this, these macro-parameters, if analysed stand-alone, may be misinterpreted and be a source of bias. This is because they quantify substances that could have either natural or anthropogenic origin.

In this context, a simple and direct use of these macro-parameters could generate the so called "confirmation bias" (Newman, 2018). This is described as where individuals have the "tendency to gather evidence to confirm hypotheses rather than objectively weighing the merits of all plausible hypotheses" (Newman, 2018). The primary, and usually the only considered assumption, is that the measured concentration is due only to the related anthropogenic activities. Consequently, the conclusions derived from this conservative hypothesis could be considered not realistic as it is supported by partial and non-scientific evidence. This simplistic approach should not be acceptable in correct environmental forensics practice.

A clear example is represented by the case of PM air pollution monitored in the Veneto Region (north-east of Italy), being one of the most polluted areas for air quality in Europe (Khomenko et al., 2021). Here, during the pandemic lockdown imposed between March and June 2020, specific emissions, such as those deriving from the vehicles traffic, almost completely ceased. Therefore, peaks of PM concentrations (i.e., exceeding regulation thresholds) were not expected during this period. However, some PM peaks were registered as caused by natural sand transported by the wind from Asian regions (Pivato and Cappai, 2021). In this case, the "macro-parameter" PM concentration includes the contribution of particulate matter generated from natural processes and unfavourable climatic conditions. Therefore, considering the number of yearly exceedances of particulate matter could represent a biased tool to support restriction measures aimed at improving air quality (e.g., traffic limitations).

A less known example is addressed by the authors in this column: the macro-parameter "Total Petroleum Hydrocarbons (TPH)".

The analytical determination of TPH allows to quantify the total presence in soils (e.g., through ISO, 2004) or waste (e.g. by EN, 2004) of a large family of different hydrocarbons, substantially corresponding to substances with C > 12. In particular, the measured values do not give information on compounds' molecular arrangement (i.e., linear, branched, cyclic, and/or aromatic), composition and related toxicity.

Considering the possible source, Vecchiato et al. (2017) stated that terrestrial plants can produce hydrocarbons as components of their epicuticular waxes to protect plant tissues from adverse environmental conditions. In particular, soils from woodland and protected areas (where anthropogenic activities are absent), exceeded the threshold limits or TPH at 50 mg kg^{-1} DW. As a paradoxical consequence, soils should have been remediated because of the presence of natural hydrocarbons such as leaf wax n-alkanes.

Considering the related human toxicity, TPH includes both human carcinogens and also non-carcinogens with low toxicity to humans. Due to this, regulations should refine the procedure for classifying a waste for carcinogenicity (HP 7) or mutagenicity (HP 11) by considering only the concentration values of the carcinogenic substances, the so-called "bio-markers", i.e., dibenzo[a,h]anthracene,

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benzo[a]anthracene, benzo[def]crhysene, Benzo[e]acephenanthrylene, benzo[e]pyrene, benzo[j]fluoranthene and benzo[k]fluoranthene.

TPH should also be considered when classifying a waste for ecotoxicity through the hazardous property HP 14. In this regard, TPH substantially corresponds to the parameter "Hydrocarbons C10-C40", already classified within the Regulation 2008/1272/EC for Classification, Labelling and Packaging of products with the Hazard Statement Code H411 related with chronic aquatic toxicity. Therefore, according to the so-called "calculation approach", as established by the current Regulation 2017/997/EC, a waste containing high concentrations of Hydrocarbons C10-C40 could be classified as HP 14 Ecotoxic without any realistic assessment of its real impact on the ecosystem. This is the case, for example, of the dismantled conveyor rubber belts (see Figure 1) where the concentration of hydrocarbons "C10-C40" could be as high as 10% (w/w). In this case, the assumptions on considering all components quantified in this macro-parameter could overestimate the presence of effectively ecotoxic compounds.

To refine this overcautious waste classification, two possible approaches are proposed:

Similar to the refinement proposed for the HP 7 or HP 11, a list of substances already classified with HSCs related with aquatic toxicity can be proposed as "eco-markers" within those considered within the macro-parameter TPH or, equivalently, Hydrocarbons C10-C40;

Ecotoxicological testing represents, in these cases, the best tool to realistically assess the ecotoxicity of a waste sample and to consistently classify it. Also, it is worth mentioning that the results derived from the bioassays performed should always prevail over the classification judgement based on the chemical composition of the waste itself.

FIGURE 1: Dismantled conveyor rubber belts.

In conclusion, this column wanted to initiate a discussion on the way the use of values measured for macro-parameters can induce overprotective and unrealistic interpretation. Further, we highlighted the consequent need to go beyond their mere meaning by deepening the knowledge on the real constituents behind them.

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DETRITUS & ART / A personal point of view on Environment and Art

by Rainer Stegmann

Artists seldom provide an interpretation of their own work; they leave this to the observer. Each of us will have his/her own individual view of a specific piece of art, seeing different contents and experiencing a range of own feelings and emotions. Bearing this in mind, I created this page where you will find regularly selected masterpieces from different epochs and I express my thoughts on what the work conveys to me personally. My interpretation will refer specifically to the theme "Environment". Any comments or suggestions regarding this column should be addressed to stegmann@tuhh.de.

TABCHARANY HANI / "The Bride of Beirut" (Beirut 2020).

In memory of the Beirut port explosion victims on August 4, 2020, and from the remains of the rubble and broken glass resulting from the explosion, the young artist Tabcharany Hani from Gemmayzeh, Lebanon created and sculpted a statue entitled "The Bride of Beirut." The sculpture was made of debris collected from the explosion site, broken glass, pieces of destroyed furniture, pieces of cement, and concrete blocks all collected from the streets of Beirut following the blast. The choice of materials allows the sculpture to be a true reminder of the devastations. The statue has been placed in the centre of Beirut.

The sculpture symbolizes a beautiful girl (Bride of Beirut) who rises from under the rubble, despite the wounds that tore her body due to the broken glass. So, she selects glass beads to make a crown on her head like a garland of thorns and a robe in which she covers her nakedness. Her upright posture, beauty and self-confident appearance send the message that the people of Beirut shall not give up; on the contrary, the sculpture conveys strength and confidence for a new start.

"This monument serves as a message to the world to show the power of humans in creating beauty from chaos". "The sculpture serves to be a true reminder of the devastations and will be place to pay respect for the precious lives that were lost." (Hani)

I selected this piece of art from waste because it sends a strong message to the world, and it may help people affected by this disaster; in this way, we also show our solidarity with the people of Beirut. The sculpture raises hopes, especially to the younger generation, by choosing a young woman, somebody like themselves. This statue is a particular example of waste to art because it makes a strong social and political statement. It also shows that it does not need sophisticated materials to create this expressive sculpture; even waste can do. It requires creativity and- in this case- love to his homeland and defiance, enthusiasm and hope. I hope that the "Bride of Beirut" reminds the responsible politicians and administrators day by day never to let such a disaster happen again.

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In the next edition of DETRITUS I will show some examples of waste to fashion from the Fashion Akademie JAK in Hamburg and will have some thoughts about the fate of used clothes

THE AKADEMIE JAK / Henri-Nannen Award

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