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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

TEXTILE WASTE: WHERE IS THE JOURNEY HEADING?

In May 2018, the Waste Framework Directive (WFD) 2008/98/EC was amended by the adoption of Directive (EU) 2018/851. Amongst numerous modifications and additions, the amended WFD now also affects textiles, which have not yet been a core issue of waste management. Furthermore, textiles are also in the focus of the "European Green Deal" (EC, 2019), "a new Circular Economy Action Plan for a cleaner and more competitive Europe" (EC, 2020a) and "a New Industrial Strategy for Europe" (EC, 2020b). While it is clear that there will be massive changes in the way textile waste is handled, it is not yet foreseeable where the journey will lead.

Textiles are part of municipal waste

Up to now textiles have not been mentioned in the WFD at all. However, the Directive (EU) 2018/851 clearly defines that textiles are part of municipal waste. However, there is no clear and unambiguous definition of what is meant by the term textiles. It is not sharp to what extent products can contain non-textile components and what purpose textile products are used for. Overlaps and ambiguities may arise. In order to achieve a level playing field in the EU and to prevent national go-it-alone, it would be important for the Commission to clearly and unambiguously define which products fall under the term "textiles" and which do not.

Re-use

The revised WFD assigns significant importance to reuse and explicitly mentions in this context textiles as well. Even though (preparation for) reuse is very welcome in terms of resource conservation, the question arises as to how this goal can be achieved. The measure preparation for reuse was already placed second in the waste hierarchy in 2008, but this has not led to the reuse of products gaining the importance it deserves within the last decade. It is to be feared that fashion chains, which in many cases follow the fast fashion business model, will counteract reuse. For an actual reduction in the consumption of clothing, legal framework conditions would have to be created that make the fast fashion business model unattractive and enable companies that offer sustainable fashion to be economically successful.

Separate collection

One of the core changes in the revised WFD is the obligation of a separate collection of textiles. While it is clear that a separate collection of end-of-life textiles will become mandatory from January 1, 2025 at the latest, it is not yet defined which targets or quotas will have to be met. On the one hand, quotas could be set for preparation for reuse and recycling, as is the case for municipal waste or packaging waste. In this case, a defined minimum percentage of the clothing sold would have to be acquired by separate collection. Whereby, in addition, it has not yet been determined how high these quotas will be. On the other hand, it would be perfectly possible to stipulate that new clothing must contain a certain minimum content of recycled material. In any case, we will know more by December 31, 2024 at the latest. However, it would be necessary to announce the exact targets as soon as possible, since the member countries need appropriate preparation time for their implementation.

Recycling

Nowadays, the costs of separate collection and sorting are borne by the sale of second-hand clothing more or less exclusively. Others than reusable end-of-life textiles will rather cause costs than contribute to the financing. As a matter of fact, collectors ask for re-useable items only. This seems to be a chicken - egg problem. Currently, textiles that would be suitable for recycling are not collected because the appropriate processes are not developed or are not economical. However, since no (or only a few) recyclable textiles are collected, no adequate systems have yet been developed to recycle such fractions. EPR (extended producer responsibility) could be a way to get out of this dilemma. Even if the current collection systems are not optimal, as they only target reusable garments, an EPR system does not necessarily only show advantages either. Nowadays, many charitable organizations are involved in the collection and sorting of end-of-life clothing. On the one hand, this leads to the creation of jobs for people who are not employable on the normal labor market. On the other hand, clothing is also offered in second-hand stores for the socially disadvantaged. Finally, it must also be taken into account that many consumers have ethical concerns about throwing functional clothing in the trash. In that, an EPR system may even be disadvantageous and could ultimately lead to clothing being given the status of a disposable product such as for packaging. All these items considered, there is a need for thorough planning and not neglecting the customers' awareness in this field.

Recycling rate

Even if there are no targets for re-use and recycling for end-of-life textiles set up to now, the amendment of WFD

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

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might exhibit an indirect impact. For municipal waste, stringent targets for re-use and recycling will have to be met by 2030 (60%) and 2035 (65%). These minimum quotas are not easy to achieve and member countries will have to make great efforts to actually reach the targets. Since textiles account for around 4-6% of municipal waste, they can make a significant contribution to meeting the quotas.

Conclusions

Even though recycling in many cases shows positive effects, such as reducing the consumption of resources, it is clear that recycling in itself is not a goal. The goal is to protect the environment and minimize the consumption of resources, and recycling is only one measure to approach this goal. In practice, as with other types of waste, the right mix of preparation for reuse, recycling, thermal recovery and landfilling must be found. However, it is not the case that recycling rates should be as high as possible in order to achieve the best possible protection of the environment or maximum reduction in resource consumption. At a certain point, the effort (financial, energetic) for recycling increases to such an extent that no more benefits can be achieved with a further increase.

The new EU legislation for dealing with end-of-life clothing is to be welcomed. In part, the specifications are not yet precise and further details from the Commission will follow in the near future. It is to be hoped that the additional and further-reaching stipulations will actually lead to a significant reduction in the environmental impact of the textile industry and are not just lip service. Specifically, the Commission's action should be such as to achieve the following objectives:

- A clear definition of what is meant by the term textiles in the WFD is absolutely necessary. It is essential to avoid different interpretations within the EU27.
- Measures to encourage producers and retailers to put fewer textiles on the market that are more durable and less subject to fashion trends must be implemented. The primary goal must be to combat the causes but not the symptoms. Ideally, alternative business models are more profitable than fast fashion.
- The charitable idea of end-of-life textiles collection should be maintained to keep the motivation of the population high, diverting textiles from municipal waste. Clothing must not be placed on the same level as packaging. Therefore, possible EPR schemes must be designed as to align with this concept.
- A collection system for end-of-life clothing that allows for collection of it regardless of its quality, must be established and funded. That is, clothing that cannot be worn again, but can be recycled, should also be collected as wide-ranging as possible.
- Local reuse instead of exporting second-hand clothing to developing countries has to be encouraged. Europe should rather not export its (waste) problems.
- Producers and retailers must not only fund collection and sorting of end-of-life textiles but also the development and establishment of recycling schemes. There must be no economic advantage in thermal recovery over the recycling of end-of-life textiles. Incineration should only be used as a last resort.

A. Bartl, W. Ipsmiller
TU Wien, Institute of Chemical, Environmental and Bioscience Engineering, Austria
andreas.bartl@tuwien.ac.at, wolfgang.ipsmiller@tuwien.ac.at

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A NOVEL METHOD TO CALCULATE THE SIZE OF REPRESENTATIVE WASTE SAMPLES BASED ON PARTICLES SIZE

Giovanni Beggio [1,*] and Pierre Hennebert [2]

[1] *Department of Civil, Environmental and Architectural Engineering, University of Padova, Via Marzolo 9, 35131, Padova, Italy*
[2] *Ineris (French National Institute for Industrial Environment and Risks), BP 2, F-60550 Verneuil-en-Halatte, France*

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ABSTRACT

A novel approach to determine the size of samples of granular wastes is proposed, forwarding the concept of the "number of particles", as previously introduced by the authors. To be representative with a minimum error, it was demonstrated that at least 100 particles showing the presence of the characteristic of interest, shall be collected in the sample. Waste particles are usually characterized by size-concentration relationships. However, in waste sampling standards they are not explicitly considered when estimating the size of the sample. In this context, this paper extends this requirement to the number of particles "rare is size", belonging to the less represented size fraction in the waste to be characterized. The number of particles is then transformed into a mass by a formulation that avoids using unrealistic assumptions on particles features. Results derived from the application of the two formulations on 5 different types of waste show that their equivalency relies on how similar are, the proportions of particles rare in concentration and rare in size in the batch to analyse. Here, preliminary knowledge on particles physical features and distribution of the measurand is key to derive coherent values for mass of samples. Finally, the need to perform on-site size reduction is discussed for cases where the application of both the conventional and novel approaches could have leaded to unpractical management of too large-sized waste samples.

1. INTRODUCTION

In the European standards, the formulas proposed for the calculation of the size of a waste sample are grounded on the "binomial jar" approach (CEN, 2006). In particular, the degree of representativeness depends on the number of particles of interest within all particles caught from the lot during sampling. Here, "particles of interest" only refers to those particles showing the presence of the characteristic to be measured in the waste lot, such as chemical content or material composition. Their number in the sample strongly influences the resulting analytical value (i.e., the mean value of the searched characteristic between all particles making up the sample). The more the proportion resembles that occurring in the waste lot, the more the samples are representative, the nearer is the measured value to the real one. As proposed by the authors in a previous publication, a minimum number of particles of interest in the sample can be calculated, which, if satisfied, could lead to a controlled degree of variability of this proportion within a set of repeated samples (Hennebert and Beggio, 2021). From that number, the mass of a sample can be calculated according to some approximations.

However, the composition and material of coarse waste particles are usually different from fines (Haynes et al., 2015; Hennebert, 2020; Priya and Hait, 2021; Viczek et al., 2021b). This is due to the fact that the relationship between size and composition is not controlled in waste production processes, thus remaining in practice unknown. In waste sampling standards the particle size and the concentration are not simultaneously and explicitly considered when estimating the size of the sample. In this context, neither appealing to the so-called Theory of Sampling (ToS) as proposed by Gy, (2004) would likely help to fill this gap. About this latter, even in its narrow application in the waste field, dedicated only to material composition analysis, this issue is acknowledged but no practical solution is proposed (Wavrer, 2018).

This said, the current size-calculation approach misses to put a requirement on the granulometric distribution of the sample, which could not reliably resemble that occurring in the waste lot and thus possibly leading to an unexpected degree of variability of the measurements.

This question is not much addressed either in the scientific literature. To the authors knowledge, only two recent and well-documented publications investigate such issue,

* Corresponding author:
Giovanni Beggio
email: giovanni.beggio@unipd.it

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by discussing the results of a so-called Replication Experiment (RE) (Danish Standards, 2013), performed to assess the variability, within a set of 10 equivalent samples (i.e., collected following the same instructions), of the material composition (Khodier et al., 2020) and chemical-physical features of Mixed Commercial Waste (MCW) (Viczek et al., 2021a). For the RE, the sampling procedure was based on the Austrian Standard ÖNORM S 2127, which indicates an "empirical" formula for the calculation of the sample size, based on a minimum number of 10 increments per 200 t of waste, whose mass (in kg) is determined by multiplying 0.06 times the 95th percentile of the particle size (in mm). The two papers present data on materials and elements distribution per size class. Khodier et al., (2020) reports that the variability in material composition is greater for class sizes occurring in smaller mass fractions. These latter are represented by coarser particles, i.e., 80-100 mm, 100-200 mm and 200-400 mm, which led to high levels of Relative Sampling Variability (RSV), i.e., RSV > 50%, for most of the materials categories investigated (up to 230% for wood particles sized 200-400 mm). Consistently, Viczek et al., (2021) showed that the values of RSV of repeated elemental analysis are significantly (but moderately) correlated with particle size. In particular, positive correlation is noted, with the highest RSV (> 80%) reported for the 80-100 mm size class. Further, the RSV of elements concentrations calculated for the single particle size fractions decreases with increasing value of the mass fractions of that particles size class. Since very few parameters were measured with a low level of RSV, the results derived from the analysis of the samples collected according to the Austrian Standard risk to be not usable for testing programmes requiring high reliability (e.g., in case a parameter is usually measured in a range including a compliance limit). In practice, this situation arises when the samples do not contain "enough" particles in these size classes to reliably resemble the heterogeneity of the population in a reproducible manner (i.e., ensuring the proportion of the rare particles, which is critical for the measurement of a reliable mean value between the particles).

In this context, the authors of the two studies discuss the obtained variability referring to the theoretical framework proposed by the ToS. In particular, in Khodier et al., (2020) the variability in material composition throughout the different size classes is explained by the high degree of distributional heterogeneity occurring in MCW, i.e., influenced by the tendency of scraps to segregate spatially in a waste lot; while, in Viczek et al., (2021), the high degree of RSV linked to analytical results is discussed assuming an high value of constitutional heterogeneity shown by MCW, which is determined by the differences of chemical contents between individual fragments and prevent from the possibility to collect samples characterized by an identical composition of the lot. To tackle this unacceptable variability, both studies concluded that higher number of increments and larger samples are needed to decrease the two contributions: however, no solutions are proposed on how to determine these larger values.

To fill this gap, a practical approach is proposed here starting from the calculation of the size of a representative sample by ensuring that at least 100 particles of interest are present in it, as suggested originally by the authors in a previous paper (Hennebert and Beggio, 2021). The novelty of this contribution stands from introducing the need to also include 100 particles rare in size within the number of particles of interest that should be present in the sample. A reconciling formulation is then presented to add the requirement laid down in this work and to those previously proposed in Hennebert and Beggio, (2021). Finally, results were discussed from the application of the two proposed formulations to calculate the size of representative samples for 5 different waste types.

2. THEORETICAL DEVELOPMENT

2.1 Requirement I: minimum number of particles of interest (connection to Hennebert and Beggio, 2021)

This approach underlies the formulas included in the European standards on sampling CEN/TR 15310-1 and EN 15002 for the estimation of the minimum size of laboratory samples and test portions (CEN, 2015, 2006). Its statistical basis (i.e., the binomial probability distribution) is fully described in a previous work by the authors (Hennebert and Beggio, 2021). Briefly, assuming the minimum achievable value for the variability between a set of repeated samples of CV = 0.1, it is demonstrated that a sample must contain a number n of particles:

$$n \geq \frac{(1-p_c)}{CV^2 p_c} \approx 100/p_c \quad (1)$$

to be representative of the waste lot (i.e., the population), this latter characterized by a number fraction of "particles of interest" $p_c << 1$. Here, particles of interest are defined as the elements of the population showing the occurrence of the researched characteristic, e.g., a physical constituent, a substance or an element. When discussing waste materials, these could be thought also as particles "rare in composition". Therefore, Equation 1 simply states that the number of particles of interest $n*p_c$ that must be collected in a representative sample (and sub-samples up to the test portions) is at least 100.

The fraction p_c of particles "rare in composition" is most of the time not known but can be assumed, as suggested in the European standards, ranging from 10^{-1} to 10^{-4} according to the distribution of the particles of interest in the population (i.e., normal or rightly skewed), or even to 10^{-6} for the so-called "nugget" effect. Previous knowledge of the waste is therefore key to provide reliable estimation of p_c. This could be achieved by data derived from basic characterization campaigns of the waste material. An alternative method based on regulatory limits for compliance testing of products is proposed in Hennebert and Beggio, (2021). A further procedure useful when a lot of single particles data are available is described in the Supplementary Material.

For practical reasons, the next step is to transform the number of particles in the sample into a volume and a mass of sample. As elucidated in Hennebert and Beggio, (2021), the current approach underlying the formula in the European standards EN 15002 and CEN/TR 15310-1 is to multiply n (as introduced in Equation 1) by the aver-

age mass of particles in the population $\overline{M_p}$ (kg), this latter roughly estimated assuming an average spherical volume of particles corrected for particles size distribution and deviation from the spherical configuration:

$$M_{sam,c} = n * M_p = \frac{(1-p_c)}{CV^2\, p_c} * \frac{\pi}{6}(D_{95})^3 * \rho_p * g * f \quad (2)$$

Where $M_{sam,c}$ is the mass of the representative sample (g), D_{95} (cm) is defined as the 95th percentile of particles diameters, g is a correction factor for particle size distribution (ranging from g =1 for uniform distribution, to g =0.25 for broad distribution), f is a form factor considering deviation from a spherical configuration (ranging from 1 for perfectly spherical scraps to << 1 for sheet-like particles) and ρ_p (g cm^{-3}) is the specific mass of the particles (assumed averaged for multi-materials waste batches).

In practice, this step represents the largest practical difficulty, due to the heterogeneous distribution of shape and size of particles in waste materials. How can one estimate reliably the mean size or mass of particles in a waste lot when the relative particle mass can vary of many orders of magnitude? This issue is currently acknowledged by the European standards, which suggest to take the results from Equation 2 just as a "rough" estimate, however enough precise to know the order of magnitude of the sample size (CEN, 2006).

2.2 Requirement II: Minimum numbers of particles "rare in size" and "rare in composition"

When size-composition relationships are not known for the particles making up the lot (as it is frequently common in the waste field), the same approach can be expanded also to those particles "rare in size". These latter can be defined as those belonging to the less numerous size-class within the whole number of particles making up the population. Their number fraction within the waste lot can therefore be quantified with p_s. Consistently with the assumptions underlying Equation 1, it should be required that also at least 100 particles rare in size should be present in the sample, or equivalently, that a sample must contain a number n_s of particles of (Equation 3):

$$n_s \geq 100/p_s \quad (3)$$

However, in most of the cases, n_s cannot be calculated due to the difficult quantification of p_s. For instance, fines are frequently so numerous that it is in practice out of the resource of the sampler to count them. These numbers could be roughly estimated for each size class by converting the mass (easily measurable during granulometric analysis) into a number of particles with hypotheses of geometry and particle density. Anyway, for size classes characterized by just several particles, this number can be easily counted during granulometric analysis. In the waste field, one can expect that these fractions are most of the times the large ones.

At this point, a novel formulation is proposed to derive a consistent mass of the sample $M_{sam,s}$(kg) while avoiding strong assumptions on the average geometry and density of particles:

$$M_{sam,s} = 100 * s/S \quad (4)$$

which considers only the mass fraction of particles rare in size S (-) and the average mass of particles rare in size s (kg). Practically, s and S should be quantified during preliminary characterization through conventional granulometry and particle sizes distribution analysis, taking care to count at least the number of particles resulting on the three top sieves characterized by decreasing mesh size. According to their practical experience, the authors suggest assessing at least five mesh sizes, to be chosen so that the number of particles in the class size with the lower number of particles approaches 100 (i.e., to be representative). After having identified the size class characterized by the lowest number of particles, s and S can be calculated as the ratio between the mass of size class of particles rare in size and the counted number of particles or the mass of the sample used for granulometric analysis, respectively.

Likewise, an equivalent approach could be proposed to calculate $M_{sam,c}$ (kg), thus substituting the formulation of Equation 3:

$$M_{sam,c} = 100 * c/C \quad (5)$$

Where c (kg) is the average mass of particles of interest and C is their mass fraction (-). However, c and C cannot be routinely measured today. With the development of combined optical measurements of the composition and size of individual particles and machine learning techniques, also this approach considering the of mass fraction of particles of interest could be feasible in the future (Bonifazi et al., 2021; Kroell et al., 2021).

2.3 Further requirements

As discussed in Hennebert and Beggio, (2021), the use of the binomial distribution for the calculation of the number of particles included in a representative sample strictly requires that each sampling action shall be carried on as a casual/probabilistic event, where each particle has an uniform non-zero possibility to be collected during sampling.

In this context, the European sampling standard introduces a further requirement to avoid negative segregation of large particles during sampling, i.e., the size of the three dimensions (length, height and width) of the sampling instruments shall measure at least 3 times D_{95} (cm). Consequently, the volume of the sampling instrument should be at least (3*D95)^3 (cm^3). This corresponds to the minimum volume of the materials picked up with a sampling action, i.e., an increment.

When the results shall be representative of the average composition of the waste lot (as it is typical for waste compliance testing), and thus consider possible heterogeneous distribution (spatial and/or temporal) of the material's features (i.e, size and composition), the laboratory samples must be composed of a number of increments collected randomly throughout the lot. This number of increments should be estimated according to the actual variability of the population, as indicated in the European sampling standard (CEN, 2006).

Based on this, the mass of the laboratory sample shall be:

$$M_{sam,inc} = n_{inc} * (3*D_{95})^3 * \rho_b \quad (6)$$

Where $M_{sam,inc}$ (g) is the mass of the sample, ρ_b (g cm^{-3}) is the bulk density of the material and n_{inc} is the planned number of increments.

The theoretical development of the formulas equalizing $M_{sam,c}$, $M_{sam,s}$ and $M_{sam,inc}$ is presented in the Supplementary Material.

Furthermore, the mass of the sample should be large enough to satisfy the requirements laid down by the set of planned analytical protocols in terms of test portions, repetitions and reserves:

$$M_{sam,a} \geq \sum analytical\ requirements \quad (7)$$

Finally, by reconciliation, the mass of the sample satisfying all the conditions proposed to achieve representativeness is the following:

$$M_{sam} = max\ (M_{sam,c}; M_{sam,s}; M_{sam,inc}; M_{sam,a}) \quad (8)$$

With $M_{sam,c}$, $M_{sam,s}$, $M_{sam,inc}$ and $M_{sam,a}$ as calculated according to see Equation 2, 4, 6 and 7, respectively.

2.4 The number of particles in the Theory of Sampling

In this context, it is worthwhile noting how ToS implies the statistical concept of number of particles in its most known formulation, virtually building a bridge with the approach proposed in this paper. In particular, ToS statistical development is clearly grounded in the binomial probability distribution (Gy, 2004).

The original formula proposed by Gy, (2004) to quantify the minimum relative variability, in terms of variance, achieved by the act of sampling (i.e., called the Fundamental Sampling Error) is the following:

$$\sigma^2 = \left(\frac{1}{M_{sam}} - \frac{1}{M_l}\right) \sum_{i=1}^{n} t_i m_i \left(\frac{a_i - a_l}{a_l}\right) \quad (9)$$

where M_{sam} and M_l are the masses of the sample and the lot, respectively, t_i is the mass fraction of the i-th group of particles, each one characterized by a mean mass of m_i, a_i is the value of the measurand as measured in the i-th group of particles and a_l is the true value of the measurand in the entire lot (which is the value a sample should represent). In Equation 9, the variability is calculated as a function of the ratio between the mass of one particle (i.e., $\sum_{i=1}^{n} t_i m_i$ estimated as the weighted average among each family), divided by the mass of the sample M_{sam}, which is nothing else than the inverse of a number of particles.

To be practical, Equation 9 needs the introduction of strong assumptions to build the heterogeneity model of the material to be analysed. Accordingly, an alternative formulation was proposed Gy, (2004):

$$\sigma^2 = \left(\frac{1}{M_{sam}} - \frac{1}{M_l}\right) HI_l = \left(\frac{1}{M_{sam}} - \frac{1}{M_l}\right) cflgd_{95}{}^3 \quad (10)$$

where HI_l, the so-called Heterogeneity Invariant, can be estimated by assuming material-specific values for d_{95} (95th percentile particle size), f and g (shape granulometric factors, respectively, equivalent to those introduced for Eq. 2), the liberation factor l, measuring the degree of liberation of a substance within a matrix and originally developed in the ores field (ranging 0 to 1 from complete segregation to complete liberation) and the constitutional parameter c, which can vary from 0 to several orders of magnitude. Methods to estimate empirically these latter parameters are described in Gy, (2004), especially for ores. However, no waste-specific references are found in the literature to estimate l and c. As no "liberation" of elements should be considered when measuring total elemental content, l = 1 can be considered a realistic assumption for waste materials. Conversely, a simplified expression for c is usually introduced for simple particles (i.e., consisting either of 100% or 0% of the measurand to be analyzed):

$$c = \rho_p \frac{1 - a_l}{a_l} \quad (11)$$

where, ρ_p is the particles density and a_l, is the value of the measurand to be analyzed in the lot. This latter, when expressed as a fraction, can be considered equivalent to p_c, as defined in Equation 1. With $\sigma^2 = CV^2$ and by considering that usually $M_l >> M_{sam}$, Equation 10 becomes:

$$CV^2 = \left(\frac{1}{M_{sam}}\right) cflgd_{95}{}^3 = \left(\frac{1}{M_{sam}}\right) \rho_p fgd_{95}{}^3 \left(\frac{1 - p_c}{p_c}\right) \quad (12)$$

where, if rearranged, M_{sam} is calculated equivalently as stated by Equation 2. In other words, in a simplified version of the ToS, it can be shown that the variance is a function of the number of particles as described by the binomial probability distribution.

3. MATERIALS AND METHODS

3.1 Wastes characterization data

Physical characterization data were collected for 5 types of wastes. In particular, D_{95} (mm), D_{05} (mm), ρ_b and ρ_p (kg m^{-3}), S (% w/w), s (kg), shape and granulometric factor f and g were determined. Both experimental data and information collected from the literature were considered.

First, data from mixed commercial waste (MCW) generated in Austria were derived from those presented in Khodier et al., (2020). Besides presenting a detailed in-depth discussion on sampling issues on this waste type, this paper was chosen because it provides mass shares of the particle-size classes. These values were used to determine the D_{95} and the D_{05} by linear interpolation. Being direct measurement not available, the number of particles in each size-class was determined by dividing the resulting mass of each size class by the average mass of particles belonging to that class. This latter was estimated by assuming spherical-shaped particles (i.e., f = 1) and a value for particle density estimated based on weighted average of densities of the materials constituting that size class. In this way, both s and S could be finally determined.

Further, the particle and bulk density together with granulometry were determined in lab by the authors on 4 additional waste samples: plastic shreds from waste of electric and electronic equipment (WEEE) generated at a treatment facility located in France (Hennebert, 2020); automotive shredder residue (ASR) produced by a private plant treating end-of-life vehicles for metal recovery located in central Italy and previously analysed (Pivato et al., 2019); 50mm undersieve bottom ashes (BA), collected after metal separation at the output from an incinerator located in France

recovering heat from the thermal treatment of municipal solid waste; recovered aggregate (RA), derived from the treatment of a mix of bottom ash from incinerated municipal waste, construction and demolition waste and foundry slags from a treatment plant located in the north-east part of Italy.

In particular, particle size distributions were derived by granulometric analysis, conducted on each investigated material through sieving and weighing the resulting sieved fractions. The adopted mesh-size series was 1-2-5-10-20-50-100-200 mm. For each waste type, size-class mass shares were used to determine D_{95} and D_{05} by linear interpolation. Particles number and weight were measured on the resulting fractions characterized by the 3 bigger size-classes to determine S and s. In particular, mean mass of particles for each of the coarser size-classes was estimated as the average weight between the counted and weighted particles. For each of the finer size classes (i.e., stopping at smaller mesh sizes) the number of particles was estimated by dividing the measured mass with the mean mass of particles, these latter assumed spherical and characterized by ρ_p.

3.2 Calculation of size of representative samples

Waste characterization data have been used as input values to compare the resulting values for $M_{sam,c}$ and $M_{sam,s}$, calculated according to the proposed formulations (Equation 2 and 4, respectively). In particular, when using Equation 2 different p_c values were used, according to the specific waste types and to the possible objectives of the dedicated testing programmes:

- For MCW, the primary objective of the characterization campaign was to estimate the materials composition of the waste lot in terms of mass fractions, focusing on the largest mass shares, apart from peculiar hazardous materials (e.g., batteries, toners, chemicals, etc.). In Khodier et al., (2020), the values (expressed as mass fractions) observed in the whole samples (i.e., not referring to the size classes) were 0.039 for textiles, 0.041 for inert material, 0.043 for paper, 0.044 for metals, 0.055 for 2D plastics, 0.071 for wood, for plastics 3D (0.122), for cardboard (0.128), and for the residual fraction (0.458). The observed p for the materials per size class are of course much lower, 26 out of 57 being < 0.01. Therefore, two cases are presented here, with p_c = 0.01 (considered as a safety approach) and with p_c = 0.04 (representing the rounded frequency of textile fraction with p_c = 0.039);
- For WEEE, assuming the quantification of Flame Retardants (i.e., PBDEs) as a possible aim of a dedicated testing programme, a value of 0.001 for p_c was set by using the ratio between the concentration limit of the specific POP additive and their functional concentration, as suggested in Hennebert and Beggio, (2021);
- Similarly, for ASR, BA and RA a p_c value of 0.001 was used as suggested from EN 15310-1 to take into account the effect of few concentrated particles within heterogeneous waste lots (CEN, 2006).

4. RESULTS AND DISCUSSION

4.1 Comparison between $M_{sam,c}$ and $M_{sam,s}$

Besides the requirement on minimum mass of the increment, the novelty of the approach of this work lies on the proposition of two formulas enabling the sampler to calculate as many masses of sample that should include 100 particles considered rare in terms of both presence of measurands and size, respectively. The mass of the sample that should be used will be therefore the maximum between the calculated values. Here, several waste characterization data were collected by the authors and used to calculate the mass of laboratory sample for five types of wastes, according to the approach proposed by this work, to compare and discuss the obtained values. Results are presented in Table 1.

Investigated samples are characterized by a ratio D_{95}/D_{05} covering a wide range of values. Lower values for D_{95}/D_{05} mean broader, i.e., more heterogenous, particles size distribution (in mass). Therefore, investigated materials can be ordered on a scale of increasing size distribution heterogeneity starting from WEEE samples, characterized by $D_{95}/D_{05} \approx 2.5$, MCW with $D_{95}/D_{05} \approx 49$, , BA and RA by $D_{95}/D_{05} \approx 800$, and ASR samples by $D_{95}/D_{05} \approx 2.400$. These results indicate much higher degree of particle size heterogeneity for samples showing "fines" (i.e., D_{05} < 1 mm). Also, the range of calculated values does not to seem coherent with the one used to calculate g, used in Equation 2 to take into account broad particles size distribution when deriving the average mass of particles, which can therefore result in overestimated values.

The value for $M_{sam,s}$ is maximum for municipal commercial waste MCW, with the largest D_{95}, which is characterized by a large mass fraction of rare particles in size S (0.21 kg/kg). These are large particles (i.e., 0.1 – 0.2 m) and heavy (i.e., estimated s = 1.8 kg/particle). The weight of 100 of these particles is 180 kg and as they represent 0.21 kg/kg, the weight of waste containing these 180 kg is 841 kg, higher than the 240 kg that have been sampled by Khodier et al., (2020). Here, the estimated particles mass is remarkably higher than that found empirically by Weissenbach and Sarc, (2022), reporting for pre-shredded MCW with sizes from 80-500 mm a mean and maximum particle weight of 36.3 g and 882.5 g, respectively. This discrepancy is likely due to the calculation assumptions which considered spherical-shaped particles characterized by an averaged density, although the coarser particles of MCW are typically 2D-shaped plastic foils or textiles, while 3D particles are often foams with a much lower density (e.g., hollow materials wood particles).

The next $M_{sam,s}$ is the one of automotive shredder residue ASR, with very low mass fraction of rare particles in size S (0.003 kg/kg), mainly consisting of relatively light (s = 0.005 kg/particle) coarse hollow foam pieces (i.e., 0.05 – 0.1 m). The resulting $M_{sam,s}$ is 167 kg. The bottom ash BA and recovered aggregates RA (being characterized by a calculated D_{95} of about 2 cm) have intermediate values of S and s, resulting in samples of 45 and 27 kg, respectively. These samples are larger than the usual ones of about 10 kg which are suggested in published sampling plans (Hen-

TABLE 1: Characterization data measured for five waste types and used to calculate masses of samples containing 100 particles "rare in concentration" ($M_{sam,c}$, Equation 2) and "rare in size" ($M_{sam,s}$, Equation 4). Data on Municipal Commercial Waste (MCW) were collected from Khodier et al., (2020), while values for waste of electric and electronic equipment (WEEE), automotive shredder residue (ASR), bottom ashes (BA) and recovered aggregates (RA) were measured by the authors.

		MCW	WEEE	ASR	BA	RA
Characterization Data						
ρ_b	kg m^{-3}	350	150	300	1,250	1,520
ρ_p	kg m^{-3}	1,022	670	877	2,500	2,100
D_{95}	mm	165	95	72	16	16
D_{05}	mm	3.38	38.00	0.03	0.02	0.02
f	-	1	0.06	0.18	1	1
g	-	0.25	0.5	0.25	0.25	0.25
S	(kg/kg)	0.214	0.026	0.003	0.02	0.086
s	kg	1.800	0.004	0.005	0.009	0.023
s/S	kg	8.41	0.15	1.67	0.45	0.27
Calculations of the mass of the representative sample						
$M_{sam,c}$	kg	6,009 (p_c=0.01) 1,502 (p_c=0.04)	902	771	134	113
$M_{sam,s}$	kg	841	15	167	45	27

nebert and Beggio, 2021). The waste of electrical and electronic equipment WEEE shreds have a rare small fraction with a low mass fraction S (0.026 kg/kg) and a low mass of particle s (0.004 kg/particle). This results in a sample of 15 kg (or a volume of about 100 L), significantly higher than what is recommended in the CENELEC CLC/TS 50625-3-1 (CENELEC, 2015).

The estimated total number of particles in the $M_{sam,s}$ for the different wastes was variable (results not shown). Samples of BA and RA, which were characterized by the presence of "fines" (assumed here as particles < 1 mm), have number of particles in the order of magnitude of billions. Further, samples of MCW and ASR residue have particles in the range of millions. Instead, WEEE sample contain just thousands of particles, as a results from the more "homogeneous" granulometry if compared to the size distributions characterizing the other analysed materials (Figure 1).

$M_{sam,s}$ is always lower than $M_{sam,c}$ (Table 1). Two groups can be identified: $M_{sam,c}$ for WEEE is 61 times higher than the corresponding$M_{sam,s}$, while a ratio 2 – 7 can be calculated for the four other materials. Note that this depends on the value of assumed p_c. The two calculated masses could be equal if p_c is increased by the factor $M_{sam,c}$ / $M_{sam,s}$. Excepted for WEEE (as discussed below), the resulting p_c (i.e., multiplied by a 2 – 7 factor) is p_c = 0.08 for MCW and p_c = 0.003 – 0.005 for the other wastes. Where the objective of the analysis is material characterization (as in Khodier et al., 2020), a p_c value of 0.08 means that every material fraction present at a lower percentage (in number of particles) than 0.08 in the lot will occur with a variability greater than 10% in a set of equivalent samples, which could be convenient for a rough characterisation. A p_c value of 0.003 – 0.005 has the same meaning for much rarer fractions, leading then a much more precise characterisation.

The $M_{sam,c}$ / $M_{sam,s}$ ratio's range of 2-7 seems very realistic since the calculated mass of $M_{sam,s}$ has the same order of magnitude than the calculated $M_{sam,c}$. When looking at the number of particles in the samples, the $M_{sam,c}$ contain about 100 to 10,000 more particles than the targeted 100,000 particles (i.e., by assuming a p_c of 0.001 in Equation 1). This could suggest that the conversion of the target number of particles into a mass by using the size of the largest particles D_{95} (Equation 2), even if optimized by the parameters f and g, results in a conservative approach, which is probably unavoidable. In practice, Equation 2 seems to overestimate the mean mass of particles, and this is more evident considering the presence of fines in all tested materials excepted for WEEE. For this latter, characterized by the absence of fines, the two approaches are complementary: 2,000 particles in $M_{sam,s}$ and 100,000 particles for concentration (assuming a p_c of 0.001), because the particles rare in size are in practice not "rare" (i.e., S = 0.214). To equalize the two masses, p_c should be 0.05 that is 50 times higher. That frequency of 0.05 is meaningful in unsorted shreds (for polymers, for metals, for additives), but could result in too high variability for quality assessment and impurity quantification of secondary raw material for the circular economy (Hennebert, 2020).

4.2 Decreasing the mass of the laboratory sample: particles size reduction and sub-sampling

It should be noted that the values for $M_{sam,c}$ in Table 1 are larger than what is recommended in usual sampling plans (Hennebert and Beggio, 2021). Consequently, considering the costs related with collecting and transporting such samples to the laboratory, the values in Table 1 could be estimated as unpracticable by the actors involved in the waste characterization. These calculated samples are large because the value of p_c used for the calculations are assumed conservatively low, as suggested by the European standards on sampling (CEN, 2015, 2006). Again, the method performed to better assess p_c is a key factor in optimizing the mass of a sample: ideally, this could be done

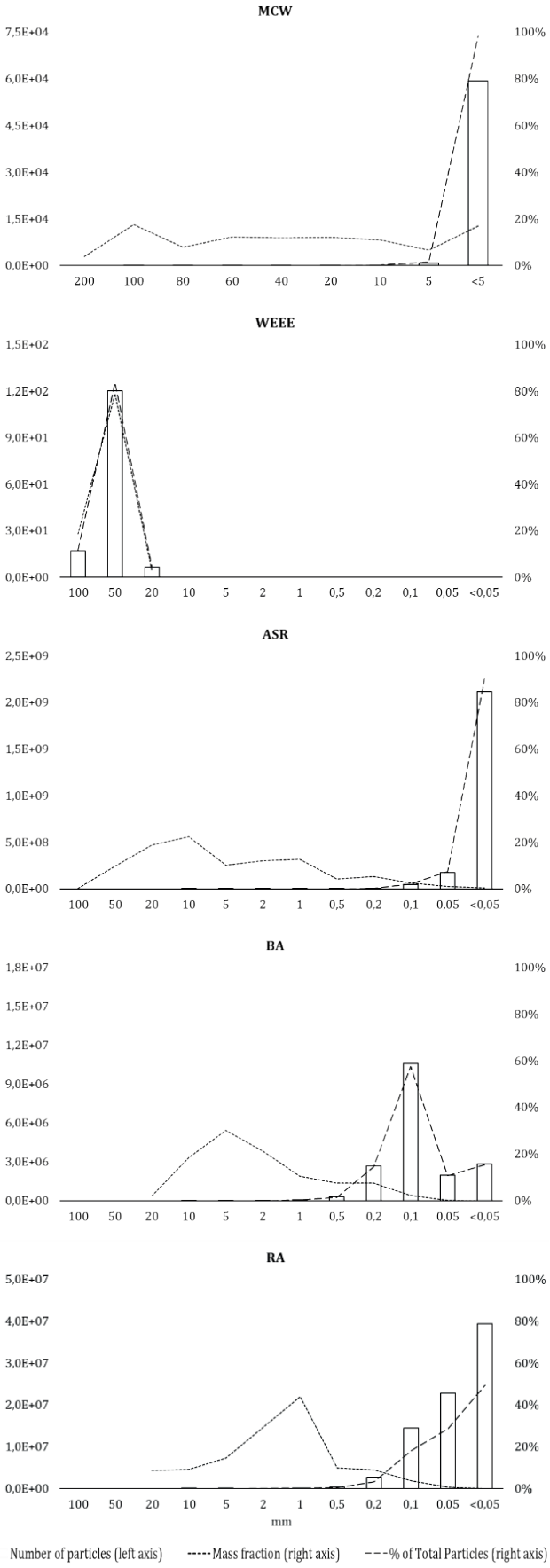

FIGURE 1: Particle sizes distribution for five types of waste, expressed as number of particles per size-class (left axis) and fraction of particles in the size-class on total number of particles (right axis), and in mass (right axis).

by checking the occurrence of the property of interest particle per particle, manually or by automated analyser. However, whether p_c values cannot be estimated more reliably, the solution to reduce the mass of the laboratory sample is on-site particles size reduction and further sub-sampling of the "primary samples" indicated in Table 1.

In practice, the sample masses calculated in Table 1 should be assumed as the minimum values allowing the samples to contain the minimum number of particles as calculated by Equation 1. Smaller samples would be characterized by lower number of particles thus leading to higher variability of repeated analyses on a set of identical samples. In this context, to maintain this variability within the required threshold, smaller samples must contain the same minimum number of particles as the primary samples. This could be done by increasing the number of particles in the primary samples by particles size reduction (i.e., shredding, grinding, cutting or milling according to the physical features of the materials) and sub-sampling (e.g., by riffle splitters or quartering and coning). Ideally, this process allows to achieve a sample size suitable for a laboratory sample characterized by the same p_c of the primary sample (Figure 2). Equivalently, particles size reduction allows to decrease D_{95} together with the mean mass of particles as estimated in Equation 2.

Considering the features of the 5 materials analyzed in this study (Table 1), Table 2 presents the values of particles size $D_{95,r}$, calculated rearranging Equation 2, needed to decrease the $M_{sam,c}$ to 20 kg while maintaining the same values of p_c. Here, $D_{95,r}$ can be reached by applying size reduction to the whole mass of the primary sample. By decreasing the size of particles, the values of g could also vary, as visible in Table 2 for WEEE, where $D_{95,r}$ was calculated assuming g = 1, derived by the fact that $D_{95,r}$ results lower than D_{05} (see Table 1). Furthermore, the smaller particles could be more spherical than their parent particles. Therefore, as the size decreases, f also increases towards 1 as elongated and flat particles are reduced to more compact shapes (cuboids, spheroids).

A typical argument is that reduction of the entire mass of the primary sample can be very expensive and time consuming. However, according to confidential information collected by the authors, frequently waste characterization campaigns must be redone because of the achieved excessive variability between equivalent samples (i.e., "outliers") due to too small laboratory samples and incorrect laboratory preparation. These additional costs would be much higher than those dedicated to the on-site reduction of some hundreds kgs of waste.

Further, one can observe that the large particles are those that will be mostly reduced (USEPA 2002), thus increasing the frequency of particles "rare in concentration". However, taking a sample with the same number of particles, this increase in p_c in the primary sample would just reduce the variability between multiple equivalent samples (Hennebert and Beggio, 2021). A reverse case is observed for malleable and ductile metals (mainly copper and lead particles), which do not fragment under the force of compression, as in a jaw crusher in the case of mineral wastes, or cutting/tearing as in shredder used for mixed wastes(Bunge, 2019). The relative frequency of un-shredded particles will thus decrease together with the increase of the variability. Here, the only solution is to melt in a metallurgical furnace a large quantity of waste (with a melting additive), achieve optimal mixing, then cast a homogeneous ingot, which should be finally drilled or sawed for analysis (Bunge, 2019). This unusual method is used to assess for instance precious metals concentration in waste, with p_c of about 1 per million and consequent nugget effects.

5. CONCLUSIONS

A novel formulation was described to integrate the conventional approach for calculating the size of a waste sample as indicated in the European waste sampling standards. This latter does not consider possible size-content relationships in waste particles making up the lot, which however frequently occurs in waste materials. This gap is easily filled starting from the concept of a minimum number of particles that should be present in a sample to be representative of a waste lot with a controlled variability within repeated samples. As elucidated in a previous paper by the authors, it depends on the proportion of particles "rare in concentration", showing the characteristics to be quantified in the waste lot (the approach of the current European standard) and of those "rare in size", the less represented size-class (the approach proposed by this work). The final number of particles in a sample fulfilling both

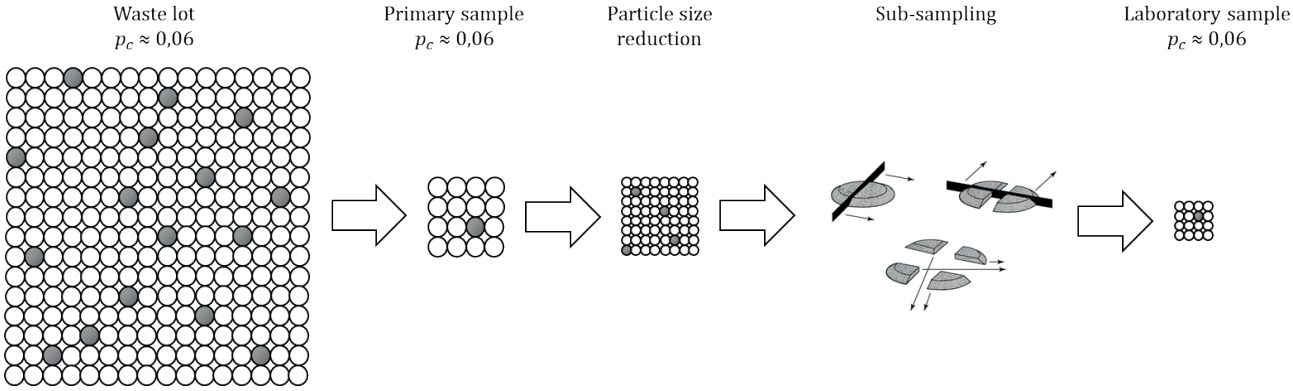

FIGURE 2: Graphical representation of the ideal process for decreasing the size of samples.

TABLE 2: Size of particles to derive a sub-sample of 20 kg from the laboratory (or primary) samples as calculated in Table 1. For each waste type, $D_{95,r}$ are calculated according to Equation 2 by assuming the same p_c of the primary sample in Table 1 and setting $M_{sam,c}$ to 20 kg.

		MCW	WEEE	ASR	BA	RA
$D_{95,r}$	mm	25 (p_c=0.01) 40 (p_c=0.04)	21.00	1.20	0.85	0.90

requirements depends on the rarity of the measurand and size chosen by the sampler to be reliably represented in the sample itself. The conversion of that number of particles in a mass relies on hypothesis on averaged geometry, shape and density of particles, whose estimation could be problematic in heterogeneous waste. To avoid unrealistic assumptions, this paper proposes an alternative approach based on values easily measurable during particle size distribution analysis.

Both formulations were applied on 5 different waste types to derive the mass of the sample to be indicated in dedicated sampling plans. Results showed that the conventional approach agrees well with the new proposition, leading to masses of sample characterized by the same order of magnitude, at least for heterogeneous particle size distributions showing presence of fines (i.e., < 1mm). For more homogeneous particle size distributions (e.g., WEEE), the sample calculated according to the conventional approach resulted one order of magnitude higher, being the proportion of rare particles in concentration far lower than those considered rare in size. The correct assessment of the frequency of particle with the property of interest is therefrom critical. A refined quantification of its value could come from particle per particle analysis. Here, optical online element analysers (eventually coupled to a sorting machine) or material fraction separator on conveyor belt are recommended to quantify a large number of particles and assess it correctly when it is expected to be low (e.g., < 0.01).

When samples masses are calculated and thought as unpractical for management, a representative sample can only be achieved after size reduction in the waste processing facilities. It is easily calculated that a laboratory sample of 20 kg should have a maximum particle size of 10-20 mm to contain 100 000 particles of this size (without considering the fines).

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UNLOCKING THE VALUE OF STOCKPILED MOBILE HANDSETS: A DELPHI EVALUATION OF FACTORS INFLUENCING END OF USE

Xavier Pierron [1,*], Ian D. Williams [2] and Peter J. Shaw [2]

[1] *Edinburgh Napier University, Craiglockhart Campus Collinton Road, Edinburgh EH11 4BN, United Kingdom*
[2] *University of Southampton, Highfield, Campus, Southampton SO17 1BJ, United Kingdom*

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ABSTRACT

Meeting consumers' demands for electrical and electronic equipment (EEE) products in the face of diminishing natural resources necessitates a shift from take-make-dispose to circular economy approaches. Mobile handsets are ubiquitous but only a fraction are returned into the economy at the end; many are locked in consumers' households. These small EEE hold residual value as well as critical resources, such as Rare Earth Elements. Incentives for destockpiling exist but are insufficient to alter long-term end-of-use behaviour. Household recycling behaviour tends to be used as a template for EEE end-of-use. But established explanatory factors for household recycling might not be fully relevant for small electronic devices: their size permits stockpiling, whilst their continued utility can encourage retention as back-up or "safety" devices. This study aimed to elucidate the relevance of factors specific to the nature of small EEE, notably their physical characteristics and working order. A panel of academics and professionals from the global waste and resource management sector was consulted using Delphi methods. The results show that factors commonly applied to foster recycling, such as altruism or pro-environmental behaviour, do not necessarily apply to small EEE. On the other hand, the device's features and working order are critical factors in the end-of-use decision-making process. This study concludes that practical and situational factors should be used to favourably alter decisions for small EEE, including devices' characteristics. In effect, updated situational factors could unlock a global "destockpile lifestyle" to realise full value from the reuse and recycling of small EEE.

1. INTRODUCTION

Global demand for and ownership of electric and electronic products are at unprecedented levels. The COVID-19 pandemic has generated further demand due to requirements for home working and schooling. In 2020, more than 50 million tonnes of such products were placed on the global market (UNEP, 2021). Since 2014 there have been more mobile and smart phones than humans on earth (The Independent, 2014); more than 2 billion mobile/smart phones were shipped in 2020 (IDC, 2021). The ubiquitous distribution of mobile phone handsets contributes to high ownership levels: in 2010, 99% of the 2.4 million students in the United Kingdom (UK) owned at least one mobile handset and average ownership was 1.5 per individual (Ongondo & Williams, 2011a). The replacement of mobile handsets is rapid. Students in higher education, for example, typically replace their mobile handsets within three years of purchase (Ongondo & Williams, 2011b), at which point functionality is often still usually retained.

High levels of ownership and relatively short periods of use lead to the generation of high volumes of end-of-use and end-of-life electrical and electronic equipment (EEE), particularly for mobile handsets. Globally, the production of waste EEE ("e-waste" or "WEEE") is predicted to reach 120 million tonnes by 2050 (UNEP, 2021); WEEE is considered the fastest growing solid waste sector (Oswald & Reller, 2011). The global situation is driven by actions at a discrete scale: when an individual no longer needs or wants an item of EEE such as a mobile handset, there are different potential fates with contrasting impacts and challenges.

In broad terms, an end-of-use or end-of-life mobile handset could be (1) disposed of as waste; (2) recycled as a means to recover materials for the manufacture of new goods, (3) sold or given to another owner and reused; or (4) retained by the owner but no longer used. The fate of such products is related to their physical condition and functionality. In the context of this study, we use the term WEEE to identify end-of-life mobile handsets as opposed to "used EEE" (UEEE) which identifies end-of-use mobile handsets.

* Corresponding author:
Xavier Pierron
email: x.pierron@napier.ac.uk

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For all end-of-use and end-of-life mobile handsets, disposal severely restricts the potential for beneficial outcomes. Potentially recoverable materials within WEEE and UEEE products that are destined for landfill or incineration are lost, failing to re-enter the manufacturing loop, and thereby failing to produce financial or material value (Ongondo & Williams, 2012). The metals, plastics, fire retardants and other contaminants contained within WEEE and UEEE (Bonifazi et al., 2021; Hennebert, 2020) can cause environmental contamination when disposed of to landfill or incinerated (Barba-Gutiérrez et al., 2008). There is scope for considerable improvement in this regard; in 2010 more than 130 million mobile phones were discarded in the US (Electronic Takeback, 2016). In the UK alone, there are 40 million unused electronic devices in working condition (Royal Society of Chemistry, 2019). These millions of unused, and often in working condition devices, represent untapped value. Either in lost opportunities to resell a device in working condition on the secondary market or to recycle unworking devices to harness critical materials such as rare earth elements (Omodara et al., 2019).

Items that are beyond viable repair, in either technical or economic terms, will not have the potential for reuse: mobile handsets of this ilk would be considered end-of-life, i.e. WEEE or e-waste. In this case, the aims and principles of the waste hierarchy (Directive 2008/98/EC) and circular economy (Ellen MacArthur Foundation, 2013) infer that recycling would be preferred to disposal. Achievements in this respect appear poor (Stegmann, 2021). For developed economies, it has been estimated that typically only 10-20% of mobile/smart phones are recycled (Ellen MacArthur Foundation, 2013; US EPA, 2014; Green Alliance, 2015). Small WEEE items (smaller than 25 cm^3; EC Directive 2012/19/EU) are considered one of the least recycled WEEE categories (Bartl et al., 2018; Ellen MacArthur Foundation, 2013). There is potential for recycled mobile handsets to provide large quantities of valuable materials (e.g. Rare Earth Elements [REE]); to achieve this, a high number of discarded devices, each containing small quantities of REE, would have to be collected and the materials therein recovered (Oswald & Reller, 2011; UNEP, 2011; Alamgir et al., 2012). There is obvious merit in increasing efforts to improve WEEE collection rates and recycling technologies, e.g. for REE (Toyota, 2014). At the same time, poorly regulated facilities and processes for recycling WEEE present risks to human health and can lead to environmental contamination (Robinson, 2009; Milovantseva & Saphores, 2013; Awasthi et al., 2018).

Mobile handsets that retain functionality should be considered end-of-use (UEEE) as opposed to end-of-life (WEEE). For UEEE, reuse would be the preferred fate (Directive 2008/98/EC; Ellen MacArthur Foundation, 2013). Recycling mobile handsets that retain utility fails to make full use of the energy and materials used in their production, packaging and delivery to the point of sale, and could be considered premature. Opportunities for reuse include direct sale to individuals or commercial businesses, and donation to individuals or charitable organisations; the latter option is prevalent in the UK but not generally elsewhere.

Retention of UEEE or WEEE by the current owner without continued use is also suboptimal: the ongoing utility of UEEE remains dormant, as do the potentially recoverable materials within WEEE. Storage of end-of-use or end-of-life mobile handsets is facilitated by their relatively small size; several devices may be stored with negligible impact on space within the owner's dwelling. Storage of devices retains resources in hibernation, resulting in continued demand for virgin raw materials for the production of new devices, and associated impacts. Storage appears common and widespread: a decade ago, an estimated 3.7 million mobile handsets were stockpiled by students in higher education in the UK (Ongondo & Williams, 2011b) and an estimated 50-90 million devices have been stockpiled globally (Silveira & Chang, 2010). Indeed, Shittu et al. (2021) reported that 97% of EEE collected from a distinct urban mine in a recent trial was reusable and subsequently donated to charities for sale and reuse.

Environmental, health and resource consequences of UEEE and WEEE are intrinsically linked to consumers' behaviour. The stockpiling or disposal of mobile handsets, in particular, is a lost opportunity for recycling or reuse. The evident loss of mobile handsets to disposal and failure to recirculate stored devices through reuse or recycling suggests that existing models and frameworks intended to support collection systems merit improvement. In this context, improved understanding of those factors influencing consumers' end-of-use or end-of-life behaviour concerning mobile handsets could inform and guide the design of collection systems and incentives, and thereby contribute to the achievement of higher collection rates of WEEE and UEEE, and associated environmental, economic and social benefits.

2. MOTIVATORS OF CONSUMERS' BEHAVIOUR IN RELATION TO WEEE AND UEEE

To consider the potential for improving understanding of those factors influencing consumers' end-of-use or end-of-life behaviour, it is instructive to review received wisdom with regard to motivators of consumers' more general behaviour in the context of waste and resources. Differentiation of influencing factors into "intrinsic" (personal factors) and "extrinsic" (situational factors) (Schultz et al., 1995) provides a framework that provides background and insight to direct efforts for enhancement of end-of-life and end-of-use mobile handset collection.

2.1 Extrinsic motivators and monetary incentives

Extrinsic motivators are illustrated by monetary incentives in the form of either financial penalties (e.g. taxes) or rewards. Willingness-to-pay (WTP) and pay-as-you-throw (PAYT) studies have demonstrated the difficulties in associating monetary incentives with "waste" (Afroz et al., 2013; Le Bozec, 2008; Song et al., 2012; Xu et al., 2018). Given the often low monetary value of residual materials, financial incentives are necessarily low and taxes are unpopular by definition. Other studies, mainly in the United States, have investigated consumers' willingness to pay Advanced Recycling Fees (ARF) to finance WEEE collection schemes

and develop subsidies to incentivise consumers. Nixon and Saphores (2007), for example, found that consumers were willing to pay 1% of the item's retail price on average but this amount is insufficient to create a sustainable collection scheme. Taiwan has attempted to tackle the issue of market-based incentives for packaging containers, which have very little intrinsic monetary value attached to them (Bor et al., 2004). With a complex system of ARF associated with the involvement of local government and subsidies, Bor et al. (2004) suggest developing a specific market for these containers, by creating new rules to influence the behaviour of producers, consumers, and local government. Whilst the ARF approach is laudable, the actual implementation remains to be demonstrated. There are also differences between developed and developing countries regarding intentions and behaviour towards WEEE (Shahrasbi et al., 2021). Consumers in developed economies are more in favour of monetary incentives. Whereas consumers in developed economies feel stronger towards intrinsic incentives related to environmental and social aspects.

Jones et al. (2010) investigated social factors influencing perceptions of willingness to pay based on social capital for household waste (i.e. social trust, institutional trust, social networks, compliance with social norms); participants in this study were willing to pay ca. €0.5 for each waste bag. Specifically for WEEE, a survey in China estimated that 52% of respondents refused to cover a fraction of recycling costs and ⅔ of those respondents willing to pay were prepared to pay up to 5% of the recycling costs (Yin et al., 2013). The higher the monthly income, the more likely respondents were willing to pay; 35% of respondents wanted to pay at the time of purchase, either explicitly as an advanced recycling fee or simply embedded or hidden in the product price; only 11% were willing to pay this fee directly to recyclers (Yin et al., 2013). In Macau, the estimated household average willingness to pay for WEEE recycling is US$ 2.50 per month (Song et al., 2016). There are three possible payment modes for WEEE Advanced Recycling Fees: (1) the cost of participating in a take-back scheme is usually transferred down to consumers (e.g. in the EU); (2) a pre-disposal fee (e.g. in Japan), and (3) a monthly recycling fee for general waste or frequent recyclables (Song et al. 2016). We note that a monthly recycling fee is not relevant for WEEE as its generation is likely episodic rather than persistent (Shaw et al., 2006).

In the UK, Ongondo and Williams (2011a) identified consumers' willingness to increase their WEEE recycling behaviour in response to economic incentives. Even though the existing WEEE legislation offers free take-back schemes, consumers still need to be offered incentives to overcome the associated perceived cost to take back their WEEE (Ongondo & Williams, 2011a). However, when WEEE has little or no residual monetary value, it is not profitable for collection organisations to offer incentives. Furthermore, if EEE still has some residual monetary value, for example when unbroken, consumers can use peer-to-peer (Consumer to Consumer, C2C) websites such as eBay or Amazon Marketplace to resell their unwanted devices. There are also a significant number of for-profit and not-for-profit organisations offering to buy unwanted mobile/smart phones. Online WEEE recycling participation is influenced by consumers' perceived value of monetary incentives and how soon the reward will be triggered (Wang et al., 2021). These studies on WEEE and monetary incentives confirm that monetary rewards have a role, but they are strictly bounded by WEEE secondary monetary value. By essence, this value is decreasing over time, diminishing associated incentives.

Obsolete EEE has limited residual monetary value (Casey et al. 2019). Economic incentives attached to WEEE are necessarily very low as monetary value is estimated on materials, not on potential reuse. Moreover, collection patterns are necessarily different to general waste due to the episodic pattern in which small WEEE and UEEE are generated. Higher monetary incentives for destockpiling of mobile/smart phones exist but for a reuse purpose: if a device is in working order, it still has a monetary value and can be resold, often with little or no need for repair. However, if a device is broken or unusable as is, its estimated value is associated with the value of its secondary material content, which represents only a fraction of the value of working devices (Ongondo & Williams, 2011b). Furthermore, if consumers were satisfied with the resale price for their unwanted and unbroken devices, they would likely use these services more often. Estimates of the refurbished smart phone market differ widely but the numbers of devices are likely to exceed two hundred million (IDC, 2021). Compared with the more than 2 billion units shipped in 2020 and an average 15% recycling rate in developed economies (Ellen McArthur Foundation, 2015), data indicate that many broken and unbroken devices are not being brought back to a collection point.

2.2 Intrinsic motivators

Given the low financial value of end-of-use or end-of-life mobile phones, extrinsic economic incentives appear unlikely to contribute to the collection of unwanted working devices; intrinsic incentives such as environmental or altruistic values are thus more usually considered as a means to enhance collection rates. Intrinsic incentives are more varied than monetary incentives and more complex to define.

The current understanding of incentives for releasing small WEEE or UEEE from stockpiles stems largely from the waste and resources management literature and, more specifically, from household waste recycling studies (Barr and Gilg, 2005; Liu et al., 2019; Nduneseokwu et al., 2017). The factors usually associated with household recycling behaviour include environmental, ethical or altruistic values, and experience in or awareness of recycling schemes. However, the same factors are not necessarily relevant to both household waste recycling and small WEEE such as mobile/smart phones. Echegaray and Hansstein (2017), for example, found that respondents having a positive attitude towards the environment did not necessarily engage in WEEE recycling behaviours.

The intention-behaviour gap is widely acknowledged (Sultan et al., 2020) and has been widely studied (Armitage & Conner, 2001; Echegaray and Hansstein 2017; Wang et al. 2021). Efforts to reduce this gap commonly address

factors that are directly linked to behaviour. In this regard, 'behavioural economics' (the study of emotions and perceptions of decisions) (Kahneman and Tversky, 1984; Thaler, 1980) has the potential to contribute to improving incentives to prevent and exploit existing stockpiles.

In this context, the 'endowment effect', a concept within behavioural economics, is pertinent: this concept evaluates the influence of ownership on value evaluations from individuals: "People typically demand more to relinquish the goods they own than they would be willing to pay to acquire these goods" (Morewedge et al., 2009:947). The endowment effect is influenced by the 'status quo bias' (Samuelson & Zeckhauser, 1988) and 'loss aversion' (Kahneman & Tversky, 1984). Individuals tend to prefer remaining in a status quo situation rather than engaging in a transaction with the possibility of losing some attributes associated with owning an object. For example, someone parting from their small WEEE in working order might regret the decision at a later stage but will not be able to reverse it.

2.3 Research aim

This study aims to bring together perspectives in relation to end-of-use/life behaviours and their role in the prevention and exploitation of existing stockpiles of small WEEE and UEEE, with a focus on mobile and smart phones. We aim to evaluate and propose a set of factors that are pertinent to investigation of small WEEE and UEEE end-of-use/life decisions and that present opportunities for enhancement of collection of small WEEE and UEEE for recycling or reuse.

3. METHODOLOGY

To explore and evaluate end-of-use/life behavioural factors in relation to mobile/smart phones, waste and resources management academics and practitioners from around the world were consulted. A list of candidate factors from the literature was compiled and consultees were asked to determine which of these factors were the most relevant for small smart and mobile phones. Online Delphi was used to gather consultee panel input across a large geographical area and to minimize bias induced by other respondents' input.

3.1 Delphi methods

Qualitative data can be accurately generated with Delphi methods (Hsu & Sandford, 2007). It is a consensus-building process developed for the Research And Development (RAND) Corporation in California, USA by Dalkey and Helmer (1963) designed to elicit an expert opinion. Several waste management studies have used this method (Bouzon et al., 2016; Raut et al., 2016) but only one specifically with WEEE (Kim et al., 2013). Panel members are invited to take part in a data collection process involving at least two rounds. Rounds are used to establish consensus iteratively. Data can be collected via interviews, open or semi-open questionnaires or Likert scales to rank factors (Hsu and Sanford, 2007). To avoid groupthink and potential influences in responses, panel members are not aware of others' presence. After a completed round, the information generated by consensus is shared with all panel members. This information is then used by the researcher to elaborate on subsequent rounds. Data collection stops once consensus on the overall aims is achieved. Cut-off points are established by the research team to determine an anticipated level of consensus (Hsu and Sanford, 2007). A limitation of Delphi data collections is the time-consuming process for the panel to convene at certain points in time and the time required for the research team to process the data. However, relevant technology can be used to limit this drawback.

Online questionnaires are regularly used to gather expert opinions in a Delphi setting (Gijsbers et al., 2016; Steinert, 2009; Yeh & Cheng, 2015). Data to be collected are structured by the researcher within web-based survey tools (Gill et al., 2013). Usually, Likert scales are used to rank factors and open / semi-open questions are included to enrich the data collected. This approach reduces survey administration time, enhances opportunities for data analysis, reduces errors and removes physical barriers to participation (Bloor et al., 2015). However, online Delphi has limitations (Donohoe et al., 2012). Some panel members might not have access to the Internet. Hardware or a web-based survey tool could fail and data could be lost. Data collection needs to be scheduled within appropriate time frames as would be done for a physical, onsite data collection event. It also cannot be ensured that invited respondents are those completing the questionnaire; this issue can be mitigated by sending individualised links to respondents. Web-based methods attenuate time-consuming issues associated with other established Delphi methods and, if appropriately selected and designed, can enrich the value of the data collected by using innovative methods associated with decision science.

3.2 Sampling

Using convenience sampling, two hundred and five waste and resource management practitioners as well as researchers from academia, government agencies and the private sector were selected. The potential panel members were part of the co-authors' professional network and were contacted via email inviting them to the study with a personalised message. The potential bias was compounded by the very Delphi method itself: the panel members did not know who were the other participants. The prospective sample had experience and knowledge in WEEE as this segment is an integral part of waste management concerns since so much WEEE fails to be recycled. In 2018, 38.5% of WEEE was landfilled in the European Union (European Commission, 2019). The behavioural aspects of the study did not require any expertise in behavioural science. The questions were related to end-of-use intentions (Table 1) and these results were analysed by the researchers from a behavioural perspective. The prospective panel members were from Western Europe: Germany, Belgium, France, Portugal, Ireland, Austria and the UK. They were presented with the two-round data collection process and invited to take part in the study. Participants were incentivised to engage by accessing early data between rounds one and two. Only members who had participated in round one were invited

TABLE 1: Summary of factors investigated stemming from waste management and behavioural economics literature.

Category	Factors	Source reference
Norms and attitudes	Lack of social pressure	Barr et al. (2001)
	Lack of ethical values	Chan and Bishop (2013)
	Lack of environmental values	Barr et al. (2001)
	Lack of altruistic values	Shaw (2008)
	Lack of positive attitude towards recycling	Thogersen (1994)
Experience and self-efficacy	Limited experience	Barr et al. (2001)
	Complex process	Harder and Woodward (2007)
	Limited awareness	Gutierrez et al. (2010)
Convenience and time	Inconvenient process	Chan and Bishop (2013)
	Time in storage	Gutierrez et al. (2010)
	Time consuming / saving	Saphores et al. (2009)
	Immediate decision	Gutierrez et al. (2010)
	Delayed decision	Gutierrez et al. (2010)
Device characteristics and status	Small size	Perez-Bellis (2015)
	Unbroken device	Barr et al. (2013)
	Quantity in storage	Karim Ghani et al. (2013)
	Device obsolescence	Gottberg et al. (2006)
Behavioural economics	Utility	Thaler and Sustein (2008)
	Regret felt	Tversky and Kahneman (1992)
	Emotional loss	Johnson et al. (2012)
	Lack of positive emotional reward	Carrus et al. (2008)
	Irreversible decision	Ramani and Richard (1993)

to take part in round two. Both rounds took place between February and June 2015.

3.3 Survey design and piloting

Both rounds were piloted among academic and research colleagues with experience and expertise relating to waste and resource management; ten individuals assisted in piloting round one and five for round two. The entire Delphi was administered online. Round one questions were divided into four themes: resell, reuse, recycle and discard; questions were presented in this order to respondents. Factors investigated were selected from the waste management and behavioural economics literature as well as factors related to mobile and smart phone characteristics (Table 1). For example, factors relating to behavioural economics - such as emotional loss, irreversibility of decision, device utility - were included. All categories of questions included characteristics potentially influencing end-of-use/life decisions, such as device size (convenience of storage), time in storage and device obsolescence. For recycling and discarding decisions, environmental values, altruistic values and ethical considerations were presented to panel members (Table 1).

Aspects specific to each category were then investigated, e.g. limited experience or awareness of reselling processes, emotional rewards for giving away a mobile or smart phone, recycling decisions and device status, or convenience of discarding methods. Respondents were also able to make free-text comments. In total, 69 factors were scored by each panel member in round one: 18 for “resell”, 9 for “reuse”, 23 for “recycling” and 19 for “discarding”. For closed questions, a 5-point Likert scale that ran from “strongly agree” to “strongly disagree” was used. During the second round, the PAPRIKA methodology was used (Potentially All Pairwise RanKings of all Alternatives; Hansen & Ombler, 2008), which presents respondents with pairs that are undominated and ranks automatically pairs that are strictly dominated, following transitivity principles (if A>B and B>C, then A>C), which results in fewer decisions for Delphi panel members (Hansen & Ombler, 2008). PAPRIKA derives from the Analytic Hierarchy Process (AHP; Saaty, 1982), a widely-used methodology to organise complex decisions but which results in more decisions (Hansen & Ombler, 2008).

With AHP, three criteria with four alternatives require 64 decisions in total by each panel member (4 x 4 x 4). By comparison, PAPRIKA requires 32 decisions, as the method only presents undominated pairs requiring a decision. To achieve this efficiency PAPRIKA requires criteria to be ranked before data collection. Respondents are presented with pairs that are undominated and the software ranks automatically pairs that are strictly dominated (Hansen and Ombler, 2008). PAPRIKA offers a more natural decision-making process than AHP. Instead of using 10-point Likert scales, panel members are presented with pairs of alternatives and select which pair dominates, or if they are equal. PAPRIKA is a proven methodology that has been used in several studies (Martin-Collado et al.,

2015; Nielsen et al., 2014; Smith et al., 2014) and has been made widely available to academics for dissemination (Table 2).

3.4 Procedure and ethical considerations

Participants were given four weeks for each round and a reminder was sent after two weeks. The participant information sheet at the beginning of the survey informed potential participants the survey would require approximately 20 minutes of their time; that they could resume at any time; that all results would be anonymous; and they could withdraw at any time without prior consent. Prospective participants were all informed that by entering the survey they were registering their informed consent.

3.5 Data analysis

Once round one data collection was completed, relevant and non-relevant factors were separated using the Content Validity Ratio (CVR) formula (Lawshe, 1975), according to aggregated Likert scores. This analysis formed the basis for structuring round two of the Delphi survey. A positive CVR value indicated that at least half the panel members were in agreement or in strong agreement with any statement made in the survey. Following Lawshe's (1975) recommendations for panel members above 40, the cut-off point was set at a CVR value of 0.29. Kim et al. (2013), in their Delphi-AHP survey for selecting e-waste priorities, used the same method and cut-off value. The objective of round two was to weigh the importance of factor categories during mobile and smart phone end-of-use decision-making process by comparing them against one another. Following Hansen and Ombler's (2008) PAPRIKA method, factors were ranked according to their Likert scale scores.

4. RESULTS

4.1 Participation in the Delphi survey

Of the two hundred and five participants who were invited to take part in the Delphi study, 103 participants accessed the first round survey and 77 completed both rounds. To be valid, a Delphi data collection requires at least ten panel members (Hsu and Sanford, 2007). Out of all the waste and resources management researchers and practitioners, 39% were from the private sector, 33% from academia and 28% from dedicated government agencies. Most of the panel members came from Western Europe (Table 3). Of these respondents, 44 subsequently completed round two. Response rates were thus 38% and 57% for round one and round two respectively. More than half of respondents had more than ten years of experience in the field of waste and resource management and more than three quarters had more than five years of experience (Table 4).

4.2 Delphi round 1

Based on round one of the Delphi survey, participants cumulatively identified which of the factors extracted from the literature (Table 1) they considered to be relevant to end-of-use/life decisions in relation to mobile/smart phones. Responses received in the first round of the Delphi survey indicated that none of the five factors relating to "norms and attitudes" were considered relevant by the participant group (Table 5). Two of the three factors pertaining to "experience and efficacy" were deemed relevant in this context (Table 5); limitations with regard to reselling were highlighted. Although five factors relating to "convenience and time" were presented, only the time consumed in end-of-life/use actions was considered relevant by the participant group (Table 5). In contrast, several factors relating to "device characteristics and storage" were considered relevant in this context; size, time in storage and utility status were highlighted (Table 5). With regard to the five "behavioural economics" factors, only utility was deemed relevant (Table 5).

4.3 Delphi round 2

The second Delphi round provided an outcome in the form of factors ranked by their importance concerning end-of-use/life decisions for mobile/smart phones (Table 4); ranking was determined using the PAPRIKA method (Hansen and Ombler, 2008). Second round Delphi outcomes were clustered into: (1) factors favouring discarding, (2) factors preventing recycling, and (3) factors preventing reuse (Table 6).

TABLE 2: Decision example for the PAPRIKA method (Hansen & Ombler, 2008).

Decision		
Factors preventing recycling / Device has still utility for the user	> or < or =	**Factors preventing recycling** / Device stored for a significant amount of time
Factors favouring discarding / Time-saving process		**Factors favouring discarding** / Several devices have been stockpiled

TABLE 3: Round 1 panel members' origins (N=103).

Panel members' origin	Proportion
UK	37%
Germany	22%
Belgium	16%
Austria	7%
Portugal	4%
Finland	4%
Ireland	3%
Other	7%

TABLE 4: Round 1 panel members' experience in waste and resources management (N=77).

Round 1 panel members' experience	Proportion
None	3%
1-3 years	3%
3-5 years	16%
5-10 years	23%
>10 years	55%

TABLE 5: Factors identified by Delphi (Round 1) participants as being relevant in end-of-use/life decisions in relation to mobile/smart phones.

Category	Relevant factors identified
Norms and attitudes	None
Experience and self-efficacy	Limited experience in reselling electronic items Limited awareness of reselling opportunities or recycling processes
Convenience and time	Time-consuming
Device characteristics and status	Small product size allows for multiple items to be stockpiled Long time in storage induces a discarding decision Unbroken status prevents recycling decision
Behavioural economics	Low utility for item

TABLE 6: Factors influencing end-of-use/life behaviours for mobile/smart phones. Influencing factors within each cluster are ranked in decreasing order of importance as determined in the Delphi second round applying the PAPRIKA analysis (Hansen and Ombler, 2008).

Cluster	Influencing factors
Factors favouring discarding	1. Discarding is a time-saving/convenient action
	2. Several devices are stockpiled
	3. Device utility is close to zero
	4. Device has been stored for a significant time
Factors preventing recycling	1. Device has been stored for a significant time
	2. Device is not broken
	3. Device retains some utility for the user
	4. Awareness of recycling schemes is limited
Factors preventing reuse/resell	1. Device size allows convenient storage
	2. Reselling is a time-consuming process
	3. Experience in reselling is limited

5. DISCUSSION

The key outcomes of the two Delphi rounds (Table 6) identify, in ranked order, those factors most likely to influence consumers' end-of-use/life decisions regarding mobile/smart phones. These influencing factors are evaluated with previously reported recycling and reuse/resell behaviours.

5.1 Factors favouring discarding

One of the most prominent outcomes from the Delphi survey suggests that discarding is a convenient approach, usually undertaken to destockpile several unused devices, and that the utility for the unused devices is negligible (Table 6). This is in line with several previous WEEE studies.

Wagner et al. (2013) defined 'convenience' according to five main attributes: knowledge of collection system, proximity of collection points, opportunity to engage in the activity, attraction of collection site or method, ease of process. Ongondo and Williams (2011b) support the aspects related to ease of use and identification of collection points, as well as their proximity to points of consumer traffic such as in libraries, banks, or shopping malls. Bouvier and Wagner (2011:1058) advocate a "concerted approach to reduce inconvenience" but the multiplicity of factors and actors required to reduce inconvenience is hard to tackle.

Their small size, frequent replacement cycles and the low numbers of phones reused and recycled imply that more than one device tends to be stockpiled by users (Table 6). This aspect aligns with observations by Ongondo and Williams (2011) who found that 59% of students surveyed stockpiled at least one mobile device; an estimated 3.7 million devices were stockpiled by 2.4 million students in UK higher education in 2011. Several stockpiled devices increase the burden they represent for consumers. An additional phone might serve as a backup but stockpiling at least two additional devices implies excess and redundancy. These unnecessarily stockpiled phones have a high likelihood of being disposed of in general refuse (Gutierrez et al., 2010). Unused stockpiled phones, when stored for a significant time, would more likely be obsolescent, depreciate in value as well as utility.

Unbroken phones tend not to be recycled thereby increasing the number of stockpiled phones (Table 6). When a device is unbroken it has more value as a usable handset, compared with a phone destroyed to retrieve the secondary market value of its components. Ongondo and Williams (2011) estimated that 59% of students replaced their phones because they were broken. Consumers' behaviour is highly influenced by changes in the mobile and smart phone sector in terms of shifts in demand and product preferences. In 2011 Nokia was the global mobile phone market leader with 27% market share and smart phones were barely emerging; Apple had a 3.5% market share at this time (Statista, 2020). At present, Apple and Samsung release flagship models frequently during much-publicised global events largely anticipated by consumers and technology specialists (CES, 2020). In 2019, 1.7 billion smart phones were shipped from factories (IDC, 2020). Whilst the estimated average life span of a mobile phone is significantly longer than smart phones, smart phone shipments exceeded mobile phone shipments in 2013 and the trend is not set to be inverted as consumers use them to "remote control their life" (Economist, 2016). Large manufacturers invest substantial resources in design and performance. These rapid improvements render smart phones released a couple of years ago obsolete and not fit-for-purpose. These factors support the claim that, even though limited data are available on the number of unbroken smart phones, stockpiled mobile devices tend to be unbroken, compared with a trend observed relatively recently by Ongondo and Williams (2011a).

5.2 Factors preventing recycling

Panel members indicated that factors preventing recycling were mostly influenced by the duration the stockpiled mobile device had been left unused, the device's working order status, the residual utility users might have for the device, and the limited awareness some users might have of recycling schemes (Table 6). End-of-use mobile or smart phones, as opposed to end-of-life devices, still have remaining utility and are not considered as waste by consumers (Table 6). These devices at the end of their useful life are stockpiled for potential future use, as a back-up or spare (Ongondo and Williams, 2011b). However, the longer these devices are stockpiled, the more likely they are destined for general refuse as opposed to being recycled (Gutierrez et al., 2010). When devices are collected by take-back schemes, if they are in working order they will likely be reused; if not they will be recycled (Table 6). Recycling is a destructive activity and devices with a residual utility will be stockpiled for a probable future usage. Despite the incentives offered by take-back schemes (Ongondo and Williams, 2011b), such as an offer close to the market valuation or free postage for phones with no monetary value left, users tend not to use such schemes. Ongondo and Williams (2011b) estimated that a majority of online mobile phone take-back schemes are convenient to use but, for students in higher education, usually lack a physical collection point next to high consumer traffic areas such as shopping malls, libraries or campuses.

5.3 Factors preventing reuse and reselling

Among the factors preventing reuse, the device size and the perception of reuse being a time-consuming activity appeared as significant barriers (Table 6). The size aspect connects with the earlier factors favouring discarding as several devices can be stockpiled (§5.1). The small size of mobile and smart phones makes them an ubiquitous item used every day, but when these devices reach their end-of-use/life, they can be stored without any marked impact on storage space (§5.2). This underlines the importance of the device characteristics in the decision-making process. New smart phone prices decline rapidly (Compare and Recyle, 2021). In November 2017 Apple's flagship device, the iPhone X, entered the market but within 3 years its value had halved. There appear to be no studies yet evaluating users' perceptions of second-hand prices. However, we suggest that some consumers might prefer not reselling at a price they believe is significantly lower than their expectation or perhaps considered unfair.

Panel members believe that limited experience of reuse processes has an impact on stockpiling (Table 6). However, experience in mobile and smart phone reuse is increasing. Global smart phone manufacturers now offer refurbished devices alongside new product sales. Van Weelden et al. (2016) argued that designers and marketers should take the lead to change consumer perceptions concerning refurbished mobile phones. The more users are exposed to reuse schemes and hear positive experiences from close friends or relatives or via social media, the more likely they engage with reuse. Stromberg et al. (2016) recommended that trials are necessary to trigger an intended behaviour.

5.4 Overview and recommendations

To fully understand the barriers preventing the collection of UEEE, factors stemming from behavioural studies, such as norms and attitudes or experience and self-efficacy or utility, as well as factors associated with the device characteristics, must be considered. This study finds that new sets of situational factors are required to facilitate desired end-of-use behaviours that enable enhanced resource efficiency for small WEEE and UEEE.

5.4.1 Norms and attitudes

The factors usually investigated infer barriers that are inherent to a lack of values (ethical, environmental, altruistic), lack of social pressure, or lack of positive attitudes towards recycling (Barr et al., 2001; Chan and Bishop, 2013; Shaw and Maynard, 2008; Thogersen, 1996). These studies are mostly aimed at household recycling behaviour and rarely directed towards WEEE or UEEE (e.g. Le Hoang, 2013). Data collected from waste and resources management practitioners and scholars indicate these factors are not relevant when investigating end-of-use decisions or small WEEE and UEEE (Table 6). Echagaray & Hansstein (2017) support the view that household recycling behaviour does not necessarily translate into a similar behaviour for small WEEE and UEEE. The very nature of electronic items, particularly when they retain some form of functionality, may not be considered as "waste" per se.

5.4.2 Experience and self-efficacy, convenience and time

The Delphi panel indicated that a lack of experience and awareness might be contributing factors to small WEEE and UEEE stockpiling decisions (Table 6). This aspect is supported by Barr et al. (2001), Harder and Woodward (2007) and Gutierrez et al. (2010). Lack of practice might hinder a willingness to dispose safely of small end-of-use/life EEE that might still be in working order. The prospect of the necessary process(es) might dissuade users to engage and simply prefer to keep it in a bottom drawer, in effect stockpiling it, perhaps for future use. This aspect is supported by the Delphi panel outcomes indicating that time and convenience are factors that can influence end-of-use/life behaviour (Table 6; Chan and Bishop, 2013; Gutierrez et al., 2010; Saphores et al., 2009).

5.4.3 Device characteristics and status

Several elements taken from the literature were corroborated by the panel members (Table 2; Perez-Bellis, 2015; Barr et al., 2013; Gottberg et al., 2006; Karim Ghani et al., 2013). The size of mobile/smart phones and their working/non-working status are factors that have a strong influence on stockpiling decisions and can be grouped with factors associated with convenience and time. The effect of time on ultimate end-of-use/life decisions is of particular concern (Table 6; Gutierrez et al., 2010). At some point in time, some users will prefer to dispose of their small WEEE or UEEE with general refuse because it has lost its utility and/or is no longer desirable as a possession.

To increase small UEEE and WEEE collection rates, the barriers should be understood to be specifically addressed. Overall, it appears that factors preventing small UEEE and WEEE to be reinserted into the economy, either by reusing, reselling or recycling them, seem to be more closely aligned with the device's characteristics and the utility users have for the device, in addition to factors already acknowledged by the literature (i.e. convenience, awareness and experience). We conclude that (1) factors relating to device characteristics and utility influence end-of-use/life decisions for small UEEE and WEEE, and (2) initiatives to enhance destockpiling of small UEEE and WEEE should therefore recognise and incorporate device-specific characteristics and utility. We recommend that efforts to improve used small UEEE and WEEE collections rates should not overly rely on factors established to be relevant to household recycling behaviour.

6. CONCLUSIONS

This study has successfully revealed the key behavioural factors relating to end-of-use/life mobile/smart phones. A better understanding of the barriers to recycling, reusing and reselling can help to enhance the design of incentives and policies to increase collection rates, effectively unlocking a global "destockpile lifestyle" to realise full value from the reuse and recycling of small UEEE and WEEE. By circulating more UEEE and WEEE devices back into the economy, positive impacts on resources consumption and reduction of environmental impacts will ensue. Insights from global experts in the waste and resources management sector have challenged established views about consumers' end-of-use/life behaviour relating to smart and mobile phones. Factors such as altruism or pro-environmentalism appear to be relatively weak as determinants of end-of-use/life behaviour for smart and mobile phones, but extrinsic, situational factors such as convenience, utility or phone working/non-working status need to be considered with initiatives to enhance small UEEE and WEEE collection rates. The importance of these factors highlights the need to design incentives and policies adapted to specific types of UEEE and WEEE. Applying frameworks stemming from the study of household recycling behaviour appears to be inappropriate when considering smart and mobile phone devices in working order and for which users still have some potential utility. This finding probably applies to other small similar personal and household items. Future research could quantitatively measure the influence these factors have on small UEEE and WEEE stockpiling levels.

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CEMENT COMPOSITES WITH WASTE INCORPORATION UNDER ACID RAIN ATTACK

Adriana Estokova *, Robert Figmig and Nikola Galanova

Technical University of Košice, Faculty of Civil Engineering, Vysokoskolska 4, Kosice 042 00, Slovakia

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Fly ash

ABSTRACT

The paper is aimed at the study of the resistance of cement pastes containing various secondary materials (fly ash, zeolite, zeoslag, slag and microsilica) in the model environment of acid rain. Changes in characteristics of the studied materials due to acid rain, such as compressive strength of cement composites, water absorption, penetration of aggressive ions, pH of material and its chemical composition were analysed. Model acidic environments represented solutions simulating acid rain with different pH values (2, 4 and 6). Natural acid rain, deionized water and saturated solution of $Ca(OH)_2$ were used as reference media. Based on the experimental findings, it can be stated that a positive effect of the secondary materials on increasing the resistance of cement pastes has been proven. The cement pastes with added additives resulted in a significant reduction in permeability in each model environment. This fact has an impact on the overall durability due to the fact that the amount of aggressive ions in the internal structure is reduced, causing corrosion and subsequent deterioration of cement composites. Based on the innovative methodology for the ion-penetration test of cement pastes, a coefficient was designed, which characterizes the effect of the used admixture in terms of pozzolanic resp. latent hydraulic activities. Based on this coefficient, the most significant positive effect was manifested by the use of an admixture of ash and zeolite. The rapid chloride penetration (RCP) test method has thus proved to be much more relevant in comparison with, for example, water absorption.

1. INTRODUCTION

Construction is one of the sectors that contributes significantly to the pollution of the environment in which we live (IPPC 2007). In addition to the production of high emissions of greenhouse and acidifying gases, the depletion of raw material resources and the generation of waste are also associated with this sector (Megdal 2018, Asif et al. 2007). One of the ways to reduce the mentioned negative environmental impacts and apply the principles of sustainability in construction is to try to extend the life of structures and buildings by increasing the durability of building materials (Pietrucha-Urbanik et al. 2019). Acid rain, which is caused by heavy air pollution, is currently a pretty big problem not only for people, but also for the materials that this rain affects. Therefore, it is especially important to pay attention to what material is used to withstand this effect.

The problem of acid corrosion has been addressed by several authors, paying particular attention to laboratory experiments where the effects of acid rain on cement composites were studied by immersion tank or spray tests using laboratory-prepared acid solutions simulating natural acid rain. Zeng et al. (2020) investigated the effect of acid rain on emulsified cement-asphalt mortar, which is used in China as a basic building block in railway construction. Zhihong (2017) et al. studied the deterioration of strength characteristics of concrete composites, based on ordinary Portland cement, due to the action of a simulated acid rain solution with different pH values (1.5, 2.5 and 3.5). The results showed that the action of acid rain caused surface disturbance and gradual crushing of concrete materials. Other authors (Shaodong Xie et al. 2004, Fan et al. 2010) dealt mainly with the confirmation of the positive effects of various pozzolanic admixtures on increasing the resistance of cement composites to acid rain using accelerated laboratory tests. The authors found that cement composites with slag cement and fly ash were more resistant than composites with ordinary Portland cement due to changes in compressive strength values. In addition, the experimental results showed that the corrosion rate was higher when soaking the samples compared to spraying the acidic solution. The rate of weight loss increased gradually with increasing immersion time of the sample. The changes were more significant for samples exposed to pH 1.5 solutions

* Corresponding author:
Adriana Estokova
email: adriana.estokova@tuke.sk

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than for samples in pH 2.5 and 3.5 solutions. The influence of nanosilicates, as another mineral admixture, on the properties of cementitious materials under acid rain conditions was studied in (Mahdikhani, 2018). The nanosilicates proved their positive effects on the mechanical properties and durability of concrete samples. The attention was paid also on monitoring the effects of acid rain on the filler component of concrete. Caifeng Lu et al. (2020) dealt with changes in the mechanical properties of recycled aggregate concretes due to acid rain. The authors confirmed that the appropriate addition of fly ash and silica fume increased strength and resistance to acid rain, while higher replacement of recycled aggregates appeared to be unfavourable as these samples were less resistant to acid rain.

The main objective of this work was to compare the resistance of cement pastes containing waste and mineral admixtures of fly ash, zeolite, zeoslag, slag and microsilica in order to increase their resistance in the model environment of acid rain. The novelty of the work was in applying the ion-penetration test to assess the durability of particular pastes based on the new proposed permeability reduction coefficient.

2. MATERIALS AND METHODS

2.1 Pastes with secondary materials

For the study of acid rain attack, 5 different types of cement pastes were produced. The ordinary Portland cement CEM I 42.5 R (CRH, Turňa nad Bodvou, Slovakia) was used in the pastes and part of the cement was replaced by secondary raw materials and wastes, which are recommended as a measure to increase the resistance of composites in acidic environments. The chemical composition of cement and individual secondary materials, studied by XRF analysis, are given in Table 1. The specific densities of materials were as followed: 3050, 2440, 2900, 2200, and 2800 kg/m^3 for cement, zeolite, zeoslag, microsilica, and fly ash, respectively. The sizes of materials, represented by the average grain, were in the interval 15.1 to 36.3 micrometers.

Microsilica and zeolite as pozzolanic materials have a significantly higher proportion of SiO_2 than CaO, while zeoslag with a predominant amount of blast furnace slag has a high CaO content.

In particular cement pastes samples, a 15% of cement was substituted by zeolite (Zeocem, Bystré, Slovakia), microsilica (Mapeplast, Mapei, Slovakia), combination of zeolite and slag (Zeobau 50 - 80% slag and 20% zeolite) and fly ash (TEKO, Košice, Slovakia) – Table 2. The recipes of the cement samples were set to the water-to-binder ratio (w/b) of 0.45 as required per the extremely aggressive acidic environment (XA3 class) according to the standard EN 206-1 (2013, 2021).

Cement pastes were prepared in the form of cubes (40 × 40 × 40) mm and beams with dimensions of 40 × 40 × 160 mm. Reference samples were made in two ways, where C0 was the very first setting target. C0 was made with a hand mixer and the sample, marked C1, was made in a standard mixer. Materials were slowly mixed for 150 s, and after 60-second pause, the mixing was continued for another 150-second period. The cement material was put into the molds, vibrated for 5 s and covered by impermeable foil to prevent specimen from drying out. After demoulding, the

TABLE 1: XRF analysis of materials.

	Concentration of the elements expressed in oxide form (wt. %)				
Oxides	**Cement**	**Microsilica**	**Zeolite**	**Fly ash**	**Zeoslag**
MgO	1.19	1.07	1.18	2.64	8.32
Al_2O_3	4.14	0.36	14.14	21.38	9.49
SiO_2	20.37	92.46	71.96	44.00	45.55
P_2O_5	0.50	0.05	0.05	0.28	0.04
SO_3	6.96	0.07	0.01	0.23	0.46
Cl	0.11	0.14	0	0	0.02
K_2O	1.10	0.99	2.27	2.13	0.84
CaO	61.88	0.27	3.16	5.89	32.27
TiO_2	0.22	-	0.51	1.90	0.40
MnO	0.04	0.58	0.03	0.14	0.59
Fe_2O_3	2.67	1.24	3.61	12.35	1.15

TABLE 2: Cement pastes composition and labeling.

Cement paste sample	**Labelling**	**Cement content (g)**	**Water content (g)**	**Secondary material (g)**	**w/b**
Reference sample	C0, C1	3850	1732.5	-	0.45
Paste with zeolite	Z	3272.5	1732.5	577.5	0.45
Paste with microsilica	MS	3272.5	1732.5	577.5	0.45
Paste with zeoslag	ZS	3272.5	1732.5	577.5	0.45
Paste with fly ash	P	3272.5	1732.5	577.5	0.45

samples were cured in $Ca(OH)_2$ solution for 28 days and then each sample was labelled, dried to constant weight and its final weight was recorded. The saturated solution of $Ca(OH)_2$ was used to avoid the process of leaching of portlandite during the curing period of the samples.

2.2 Model experiment of acidic corrosion

The corrosion resistance experiment on cement pastes was performed as a tank test through immersing the samples in model acidic media (Table 3), over a period of 5 months whereas the pH of the liquid phases was regularly adjusted to baseline. The volume of the test medium was calculated as ten times the volume of the cement sample. The samples were immersed in plastic containers covered with lids.

6 types of model environments with different pH values were designed, which represented different acidity of the environment as well as a reference alkaline environment. A saturated solution of calcium hydroxide ($Ca(OH)_2$) was chosen as reference medium, where the process of leaching or acid corrosion was not expected. The local natural rain was collected during the period of two weeks in plastic container. Laboratory solutions of model acid rain were prepared by mixing of corresponding solutions of 93% sulphuric acid and 65% nitric acid in a ratio of 6:4 to resemble the basic composition of acid rain as much as possible (Zabawi 2008). The action of ions other than sulphates and nitrates present in natural rain has not been studied.

2.3 Analytical procedures

Several parameters were studied on cement composites before and after the experiments: bulk density of samples, changes in weight and water absorption, penetration of aggressive ions, compressive strength tests, and the pH of the cement pastes and corrosive media. The results of the parameters tested are presented as an average of two measurements.

Consistency of fresh pastes was investigated according to EN 1015-3 (2007), where the average value of the cake formed was measured in time of 5 minutes after first contact of binder and water (zero time) on Haegerman table and then after 25 strikes.

Two methods were used to determine the bulk density. Water immersion measurement using cylinder with an aspect ratio of 1: 2 was used for fresh cement paste. For hardened paste before the compressive strength test, dimensional determination based on dimensions was used.

TABLE 3: Model solutions.

Medium	Labelling	pH
$Ca(OH)_2$	CH	12.5
Deionized water	DV	7.0
Natural acid rain	NR	6.5
Model acid rain – extremely aggressive environments	MAR2	2
Model acid rain – aggressive environments	MAR4	4
Model acid rain – slightly aggressive environments	MAR6	6

Water absorption was determined on the basis of the masses of the dry and wet cement pastes samples (see expression 1), which were weighed on analytical balances (Radwag), with an accuracy of 3 decimal places. The cement pastes were dried in laboratory oven at temperature of 105±5°C to constant mass.

$$WA = \frac{m_w - m_d}{m_d} \cdot 100 \quad (1)$$

where,
m_d –mass of dry sample (g);
m_w – mass of wet sample (g);
WA – water absorption (%).

To compare the permeability of cement pastes, the rapid chloride penetration test (RCP test) was performed, according to ASTM C1202-19. The test is based on measuring the penetration of chloride ions through the material. For each type of cement paste, two samples were tested in order to obtain a representative value. Electrolytes of 3% NaCl solution (cathode) and 0.3M NaOH solution (anode) were used for RCP testing. The voltage in the system was around 60 V and the sample was cooled during the test by a 12 V DC fan measuring 80 × 80 mm. Our measurement procedure was slightly modified so that test was performed over a period of 25-30 minutes for one test sample. The minimum and maximum current were recorded within 1 minute. After stabilization of the current value at about 15 resp. 20 minutes, two more 5-minute intervals were recorded. During the test, the temperature of the sample was measured with a non-contact IR thermometer and the electrolyte temperature was measured using temperature probes (J-type). According to passing charge result, permeability and thus the quality of cement paste can be evaluated.

Compressive strength of cement pastes was tested after 28 days of curing under saturated calcium hydroxide solution. For the final value of compressive strength, 3 samples were tested according to EN 12390 (2019) with loading speed of 0,5 MPa (equals to 0.8 kN/s).

The pH of the cement paste was determined based on the leachate of the material in a liquid medium. After the destructive compressive strength test, the samples were ground and sieved on a sieve with a size of 0.063 mm. 1 g of cement paste material was mixed with 100 ml of deionized water and stirred for 1 minute. Subsequently, a pH meter (Extech EC500) was used for pH value determination in cement samples leachate and in corrosive media as well.

The composition of the raw materials of the prepared cement pastes was analysed by the X-ray fluorescence method (XRF) using Ametec Spectro IQ analyser (Ametec, Mahwah, NJ, USA).

3. RESULTS AND DISCUSSION

3.1 Characteristics of fresh composites and hardened pastes after 28 days

3.1.1 Consistency of cement pastes

The results of the Haegerman's test measuring the flowability of the fresh cement pastes are presented in Figure 1. Replacement of cement by secondary materials

(microsilica, zeoslag and fly ash) had no significant effect on the consistency. The initial consistency of MS, ZS and P samples ranged from 170 to 188 mm while the initial consistency of reference sample was 176 mm. However, partial replacement of cement by zeolite led to decreasing in consistency of cement paste (137 mm). This may be due to the clathrate structure of the zeolite crystal lattice, which causes water to bind to the space in the middle of the host cluster (Martínez and Corma 2013).

3.1.2 Bulk density

The bulk density of the cement composite decreased with the addition of an admixture, which is due to the different bulk densities of the input materials (Figure 2). The highest values are reached by reference samples C0 and C1, where the maximum values of bulk densities of samples in the saturated state (D-ssd) were about 1984 kg.m^{-3}. This was the same for dry samples (D-28-dry), the highest values were also reached by reference samples C0 and C1. The D-mix in the figure represents the bulk density of the fresh paste after mixing. The measured values of bulk densities of cement pastes are comparable with those determined by Allahverdi et al. (2010) but lower than reported by Heikal et al. (2020) who investigated the pastes with clay nanoparticles.

3.1.3 Water absorption and weight changes

After 28 day-curing in the reference medium $Ca(OH)_2$, the weights of the samples were measured in wet and dry state to obtain the water absorption. The highest water absorption of 28.8% was reached by the sample with the admixture of fly ash (P), however, this was very close to the absorption of sample with a combination of zeolite and slag (ZS). Samples with an admixture of zeolite (Z) and microsilica (MS) achieved the lowest absorption as seen in Table 4. Allahverdi, on the contrary found that microsilica addition contribute to the increase in water absorption of the pastes.

3.1.4 Compressive strength

The highest value of compressive strength after 28 days was reached by reference samples C0 and C1, up to 63.8 MPa (Table 5). The lowest compressive strength was achieved by a sample with an admixture of fly ash (P), namely 52.5 MPa which was consistent with the study conducted by Wang et al. (2016). However, the pozzolanic properties of the fly ash and the latent hydraulic properties of the zeoslag may not have been exhibited after such a short time, as they need a longer reaction time.

3.1.5 Penetration of aggressive ions

Figure 3 shows the measured values of the current

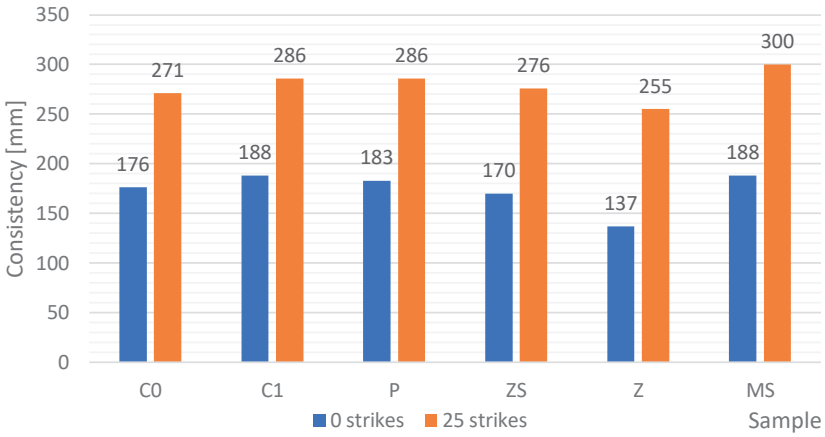

FIGURE 1: Consistency of cement pastes.

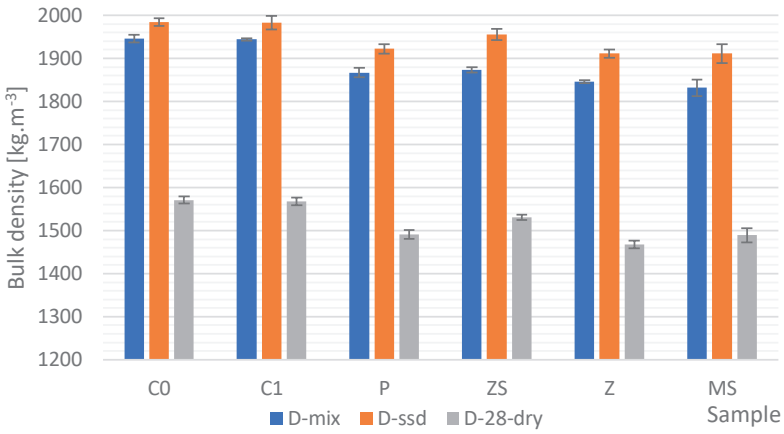

FIGURE 2: Bulk densities of cement pastes.

TABLE 4: Water absorption of cement pastes.

Cement paste sample	Water absorption value (%)		
	Average	Standard deviation	Variation
C0 - reference	26.2	0.3	1.0
C1 - reference	26.9	0.5	1.9
P – with fly ash	28.8	0.6	2.1
ZS – with zeoslag	28.6	0.1	0.3
Z – with zeolite	25.4	0.2	0.8
MS – with microsilica	24.9	0.4	1.8

TABLE 5: Compressive strength of cement pastes.

Cement paste sample	Compressive strength (MPa)		
	Average	Standard deviation	Variation
C0 - reference	61.6	1.8	2.9
C1 - reference	63.8	3.5	5.5
P – with fly ash	52.5	1.9	3.6
ZS – with zeoslag	54.6	2.6	4.7
Z – with zeolite	61.5	1.7	2.7
MS – with microsilica	56.0	1.6	2.9

passing through the individual cement pastes at the beginning of the measurement (I-0), as well as the maximum current passed (I-max), which were recorded for the cement pastes. The higher current represents a larger amount of ions penetrating into the structure of the cement paste and thus its lower ability to withstand aggressive environments. The highest values of ion penetration (0.6 A) were recorded in the sample with the addition of fly ash. The composite with microsilica reached the lowest value - 0.36 A, due to its admixture, because it acted as a filler and thus blocked the passage of ions through the sample. In comparison with the compressive strengths values of the samples presented in Figure 3, it can be seen that the values of the ion penetration corresponded to the values of the compressive strengths, where the fly ash reached the lowest value.

3.1.6 pH of cement pastes

The measured pH values of cement paste samples, determined after 28 days of samples curing, are compared in Figure 4. The highest pH values, 13 and 12.8, were observed for the reference samples C0 and C1, respective-

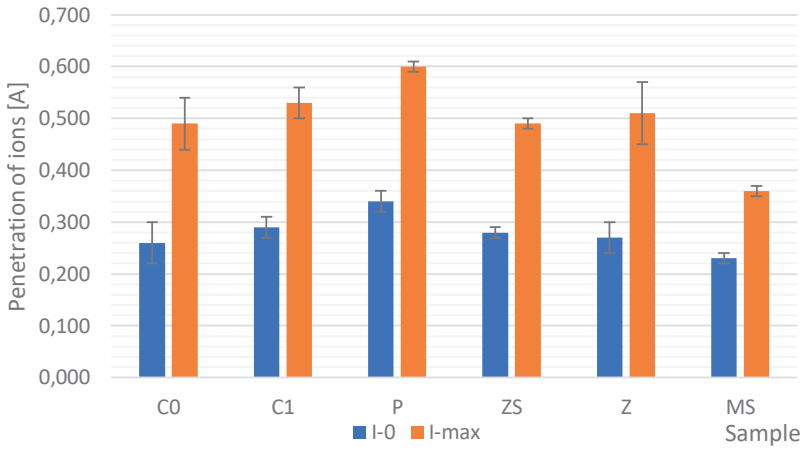

FIGURE 3: Results of the RCP test of cement pastes before the corrosion experiment..

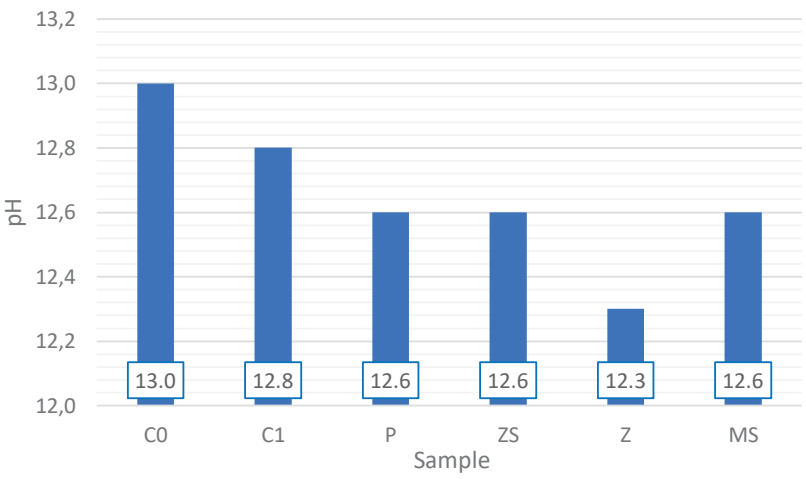

FIGURE 4: pH of the cement paste samples.

ly. The lowest value was measured in a sample of cement paste with zeolite (Z), where the pH reached 12.3.

3.2 Properties of cement pastes after exposure in model solutions

3.2.1 Increase in bulk density

After the experiment, there was noticed an increase in bulk densities (D-ssd) for most cement pastes after their exposure to a corrosive model environment. In deionized water (DV) and in natural rain (NR), the increase in the bulk density of the samples was very similar and in comparison with other environments neglible (0.05 - 0.6%) – Figure 5 b) and c). This result is related to the fact that the environment of natural rain was very similar to the environment of deionized water not only in terms of acidity, but also due to its low conductivity and minimal presence of sulphates. The changes in the bulk densities of the samples in the environments with model acid rain were several times higher, as can be seen in Figure 5 d) - f). The increase in the bulk density of the samples in an aggressive environment

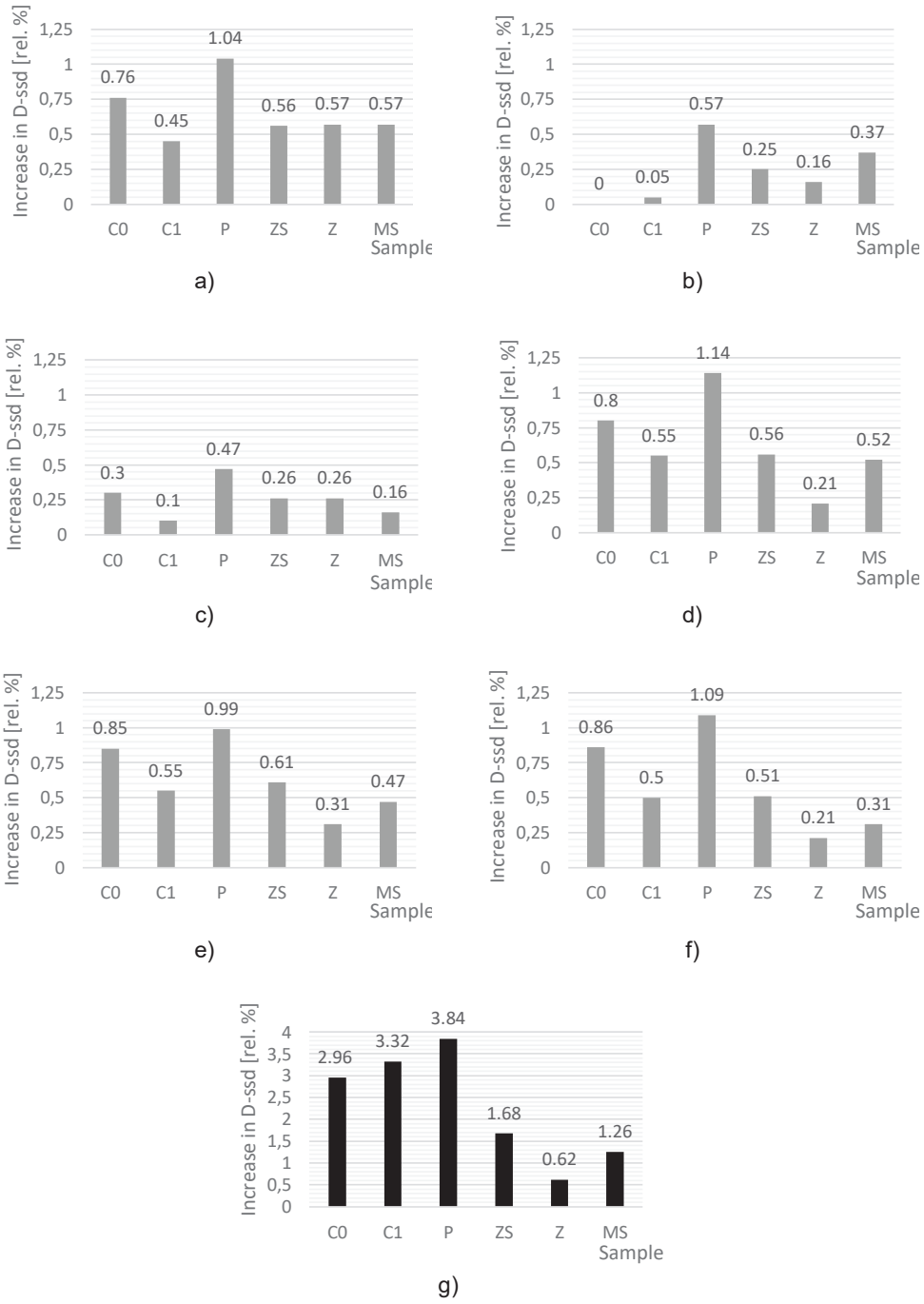

FIGURE 5: Changes in bulk densities of cement pastes after exposure to a) Ca(OH)2 reference medium, b) deionized water, c) natural acid rain, d) model acid rain with pH = 6, e) model acid rain with pH = 4, f) model acid rain with pH = 2, g) model acid rain pH = 2 – samples with precipitates.

is probably associated with the formation of new sulphate compounds not only on the surface of the sample, but also with their crystallization in the internal structure (Rozière et al. 2009; Zhang et al. 2013). These sulphate compounds were formed as a result of the presence of sulphate ions in the aggressive solution. Sulphates likely reacted with calcium ions, either directly leached in a liquid medium or even after penetrating inside of a paste with not yet leached portlandite. On the contrary, the increase in the bulk density of cement pastes in the reference environment $Ca(OH)_2$, where corrosion did not occur by leaching portlandite, is probably related to the ongoing hydration processes. The highest increase in bulk density was recorded for a sample of cement paste with fly ash (P).

3.2.2 Water absorption changes

A comparison of the water absorption (WA) of cement paste samples before (orange) and after the corrosion experiment (blue) is shown in Figure 6.

In the reference medium, the absorption values of all samples except the zeolite and microsilica pastes decreased compared to the 28-day absorption, likely due to ongoing hydration processes as the pores were filled with hydration products (Moghadam et al 2020). For samples immersed in deionized water, the absorption was approximately the same as at the beginning of the experiment, but for the zeolite (Z) and microsilica (MS) samples, an increase in absorption was again observed. Similar trends in absorption as in deionized water were observed for cement samples immersed in natural acid rain (Figure 6 c). The values reached for the reference samples and zeoslag-based samples were lower than the original ones. The value of the cement paste with fly ash increased slightly. Absorption values of Z and MS samples increased significantly. The increase in absorption in water and natural rain could be linked with the portlandite leaching from the cement matrix (Jebli et al. 2018, Carde et al. 1996). Samples in MAR6 and MAR4 media behaved the same, the values remained

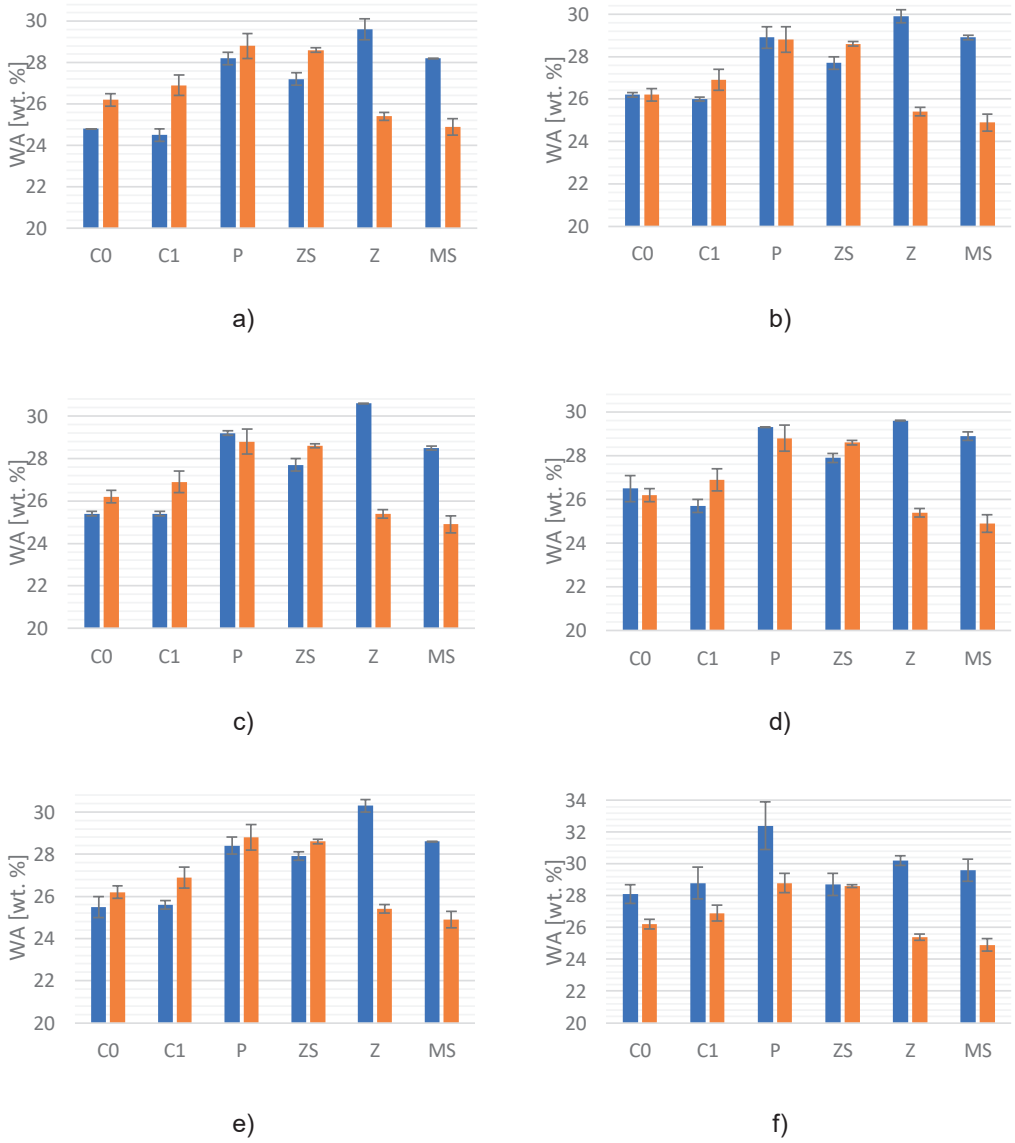

FIGURE 6: Comparison of absorption of cement pastes before and after exposure to a) reference medium Ca(OH)2, b) deionized water, c) natural acid rain, d) model acid rain with pH = 6, e) model acid rain with pH = 4, f) model acid rain with pH = 2.

at the original level, but the values for Z and MS increased. The solution of model acid rain with pH 2 was confirmed as clearly the most aggressive, in which the values after the absorption experiment increased in all samples compared to the original absorption.

The absorption of the most of samples changed only minimally due to experiment, but this was not the case for samples Z and MS. After the experiment, all pastes with zeolite and microsilica achieved higher values of absorption than the original ones. This indicates their lower resistance compared to fly ash and zeoslag pastes.

3.2.3 pH of aggressive media

The pH values of liquid experimental media of cement pastes with fly ash addition (P sample - on the left) and reference sample (C0 – on the right) are illustrated in Figure 7. As seen in Figure 7, the pH values raised dramatically in the corrosion experiment after samples immersing and reached the values above 11. The increase in pH of the media was linked to the cement components leaching, mainly of portlandite ($Ca(OH)_2$), which contributed to the higher concentrations of hydroxide ions (Beddoe et al. 2022). This finding is in correlation with the other authors and our previous research as well (Zhou et al. 2018, Estokova et al. 2018, Rozière et al. 2009). During whole experimental period, the pH fluctuated in the interval of 11-12, in spite of the fact that the pH was regularly set to the initial value. This confirmed the observation, that the leaching of the cement matrix was in progress during the whole experiment. The very similar values in pH during the exposition of samples to the various media led to the conclusion, that process of dissolution of the hydration components in cement pastes dominated in the experiment. The trends in pH for the other samples were similar to those of presented.

3.2.4 Change in permeability of pastes determined by RCP test

In every model solution, each sample achieved a lower ion penetration after the experiment compared to the penetration before, which was manifested by a decrease in permeability for each sample (Figure 8).

In the case of cement pastes immersed in DV, CH and VD, this phenomenon was probably related to the ongoing hydration process, which probably dominated the processes of leaching of basic components. Yang et al. (2018) reported that leaching by deionized water is a very slow process and it is limited by calcium concentration in the pore solution higher than 20 mol/m^3. In the case of cement pastes, which were immersed in model acid rain solutions, the reduction in the permeability of the samples was additionally affected by the formation of new sulphate compounds.

The highest initial (I-0) and maximum (I-max) current values measured for cement pastes after corrosion experiments were observed in reference samples C0 and C1. This means that in these samples, the highest penetration of aggressive ions was identified. On the contrary, in the samples with fly ash (P) and zeolite (Z) the values of ion penetration were the lowest, which in the case of cement pastes with fly ash also correlates with the results of water absorption.

Based on the measured values of ion penetration through cement pastes, the coefficient of reduction of permeability (KPR) was proposed to compare the efficiency of adding mineral admixtures (Expression 2). This coefficient was designed on the basis of comparing the values of measured maximum currents of individual samples of cement pastes with the reference sample C0.

$$KPR = 100 - \left(\left(\frac{I\text{-max}(P_p)}{I\text{-max}\ (C0_p)} \right) \times 100 \right) \quad (\%) \quad (2)$$

where KPR is permeability reduction coefficient; I-max(P_p) is the measured value of I-max of the particular cement paste in the model solution p; and I-max($C0_p$) is the measured value of I-max of the reference sample in the model solution p.

A comparison of the contributions of individual mineral admixtures to reduce the overall permeability of the sample and thus to increase its resistance in the studied envi-

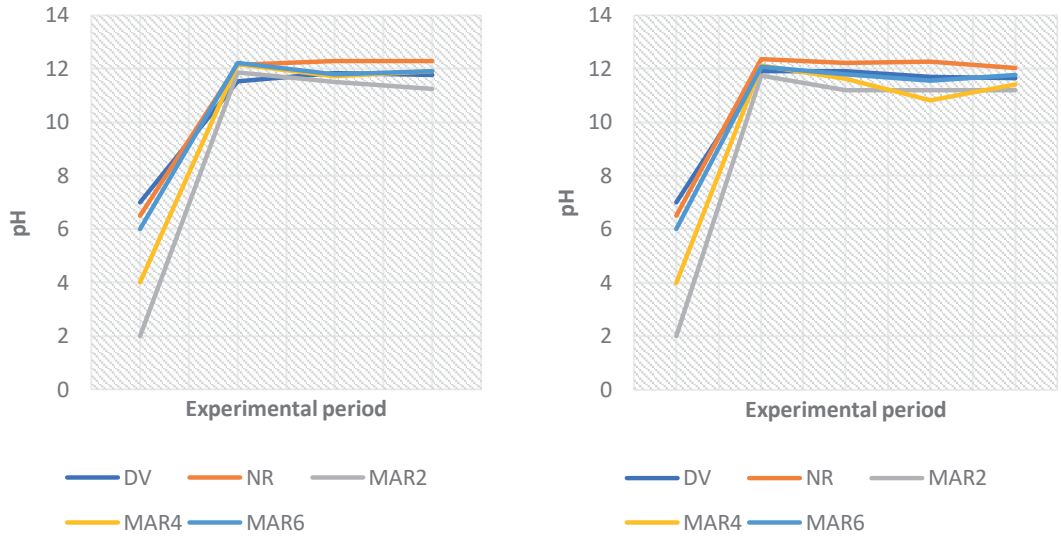

FIGURE 7: The pH trends of experimental media of samples P (left) and C0 (right).

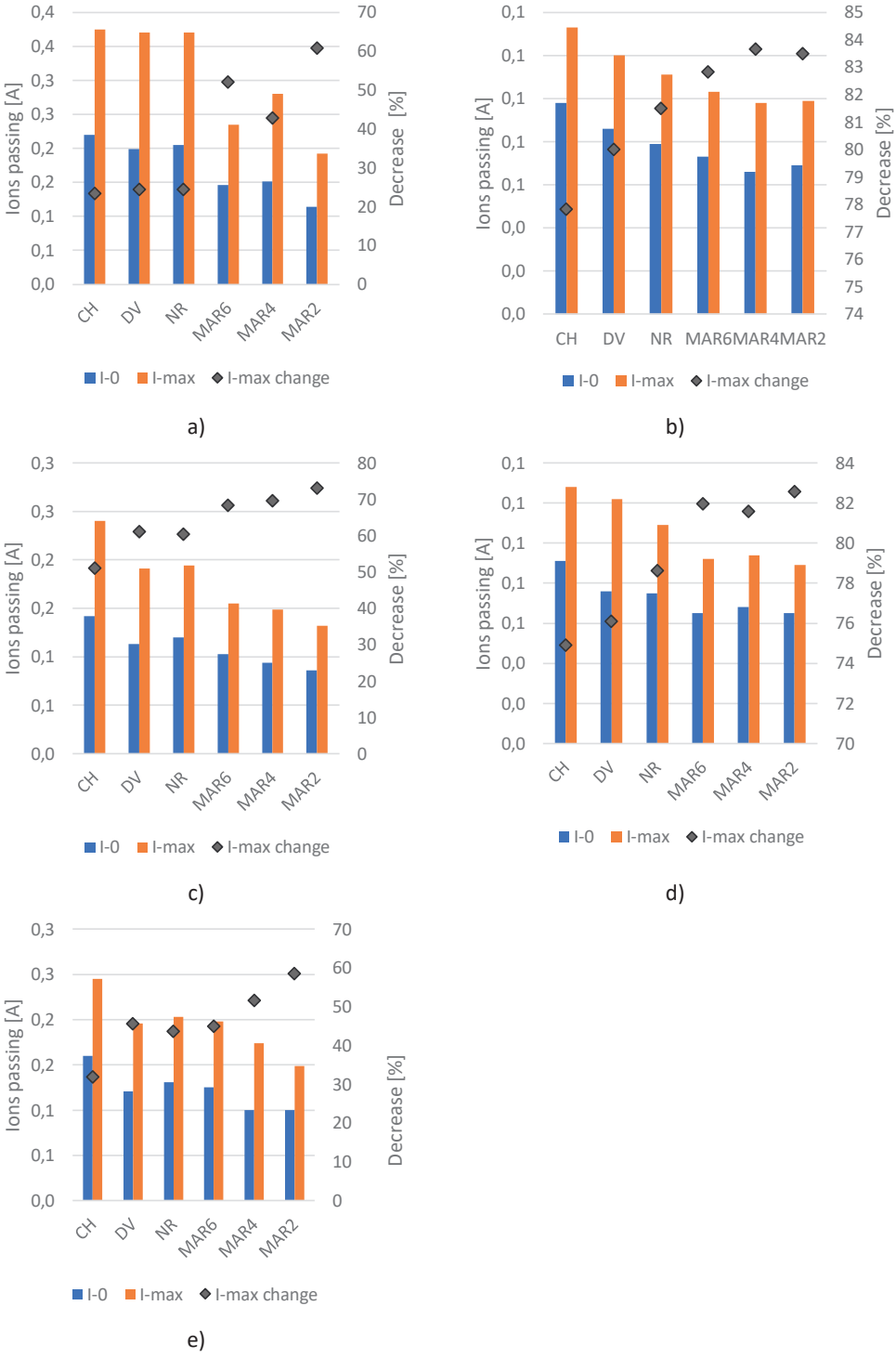

FIGURE 8: Measured I-0 and I-max of cement pastes after the experiment compared to the input values for a) C0 sample, b) P sample, c) ZS sample, d) Z sample, e) MS sample.

ronments is shown in Figure 9.

The more aggressive the environment, the less positive effect of the admixture was manifested. The most effective influence of mineral admixtures was found in the model solutions of natural rain and deionized water. As seen in Figure 5, the use of any admixture reduces the permeability of the cement paste, but the best results have been obtained by adding fly ash (P) or zeolite (Z).

3.2.5 Visual changes of cement samples

Various precipitates were observed on the surface of the cement paste samples after the acid rain exposure. The precipitates were mostly white and occurred predominantly on samples immersed in the MAR2 acid rain model solution. Figure 10 illustrates the surface of the samples that were in a model rain environment with pH = 2. The new-formed surface compounds are likely based on

the sulphates (Malolepsy et al. 2015, Zhang et al. 2013, García-Vera et al. 2018, Estokova et al. 2016).

In addition to surface precipitates, visible damage in the form of surface cracks as well as complete disintegration of the sample was observed for the samples of cement pastes, which were exposed in the model environment with pH = 2.

4. CONCLUSIONS

In this work, the effect of acid rain causing acidic, sulphate and leaching corrosion was studied on cement pastes with various mineral admixtures. Cement pastes with added additives based on waste and supplementary cementitious materials resulted in a significant reduction in permeability in each model solution. Based on the RCP test, an innovative approach was designed to evaluate the effect of the particular admixtures on the improving of permeability of the cement pastes, in terms of their pozzolanic and latent hydraulic activities. Results revealed that the most significant positive effect was manifested by the use of admixtures of ash and zeolite. The RCP testing of the pastes has thus proved to be much more consistent in comparison with, for example, water absorption testing when comparing the influence of the individual admixtures.

AKNOWLEDGEMENTS

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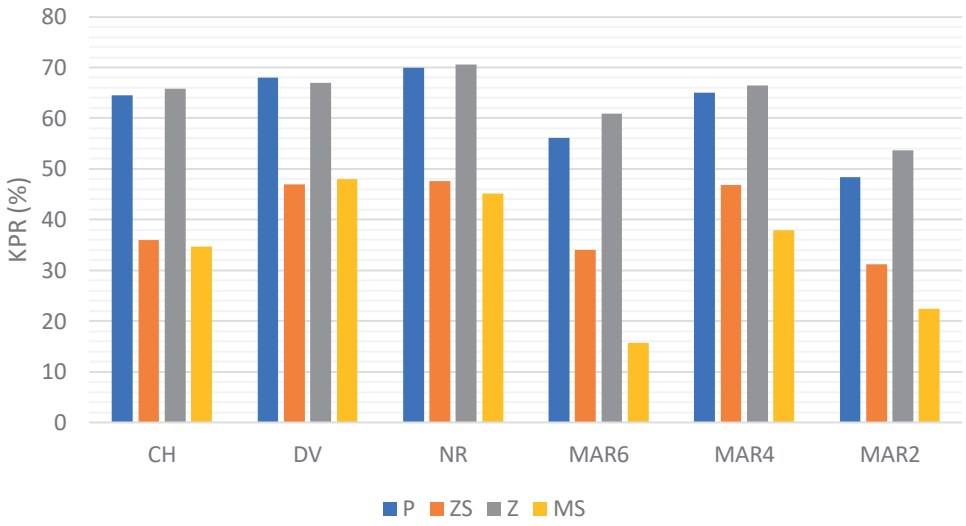

FIGURE 9: Comparison of KPRs of cement pastes.

FIGURE 10: Samples exposed to MAR2 environment a) P sample, b) MS sample.

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PILOT-SCALE VERMICOMPOSTING OF DEWATERED SEWAGE SLUDGE FROM MEDIUM-SIZED WASTEWATER TREATMENT PLANT (WWTP)

Petra Innemanová [1,2,*], Alena Grasserová [1,3] and Tomáš Cajthaml [1,3]

[1] *Institute for Environmental Studies, Faculty of Science, Charles University, Benátská 2, 128 01 Prague 2, Czech Republic*
[2] *DEKONTA a.s., Dřetovice 109, 273 42 Stehelčeves, Czech Republic*
[3] *Institute of Microbiology Czech Academy of Sciences, Vídeňská 1083, 14220, Prague 4, Czech Republic*

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ABSTRACT

The transformation of dewatered sewage sludge into vermicompost provides an advantageous solution in cases where the sludge is not too contaminated with inorganic pollutants, especially heavy metals. In addition to the conversion of the sludge to a product with a higher-added value, undesirable organic pollutants and micropollutants are partially eliminated. Anaerobically stabilized dewatered sewage sludge from a medium-sized Wastewater Treatment Plant (WWTP) was subjected to the vermicomposting process under field conditions. Straw was used as the bedding material in the form of two mixing ratios. The almost 1 year of the monitoring of the process focused on the hazardous substances present, the concentrations of which are regulated by legislation on the use of sludge on agricultural land. In addition, the contents of macro- and micro-nutrients such as N, P, K, Mo, Ca, Mg, and the wintering of the earthworm inocula were monitored. The potential of the vermicomposting process to reduce the content of emergent pollutants from the PPCP group was described with respect to 35 detected substances, including five endocrine disruptors. The study suggested that the bio-stabilization of dewatered sewage sludge using earthworms provides an effective technology for converting noxious wastewater treatment products into nutrient-rich bio-fertilizers.

1. INTRODUCTION

Sewage sludge contains nutrients and other substances that are able to positively contribute to the enhancement of the properties of soil and overall fertility (Latare et al., 2014; Shanta Mendis et al., 2020). Its reuse, where suitable, is encouraged by European Council Directive 91/271/EEC. Treated sludge in the Czech Republic must fulfil the quality criteria set for toxic metals (As, Cd, Cr, Cu, Hg, Ni, Pb and Zn), adsorbable organic halogens (AOX), polychlorinated biphenyls (PCBs), polyaromatic hydrocarbons (PAHs) and the microbial pathogens *Salmonella sp.* and *Escherichia coli* (Ministry of the Environment of the Czech Republic, 2021). National legislation has incorporated the relevant regulations of the European Union, including Directive 86/278/EEC. Apart from those pollutants whose concentrations are regulated, a broad spectrum of so-called 'emerging' organic chemicals, including pharmaceuticals and other personal care products (PPCPs), may be transferred to residual solids during the treatment of wastewater. Thus, a reliable assessment is required of their significance and implications for the beneficial recycling of treated sewage sludge (Khakbaz et al., 2020).

Vermicomposting is a process via which earthworms act to convert organic materials (usually waste) into a humus-like material known as vermicompost. It comprises a bio-oxidative and stabilizing process for the conversion of organic material which, unlike classical composting, uses the interaction between the intensive activity of earthworms and microorganisms, and does not involve the thermophilic decomposition phase (Domínguez and Edwards, 2011; Champar Ngam et al., 2010). Vermicompost generally appears to be superior to conventionally-produced compost in terms of a number of important parameters including a higher content of available nutrients associated with the enhanced hydrolytic activity and microbial population size (Tognetti et al., 2005; Sinha et al., 2010).

Our study concerns the long-term field testing of sludge vermicomposting in two separate pits, each with a working volume of 3m^3. Straw was used as the bulking material in two mixing ratios. The research covered the testing phase of a pilot vermicomposter conducted for the purpose of

* Corresponding author:
Petra Innemanová
email: petra.innemanova@dekonta.cz

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follow-up experiments focusing on the reprocessing and sanitation of sewage sludge. The aim was to ensure a sufficient inoculum density and to test the overwintering of the system under outdoor conditions. However, even during this start-up phase, all the parameters required to be monitored by Czech legislation, as well as the contents of macro- and micro-nutrients such as N, P, K, Mo, Ca and Mg were monitored, as was the development of the concentration of selected PPCP micropollutants.

2. MATERIAL AND METHODS

2.1 Material and the design of the field experiment

The dewatered anaerobically stabilized sewage sludge with an initial dry matter content (DMC) of 24.9 ± 0.7% was taken from WWTPs of a 33 thousand population-equivalent (p.e.) located in South Bohemia. The straw was supplied by a local farmer. The earthworms (*Eisenia andrei*) were supplied by the FLORIUM s.r.o. vermicomposting plant.

The pilot-scale vermicomposting experiment is being conducted in segments A and B of a field vermicomposter (see Figure 1). The working volume of each segment (A and B) is 3 m^3. The working volume of the backup segment (C) is 3.5 m^3; this part of the vermicomposter serves as the earthworm inoculum for subsequent experiments. The drainage system of the field vermicomposter allows for the leachate sampling of each segment. The excess leachate is collected in an underground tank with a volume of 1 m^3 and subsequently disposed of at the nearest WWTP. This experiment does not include the monitoring of the leachate (Figure 2).

A perforated drainage pipe made of polyvinyl chloride was positioned at the bottom of each segment and covered with a layer of straw (36 kg for each of segment A and B). After separating this drainage layer with a geotextile material, each of the segments was filled with the test material according to the following arrangements:

Segment A: 4 layers of straw (40 kg in total) and 3 layers of dewatered sewage sludge (608 kg in total, representing 159 kg of dry matter). Straw formed the bottom and upper layers. The weight ratio of the straw to the dry sludge was 1:4.

FIGURE 2: Field experiment.

Segment B: 3 layers of straw (30 kg in total) and 2 layers of dewatered sewage sludge (the same amounts as in segment A). Straw formed the bottom and upper layers. The weight ratio of the straw to the dry sludge was 1:5.3.

After filling the vermicomposter with a substrate, two perforated polypropylene boxes containing the earthworm hybrid *Eisenia andrei* were placed in each segment. The total weight of the earthworm inoculum was 7 kg for each segment.

The layers of straw created air pockets that improved the level of comfort for the earthworms. Sludge samples

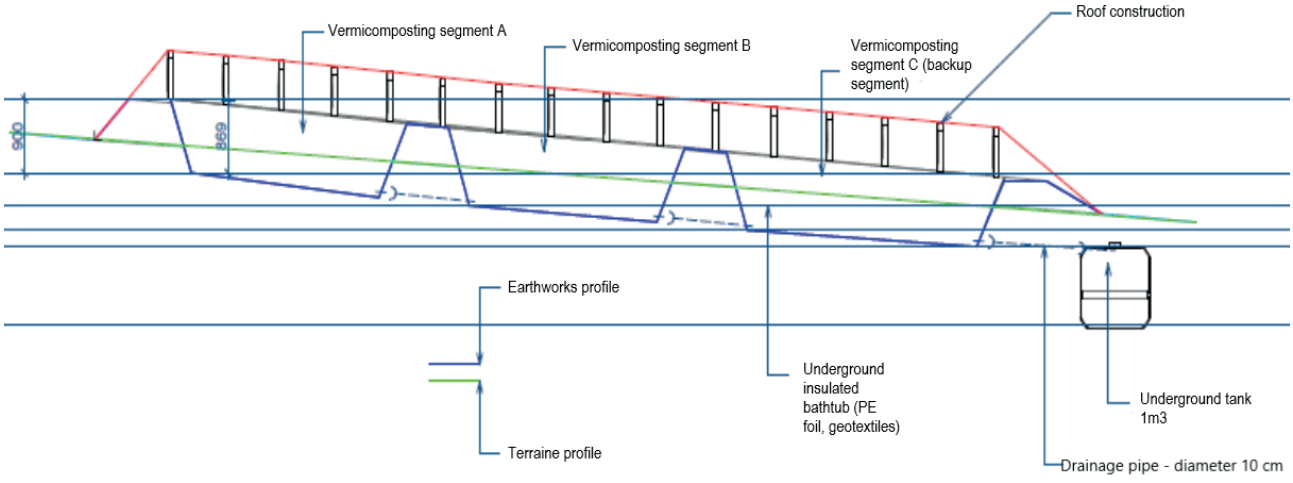

FIGURE 1: Pilot-scale vermicomposter scheme (if not directly specified, the dimensions are given in cm).

for subsequent analysis purposes were taken from the layers without straw.

The vermicomposting process commenced on 4 June 2020 and is ongoing. Both segments were sprinkled twice with the same amount of water during the dry summer of 2020. Otherwise, a perforated cover was sufficient to provide the necessary irrigation.

In November 2020, compact piles were formed from the vermicompost layers of the two segments, in the lower one-third of the segment in both cases. This arrangement allowed the earthworms to overwinter comfortably via the creation of non-freezing zones. In addition, this form of vermicompost will serve as the inoculum for the next batch of sludge in the so-called wedge system (currently in progress).

2.2 Sample analysis

The earthworm biomass was determined on the basis of the manual counting of individual worms (adults and juveniles) in a 1 l sample of vermicompost. 5 parallel samples were taken from the two segments A and B. The dry matter content (DMC) was measured gravimetrically after the drying of the samples at 120^{0}C. DMC was expressed as a percentage of the dry weight of the respective sample.

E. coli was determined according to the Czech ČSN EN ISO 9308-1 national standard. The *Salmonella sp.* was determined according to ČSN EN ISO 6579.

The determination of heavy metals, the Ca, Mg, K, P and N contents, the pH, the DMC and the content of TOC, PCBs (the sum of 7 congeners 28+52+101+118+138+153+180), PAHs (the sum of anthracene, benzo(a) anthracene, benzo(b) fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(ghi)perylene, phenanthrene, fluoranthene, chrysene, indeno(1,2,3-cd)-pyrene, naphthalene and pyrene) and AOX was conducted by an accredited analytical laboratory (Dekonta, a.s., Ústí nad Labem, Czech Republic). All the measurements were taken in triplicate.

The samples intended for the PPCP and endocrine disruptor analysis using LC-MS/MS were freeze-dried and homogenized. Each sample (weights of 1-2 g) was then transferred to an extraction cell and positioned in an Accelerated solvent extractor (ASE, Dionex). The extraction method was as follows: the preheating of the methanol solvent and the cell to 80°C with a pressure of 1500 psi; 3 extraction cycles and 5-minute static periods between the cycles. The extracts were then evaporated to 5 mL and centrifuged (6000g, 10 min), whereupon the supernatants were transferred to 2mL vials for subsequent analysis purposes. The extracts were analyzed using the LC system (Agilent 1260 Infinity) coupled with a triple quadrupole mass detector (Agilent 6470 LC/TQ). Separation was performed using a Poroshell 120 EC-C18 column (2.7 µm, 3 mm x 100 mm, Agilent) equipped with a Poroshell 120 EC-C18 precolumn (2.7 µm, 3 mm x 5 mm, Agilent); both were heated to 40°C. The mobile phase consisted of phase A (0.5mM ammonium fluoride in MQ water + 0.01% formic acid, LC-MS grade) and phase B (100% methanol, LC-MS grade). The gradient elution program was as follows (time [min], % phase B): 0, 5; 4, 50; 6, 50; 18, 100; 21, 100; 22, 5 and 23, 5. The mobile phase flow was 0.4 mL/min; one run lasted 23.50 min and the injection volume was 2 µL. In order to suppress the matrix effect, the samples were measured with automatic standard additions of 1, 5 and 25 ng/mL. The mass spectrometric parameters were optimized using MassHunter Workstation Optimizer and Source Optimizer (both Version 10.0, SR1, Agilent).

The output values of the monitored chemical parameters represented the results of the field sampling after 9 months (which included the winter season). With respect to the microbiological parameters, the sanitation efficiency of the process was evaluated after approximately 5 and 11 months of the duration of the process.

3. RESULTS AND DISCUSSON

3.1 Dry matter content and earthworm biomass

The dry matter contents of segments A and B after 11 months of processing were 28.6 ± 0.4% and 26.8 ± 0.9%, respectively. The small (but statistically significant difference, $p < 0.01$) did not lead to a differing worm density, i.e. 54.8 ± 15.2 individuals per liter in segment A and 46.2 ± 20.2 individuals per liter in segment B (mean and standard deviation of 5 measurements) 11 months after the start of the experiment. Nevertheless, the observed average weight of the adults of 0.86 ± 0.27 g in segment B was significantly higher than the value of 0.47 ± 0.18 g determined for segment A ($p < 0.01$, mean and standard deviation of 30 measurements). The slight difference in the moisture contents of segments A and B was the most likely reason for the observed differences in the body weights of the earthworms. Similar observations were described in a study by Domínguez and Edwards (1997), which described that beneath an 85% moisture level, higher moisture conditions clearly facilitated growth as measured by an increase in the individual biomass of *Eisenia andrei*.

3.2 Chemical and microbiological parameters

Adequate sanitation had not been achieved after 5 months of the process. *Salmonella sp.* was not detected in the sludge used in the experiment but concerning the *E. coli* parameter, the required limits were met after approximately 11 months of the duration of the experiment (see Table 1), thus indicating that sludge sanitation is possible in the absence of a pre-composting step with the thermal phase of the process; however, it requires a longer time period. These results are at variance with trends reported in the literature. For example, Procházková et al. (2018) observed a decrease in *E. coli* to an undetectable level after 8 weeks of the vermicomposting of apple pomace waste with an artificial bacterial load. In addition, a study by Parseh et al. (2021) described the extensive ability of *E. fetida* to reduce pathogens within 8 weeks in dewatered sludge without the need for an increase in temperature. However, the results of these studies are difficult to compare since they are usually recorded under optimal laboratory conditions. It is necessary to take into account that a longer period of time is required for complete sanitation under real conditions. This is due not only to temperature and moisture fluctuations; it was observed during the experiment that due to the inhomogeneity of the mixture, random layers without

TABLE 1: Concentrations of *E. coli* in segments A and B at the commencement and after 140 and 340 days of the process.

	E. coli in parallel samples (CFU/g)					Czech legislation limit
Input	7.8×10^4	9.2×10^4	1×10^5	2.2×10^5	2.8×10^5	Max. 10^3CFU/g for 4 samples and 5×10^3CFU/g for one sample from 5 parallel samples
A (day 140)	3.1×10^4	3.5×10^4	3.5×10^4	3.6×10^4	4.2×10^4	
B (day 140)	2×10^4	2.5×10^4	2.9×10^4	3.4×10^4	3.5×10^4	
A (day 340)	Negative	Negative	Negative	Negative	Negative	
B (day 340)	Negative	Negative	Negative	4×10^2	2.4×10^3	

the presence of earthworm settlements occurred over relatively longer time period.

As can be seen in Table 2, the treated sludge complied with the limits for hazardous substances set by Czech legislation (Ministry of the environment of the Czech Republic, 2021) for the application of treated sludge to agricultural land even before the start of the vermicomposting process. The relative stabile concentration at the most of monitored heavy metals can be explained by the combination of two conflicting phenomena: the concentration through the decomposition of the organic matter and elimination due to ingestion by the earthworms and following bioaccumulation. The predominant effect of bioaccumulation may provide an explanation for the decrease in the content of Cu and As. According to Rorat et al. (2017), *Eisenia andrei* accumulated heavy metals as follows: Cd>Cu>Zn>Ni>Cr>Pb. Kilpi-Koski et al. (2019) observed a high bioaccumulation factor (BAF) for As, but a low BAF for Cu. Moreover, other studies have provided differing information on heavy metal bioaccumulation factors (Suleiman et al., 2017; Wang et al., 2018), and further research is required in this regard. In any case, bioaccumulation cannot be considered to provide a tool for the removal of heavy metals from vermicomposted material since the continuous earthworm mortality and their subsequent decomposition during a full-scale application leads to the re-supply of accumulated metals back into the final vermicompost. Therefore, only the initial concentration of heavy metals in the sludge is a key factor in the design of the appropriate technology. The limits set for selected organic substances from the persistent organic pollutants (POPs) category were fulfilled. The AOX concentration dropped to below the detection limit for both treatments. Some studies (for example Khakbaz et al., 2020) have used sludge parameter extractable organic halogens (EOX) for the quantification of organic halogens in sewage because of the suitability of this parameter to characterize complex two-phase matrices as a sludge (Rizzardini and Goi, 2014). Our study followed the requirements of the Ministry of the environment of the Czech Republic (2021) according to which, in addition to the AOX, the monitoring of PCBs (the sum of 7 congeners: 28+52+101+118+138+153+180) and PAHs (the sum of anthracene, benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(ghi)perylene, phenanthrene, fluoranthene, chrysene, indeno(1,2,3-cd)-pyrene, naphthalene and pyrene) is mandatory. While PCBs were under the detection limit even in the initial samples, there was no tendency for the sum of 7 selected PAHs to decrease from the initial value of 2.8 ± 1.1 ppm. The opposite tendency, i. e. concentration over time, indicates the presence of highly-persistent substances. The bioavailability of PAHs has been found to be strongly related to the number of their aromatic rings, their molecular weight and their structure (Amir et al., 2005). In this specific case, more persistent PAH representatives were probably present in the sludge while, for example, a study by Rorat et al. (2017) reported that of the PAHs regulated, indeno(1,2,3-c,d)-pyrene was not detected and the most efficient rate of removal was recorded for the two- and three-ring substances naphtalene and phenanthrene. When designing the appropriate technology, it is, therefore, necessary to take into account the relative concentrations of individual PAHs in the sum of those that are subject to regulation.

In addition to hazardous substances, the monitoring of which is required by legislation, the content of selected biogenic elements was also monitored. As can be seen from Table 2, an obvious increase was observed especially in the case of phosphorus. An elevated level was also observed in potassium concentrations. Conversely, the total nitrogen content dropped and, at the same time, a marked shift was observed in the ratio of the NH^{4+}/NO^{3-} form of nitrogen. It decreased by 4 orders of magnitude from the original value of approximately 10^4. The levels of calcium and magnesium remained at similar levels for 9 months. These trends have also been observed under laboratory conditions (Zhang et al., 2020) and even without sludge blending (Khwairakpam and Bhargawa, 2009), which indicates that sewage sludge can be recycled as a good quality fertilizer. The observed loss of organic carbon can be attributed to the loss of organic matter from feed mixtures as carbon dioxide through earthworms and microbial respiration (Garg et al., 2008). The pH dropped from the original 7.6 ± 0.1 to 5.2 ± 0.3 and 5.4 ± 0,1 which is consistent with the results of other authors (Gupta and Garg, 2008; Bhat et al., 2016). A gradual return to neutral values was observed after longer processing times (data not shown).

3.3 Development of the micropollutant concentration

Although samples were taken for analysis from the sludge layer, it cannot be ruled out that the action of the earthworms and mechanical manipulation did not result in the mixing of the substrates and, thus, a reduction in the content of the monitored substances via dilution. On the other hand, during the vermicomposting process, the mass of the mixture generally declines due to the partial mineralization of the organic matter (Suleiman at al., 2017). Thus, recalcitrant substances may become concentrated as a result. The calculation of the actual loss of pollutants is subsequently complicated. Similar laboratory studies have applied an internal standard for the recalculation of the ef-

TABLE 2: Concentration of hazardous substances, nutrients and TOC in segments A and B at the commencement and after 9 months of the process (mean and standard deviation of 3 paralel samples).

Hazardous substances (mg/kg)	Input	A – output	B- output	Czech legislation limit
As	8.0 ± 0.2	5.2 ± 1.1	6.1 ± 0.6	30
Cd	1.3 ± 0.03	1.2 ± 0.1	1.2 ± 0.1	5
Cr	42.8 ± 4.2	42.7 ± 8.2	40.9.0 ± 0.7	200
Cu	249.0 ± 11.0	201.0 ± 21.0	202.0 ± 16	500
Hg	1.7 ± 0.5	1.3 ±0.4	1.2 ±0.1	4
Ni	29.5 ± 1.9	28.5 ± 2.8	31.1 ± 5.4	100
Pb	37.6 ± 2.6	34.6 ± 4.5	34.4 ± 2.8	200
Zn	804.0 ± 45.0	754.0 ± 80.0	714.0 ± 98.0	2500
Mo	6.0 ± 0.65	5.0 ± 0.65	4.7 ± 0.6	
AOX	96.0 ± 57.0	n.d.	n.d.	500
PCB	n.d.	n.d.	n.d.	0.6
PAH	2.8 ± 1.1	3.5 ± 0.4	6.8 ± 1.4	10
P	(26.0 ± 0.5) x10^3	(39.3 ± 4.1) x10^3	(39.4 ± 4.7) x10^3	
K	(2.7 ± 0.4) x 10^3	(4.5 ± 0.3) x10^3	(3.9 ± 0.2) x10^3	
N_{total}	(8.2 ± 2.5) x10^3	(3.7 ± 0.8) x10^3	(3.9 ± 0.3) x10^3	
Ca	(23.8 ± 0.4) x10^3	(22.6 ± 1.7) x10^3	(19.5 ± 4.6) x10^3	
Mg	(5.0 ± 0.2) x10^3	(5.0 ± 0.4) x10^3	(4.8 ± 0.7) x10^3	
TOC	(308 ± 44) x10^3	(227 ± 14) x 10^3	(235 ± 10) x10^3	

n.d.: not detected

ficacy. For example, Covino et al. (2016) used a selected heavy metal, which was present in only one part of the composting mixture (wooden chips). The removal efficiency of micropollutants and hazardous substances indicated as a percentage of reduction on the basis of the initial and final concentrations without the calculation of the actual loss may thus be misleading. The declared loss of monitored substances should be considered as a combination of the processes described above. However, with regard to the subsequent applicability of the sludge, we were primarily interested in the final quality of the product. For our purposes, the final removal of micropollutants might be referred to provisionally as the "operating removal efficiency".

The initial concentrations of the monitored pharmaceuticals ranged from 0.5 ± 0.1 ppb (Sulfamethazine) to 8.0 ± 0.4 ppm (Telmisartan). The initial and output concentrations of 35 substances detected from the PPCP group are summarized in Table 3.

The operating removal efficiency of the vermicomposting process differed between 0% and 100%, with the highest values (above 90%) determined for Acesulfame, Equilin, Equol, Furosemide, Hydrochlorothiazide, Ibuprofen, Saccharine and Sulfamethazine and endocrine disruptor 17beta-estradiol. With respect to this case study, 28.7% (segment A) and 29.2% (segment B) of the most abundant micropollutant, Telmisartan, were removed. The only increased level after 9 months of processing was observed for Bisphenol S, which was probably related to the composter insulation material used. The total operating removal efficiency of all the detected micropollutants was 35.3% and 34%. To date, only a small number of similar studies have been published, a review of which has recently been provided by Chowdhury et al. (2022). The cited studies differ in terms of the specific observed substances included in the groups of pharmaceuticals and PPCPs and are, therefore, difficult to compare. It is clear that further research is essential in the field, especially concerning the overall effects on the environment, e. g. endocrine disruptivity and ecotoxicity.

4. CONCLUSIONS

During the first year of the operation of the field vermicomposter, the earthworm inoculum in the mixture of sewage sludge and straw multiplied to a sufficient extent and the culture overwintered successfully, even though frosts reached temperatures of below -20°C in the winter of 2020/2021.

The different mixing ratio of the sludge/straw exerted a slight effect on the output dry matter content, which led to a minimal difference in the density of the earthworm populations and a significant difference in the biomass of the *Eisenia andrei*. No significant difference was observed between segments A and B with respect to the monitored parameters.

The sludge used in the experiment met the respective legislative requirements for agricultural land application in terms of the content of heavy metals and that of the monitored organic substances and *Salmonella sp.*, the content of which met legislative requirements even at the outset of the process. The *E. coli* content met the criteria in the 11th month.

TABLE 3: Concentration of selected PPCPs in segments A and B at the commencement and after 9 months of the process, mean and standard deviation of 18 input samples and 6 output samples from each of segment A and B; the variance associated with the compound content via the analysis of variance (ANOVA) and its significance, *p <0.05; **p <0.01.

Pollutant	Input (ng/g)	Segment A (ng/g)	Segment B (ng/g)
Acesulfame	47.5 ± 9.0	4.1 ± 1**	3.9 ± 0.7**
Acetaminophen (Paracetamol)	10.8 ± 2.2	4.8 ± 1.5**	3.9 ± 0.4**
Amitriptyline	64.4 ± 11.5	52.2 ± 11.6	51.7 ± 7.3*
Atorvastatin	13.1 ± 4.2	10.3 ± 4	13.5 ± 5
Azithromycin	41.4 ± 11.7	59.8 ± 18.1	45.7 ± 25.4
Bisphenol A	615.5 ± 63.4	93.4 ± 23.6**	158.5 ± 24.6**
Bisphenol F	29.6 ± 4.3	21.5 ± 8.4**	17.8 ± 2.2**
Bisphenol S	27.3 ± 2.6	95.0 ± 31.5*	45.6 ± 29.1
Caffeine	50.0 ± 4.0	40.8 ± 5.2**	42.9 ± 2.3**
Carbamazepine	132.5 ± 38.4	75.8 ± 11.4**	87.9 ± 12.3*
Carbamazepine 10,11-epoxide	4.9 ± 0.4	3.2 ± 0.6**	3.7 ± 0.6**
Cetirizine	152.8 ± 9.6	84 ± 15.7**	91.5 ± 12.5**
Citalopram	421.1 ± 32.1	320.1 ± 62.8**	287.3 ± 61.8**
Daidzein	7.4 ± 1.1	2.6 ± 0.2**	2.5 ± 0.1**
Equilin	1.2 ± 1.4	n.d.	n.d.
Equol	39.7 ± 8.6	2.6 ± 0.8**	4.9 ± 4.2**
Estrone	3.5 ± 2.7	0.4 ± 1.0*	0.9 ± 1.3
Fluoconazole	1.3 ± 0.2	1.0 ± 0.2**	1.1 ± 0.1*
Furosemide	19.2 ± 2.8	n.d.**	n.d.**
Gabapentin	38.5 ± 9.8	7.0 ± 2.8**	9.8 ± 1.9**
Genistein	3.5 ± 2.7	2 ± 0.4	2.0 ± 0.2
Hydrochlorothiazide	2.6 ± 0.5	n.d.**	n.d.**
Ibuprofen	129.7 ± 79.2	7.7 ± 7.2**	n.d.**
Lamotrigine	94.7 ± 12.6	21.4 ± 7.8**	27.6 ± 5.6**
Metoprolol	135.8 ± 8.2	45.2 ± 7.5**	48.0 ± 13.1**
Mirtazapine	74.2 ± 5.7	33.8 ± 10.2**	36.3 ± 5**
Saccharine	28.4 ± 13.2	n.d.**	n.d.**
Sulfamethazine	0.5 ± 0.1	n.d.**	n.d.**
Sulfanilamide	9.4 ± 3.1	2.2 ± 0.4**	2.9 ± 0.5**
Sulfapyridine	8.1 ± 1.9	1.9 ± 0.2**	2.6 ± 0.8**
Telmisartan	(8.0 ± 0.4) x10^3	(5.7 ± 0.8) x10^3 **	(5.7 ± 0.8) x10^3 **
Tramadol	58.4 ± 4.3	28.8 ± 4.3**	31.3 ± 5.9**
Trimethoprim	10.2 ± 1.6	1.6 ± 0.1**	1.3 ± 0.2**
Venlafaxine	128.6 ± 9.6	91.2 ± 15.1**	90.5 ± 11.3**
17beta-estradiol	24.8 ± 20	n.d.**	n.d.**

n.d.: not detected

The degradation potential of selected micropollutants from the PPCP group differed. A total of 35.3% degradation of the monitored substances was observed in segment A and 34% in segment B.

Vermicomposting led to a significant decrease in the concentration of the 4 detected endocrine disruptors (Bisphenol A, Bisphenol F, Estrone and 17beta-estradiol). Conversely, an increase was observed in the content of Bisphenol S, which was probably due to the film material that was used for the insulation of the vermicomposter.

Thus, vermicomposting appears to be a useful method for processing sewage sludge from at least smaller WWTPs. It is recommended that the further potential of this process be explored in subsequent research.

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RECYCLING-ORIENTED CHARACTERIZATION OF PET WASTE STREAM BY SWIR HYPERSPECTRAL IMAGING AND VARIABLE SELECTION METHODS

Giuseppe Bonifazi [1,2], Giuseppe Capobianco [1], Paola Cucuzza [1,*], Silvia Serranti [1,2] and Andrea Uzzo [2]

[1] *Department of Chemical Engineering, Materials & Environment (DICMA), Sapienza University of Rome, Via Eudossiana 18, 00184 Rome, Italy*
[2] *Research Center For Biophotonics, Sapienza University of Rome, Corso della Repubblica, 79 04100 Latina, Italy*

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ABSTRACT

The proposed study was carried out to develop a fast and efficient strategy for plastic waste sensor-based sorting in recycling plants, based on hyperspectral imaging (HSI), combined with variable selection methods, to produce a high-quality recycled polyethylene terephthalate (PET) flakes stream. Variable selection techniques were applied in order to identify a limited number of spectral bands useful to recognize the presence of other plastic materials, considered as contaminant, inside a stream of recycled PET flakes, reducing processing time as requested by sorting online applications. Post-consumer plastic samples were acquired by HSI working in the short-wave infrared (SWIR) range (1000 - 2500 nm). As a first step, the hypercubes were processed applying chemometric logics to build a partial least squares discriminant analysis (PLS-DA) classification model using the full investigated spectral range, able to identify PET and contaminant classes. As a second step, two different variable selection methods were then applied, i.e., interval PLS-DA (i-PLSDA) and variable importance in projection (VIP) scores, in order to identify a limited number of spectral bands useful to recognize the two classes and to evaluate the best method, showing efficiency values close to those obtained by the full spectrum model. The best result was achieved by the VIP score method with an average efficiency value of 0.98. The obtained results suggested that the variables selection method can represent a powerful approach for the sensor-based sorting online, decreasing the amount of data to be processed and thus enabling faster recognition compared to the full spectrum model.

1. INTRODUCTION

Plastic is one of the most used materials in daily life, thanks to its characteristics and versatility. Moreover, plastic waste is among the most diverse materials, making their recycling very complex (Ragaert et al., 2017). Due to the growing use of plastic, the amount of produced waste tends to increase over time, reaching an unsustainable pace for environmental reasons. It is thus necessary to develop and implement the best recycling strategies for plastic waste, guaranteeing high quality standards of the produced secondary raw materials and improving competitiveness with virgin polymers (Eriksen et al., 2018). Indeed, the quality of secondary raw materials resulting from the post-consumer plastic recycling process is highly dependent on the sorting efficiency throughout the plant line (Küppers, et.al, 2019). The purity degree of secondary plastics is certainly one of the most important quality characteristics required by the market (Faraca and Astrup, 2019). Traces of contaminant inside the recycled stream of a single polymer, both as other materials and other types of polymers, can affect the final properties of the secondary raw material. As a consequence, the identification and separation steps in mechanical recycling plants for homogeneous plastic production are critical (Alsewailem and Alrefaie, 2018). Accurate separation methods are needed for plastic recycling, which allow to minimize contaminant in recycled products (Serranti et al., 2011; Wu et al., 2013; Cucuzza et al., 2021). Hyperspectral imaging (HSI), coupled with chemometric logics, can represent an important tool to perform waste plastics identification and separation, such as polyethylene and polylactic acid (PLA) (Ulrici et al., 2013), polyolefins from building and construction

* Corresponding author:
Paola Cucuzza
email: paola.cucuzza@uniroma1.it

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waste (Serranti et al., 2012), PE and polypropylene (PP) from household waste (Serranti et al., 2015a), low density polyethylene (LDPE) and high density polyethylene (HDPE) recognition along with PP, polyvinyl chloride (PVC) and polystyrene (PS) (Bonifazi et al., 2018a), plastic containing brominated flame retardants (Bonifazi et al., 2020; Bonifazi et al., 2021a). HSI is a technology that integrates conventional imaging and spectroscopy, being able to attain both spatial and spectral information from an object (Gowen et al., 2007). HSI can be used in recycling plant as sensor-based sorting method. The potential application of HSI is widely demonstrated in the literature in different sectors, in addition to plastic waste, such as food control (Serranti et al., 2013; Bonifazi et al., 2021b), demolition waste (Serranti et al., 2015b; Bonifazi et al., 2018b; Trotta et al., 2021), hazardous materials (Bonifazi et al., 2018c; 2019). Therefore, HSI techniques represent an attractive solution for characterization, classification, quality control and sorting-online application also for polyethylene terephthalate (PET) waste streams.

The proposed study was carried out to build a fast and efficient strategy to produce a high-quality recycled PET stream, based on HSI working in the SWIR range (1000-2500 nm), recognizing PET flakes and other polymers (considered as a single class of contaminant). Indeed, it is essential to continuously refine research on PET recycling, as it is one of the most used polymers for food and beverage packaging, thanks to its physical and chemical characteristics (Welle, 2011). Furthermore, the use of HSI in the SWIR range ensures the recognition of the slight spectral differences between polymers, reducing errors of misclassification (Singh et al., 2017; Lorenzo-Navarro et al., 2021). In order to increase the data processing speed, as requested by the application of the classification logic to be utilized at industrial plant level, a variable selection approach was tested, allowing to select the most useful wavelengths for the identification of PET and contaminant inside the full investigated spectrum. In fact, in the sensor-based sorting process based on HSI the wavelength selection is strictly necessary in order to obtain an identification of materials with minor time and production costs. Different variable selection methods can be applied to near infrared data analysis (Yun et al., 2019; Mehmood et al., 2012). In the proposed case study, among the most used variable selection methods, i-PLSDA (Interval Partial Least Square Discriminant Analysis) and VIP (Variable Importance in Projection) were tested. In detail, a classification model based on PLS-DA in full spectrum mode was set up to identify classes of polymers, i.e., PET and other polymers considered as a single class of contaminants. Subsequently, i-PLSDA and VIP methods were applied. Finally, the results obtained were compared in order to identify the best variables selection method with the best predictive performance close to full spectrum classification model.

2. MATERIALS AND METHODS

2.1 The investigated samples

The plastic waste flakes used for this study, collected from a recycling plant, were randomly sampled and are representative of an online sorting scenario. They have an average size of 16 mm. In detail, the samples are constituted of PET flakes contaminated by small quantities of other polymers (such as PE, PP and PS) (Figure 1).

The dataset used to build and validate the model was composed by 55 PET and 55 contaminant flakes (Figure 1a), divided into a calibration (33 PET and 33 contaminant flakes) and a validation (22 PET and 22 contaminant flakes) set, as shown in Figure 1b. Finally, the classification model was applied to 3 different test sets (Figure 1c, d and e) composed by 389 randomly sampled plastic particles collected from the same output flakes stream of the calibration and validation datasets.

2.2 Data acquisition

Data acquisition was performed at the Raw Materials Laboratory (RawMaLab) of the Department of Chemical Engineering, Materials & Environment of Sapienza University of Rome, using the hyperspectral system SisuCHEMA XL (Specim, Spectral Imaging Ltd, Oulu, Finland), working in the SWIR region (1000 - 2500 nm), with the Imspector N25E spectrograph, spectral sampling/pixel: 6.3 nm; spectral resolution: 10 nm (30 µm slit), spatial resolution: root-mean-square spot radius <15 µm (320), field of view of 20 cm with 15mm lens, scanning speed (mm/s): 72.50 and active pixels: 320 (spatial) × 240 (spectral). The lighting was reproduced by applying a diffuse line illumination unit. Images were acquired performing a line by line scan of each investigated dataset. Instrument was equipped with an integrate hardware and software spectral calibration architecture. Image data were automatically calibrated by measuring an internal standard reference target before each dataset scan.

2.3 Hyperspectral data analysis

The acquired hyperspectral images were analyzed through the PLS_toolbox (ver. 8.8 Eigenvector Research, Inc.) running in the Matlab environment (version R2020a, The Mathworks, Inc.).

As this paper aimed to identify plastic contaminants inside a flow stream of PET, independently from their nature, a two-classes model was built, based on a PET class and a single class of contaminants. A data preprocessing to improve the collected spectral characteristics and an exploratory analysis of the data based on Principal Component Analysis (PCA), were performed. PCA was chosen to perform exploratory analysis about classes variability, to identify and remove outliers (Bro and Smilde, 2014). Partial least square discriminant analysis (PLS-DA) models in full spectrum and variable selection mode were defined and applied. PLS-DA is a supervised technique that needs a prior knowledge of the data (Barker and Rayens, 2003), which is based on the reduction of dimensionality through partial least squares regression (PLS-R) with discriminating characteristics (Ballabio and Todeschini, 2009; Ballabio and Consonni, 2013).

Different pre-processing techniques and combinations of algorithms were tested following the examples usually adopted in literature (Amigo et al., 2008; Rinnan et al., 2009; Amigo, 2010; Martens and Næs, 2011; Vidal and

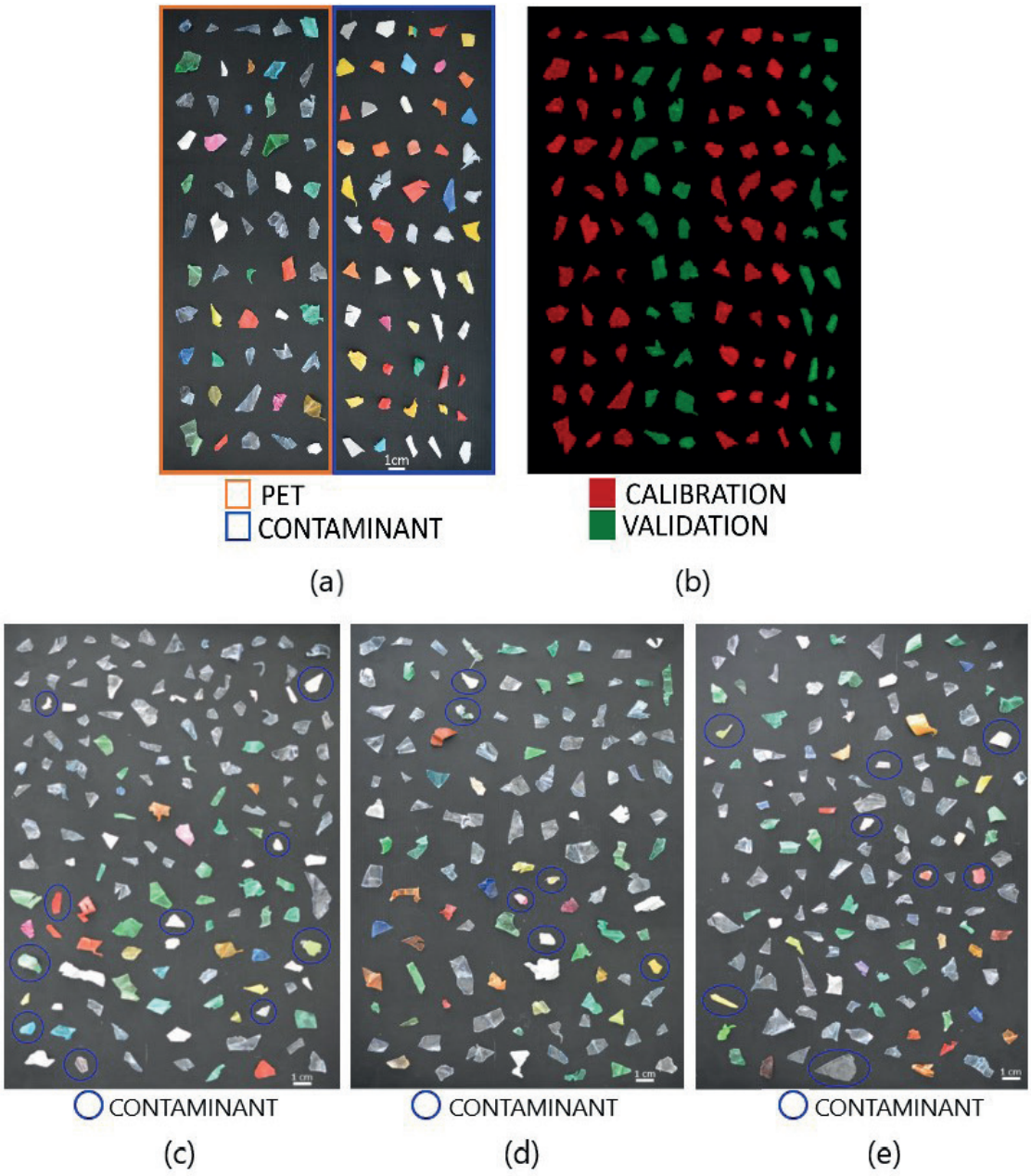

FIGURE 1: Source image of the investigated plastic samples divided in PET and contaminant flakes (a), false color image of the samples divided into calibration (red) and validation dataset (green) (b), source images of the randomly selected plastic flakes (contaminant marked by blue circles) for test 1 (c), test 2 (d) and test 3 (e).

Amigo, 2012; Calvini et al., 2016). Multiplicative Scatter Correction (MSC - median) method was used to remove scaling and offset effects, Savitzky - Golay smoothing (window 15 points) was chosen to delete high-frequency noise from samples, 1st derivative (polynomial order: 2, derivative order: 1 and window points: 21) was used to emphasize the characteristics of the bands and mean centering (MC) was applied to remove mean value and further improve the spectral differences between samples. The Contiguous Block (with a number of data splits equal to 10) cross-validation method was chosen (Figure 2) (Ballabio and Consonni 2013), in order to evaluate the complexity of models and to select the appropriate number of latent variables (LVs). Moreover, the optimal number of 3 LVs was decided by the smaller difference between RMSEC and RMSECV (Balage et al., 2018; Currà et al., 2019; Suhandy and Yulia, 2019).

Three PLS-DA classification models were built. The first model was developed using the full SWIR spectrum (1000-2500 nm), whereas the other two models using only wavelengths selected by i-PLSDA and VIP scores method. In detail, i-PLSDA selects a subset of variables by performing a sequential and exhaustive search for the best variable or combination of variables (Nergaard et al., 2000). The variable selection was made in "forward" mode, where the intervals was then included in the search, specifically

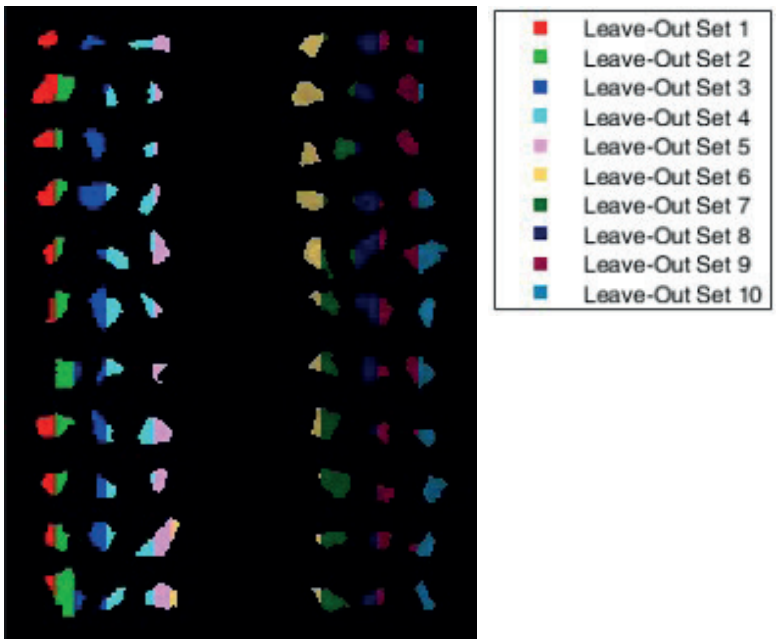

FIGURE 2: Results of the application of the contiguous block algorithm as cross-validation method on calibration dataset.

3 intervals with an interval size of 10. VIP scores estimate the importance of each variable in the projection used in a model (Chong and Jun 2005). VIP scores method was made considering 3 intervals with a dimension of 10 wavelengths. Such dimension was used as it corresponds to a wide spectral range of 60 nm, similar to that of common infrared broadband filters. In addition, 3 intervals were used to achieve an efficiency close to the full spectrum with a minimum number of wavelengths.

In order to compare the classification results, based on pixel detection, i.e., the attribution to one of the two classes (PET or contaminant) with reference to the number of pixels, the values of sensitivity, specificity and efficiency were calculated (equations 1, 2 and 3).

$$Sensitivity = \frac{True\ Positive}{(True\ Positive + False\ Negative)} \quad (1)$$

$$Specificity = \frac{True\ Negative}{(True\ Negative + False\ Positive)} \quad (2)$$

$$Efficiency = \sqrt{(Sensitivity \times Specificity)} \quad (3)$$

3. RESULTS AND DISCUSSION

3.1 Mean reflectance spectra

The average raw and pre-processed reflectance spectra of PET and contaminant classes are shown in Figure 3. PET spectrum was characterized by absorption bands of C-H_2 and C-H of the third harmonic region (1138 and 1180 nm), C-H of the second harmonic region (1400, 1660, 1720, 1830, 1910 and 1955 nm) and C-H stretching vibrations + C-H deformation of first combination region (2100, 2136, 2160, 2186 and 2261 nm). The mean spectrum of contaminant showed a complex fingerprint due the presence of different types of polymers. The main absorption bands detected for contaminant average spectrum were located around 1220, 1400, 1735 and 2320 nm. Finally, the pre-processed spectra allowed a differentiation between the two classes of materials.

3.2 Principal component analysis

PCA results are shown in Figure 4. Most of the variance was captured by the first two PCs, as shown in the PC1-PC2 score plot (Figure 4a), where PC1 and PC2 explained 74.61% and 13.76% of the variance, respectively. As shown in the PCA score plot, a separation was achieved between the clouds of PET and contaminants. In more detail, contaminant class showed higher variability, due to the presence of different type of polymers, being clustered across all quadrants in various groups mainly characterized by PC1 negative values. PET is characterized by a vertical cluster characterized by PC1 positive values. The loadings plot of PC1 and PC2 was shown in Figure 4b. The main PC1 variability is given by the wavelengths around 1170, 1375, 1705 and 2235 nm for positive values, while the negative values of PC1 are given mostly by the wavelengths 1265, 1475, 1865 and 2090 nm. PC2 is principally influenced by wavelengths around 1100, 1350, 1650 and 2100 nm for positive values, whereas negative values are more marked by wavelengths about 1235, 1470, 1750 and 2270 nm.

3.3 Full spectrum PLS-DA classification model

The results of the full spectrum PLS-DA classification model applied to the validation (Figure 5a) and test datasets (Figure 5b, c and d) are reported through the prediction images called “class predicted member”. PET and contaminant classes were correctly predicted in all datasets (cf. Figure 1 and 5).

The model correctly identified in the validation dataset 22 PET and 22 contaminant flakes (cf. Figure 1a, b and 5a), in the test 1 133 PET and 10 contaminant flakes (cf. Figure 1c and 5b), in the test 2 106 PET and 6 contaminant flakes (cf. Figure 1d and 5c), and in the test 3 126 PET and 8 con-

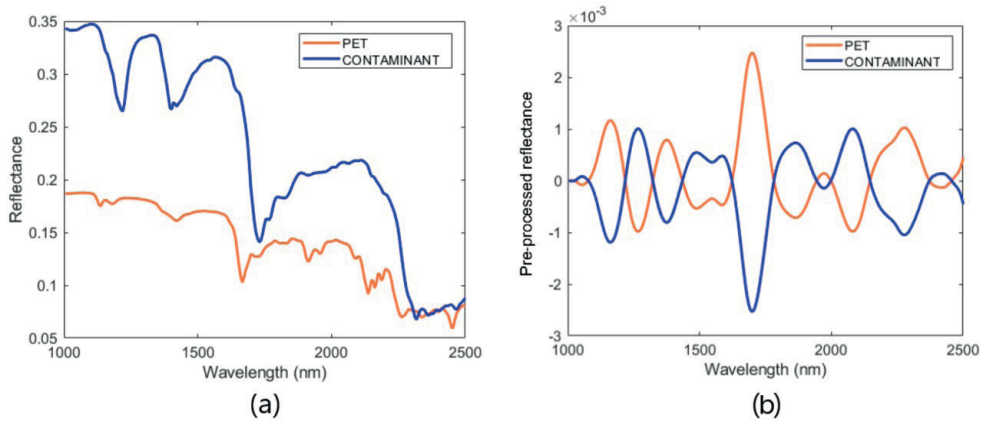

FIGURE 3: Average raw (a) and pre-processed reflectance spectra (b) of PET and contaminant classes.

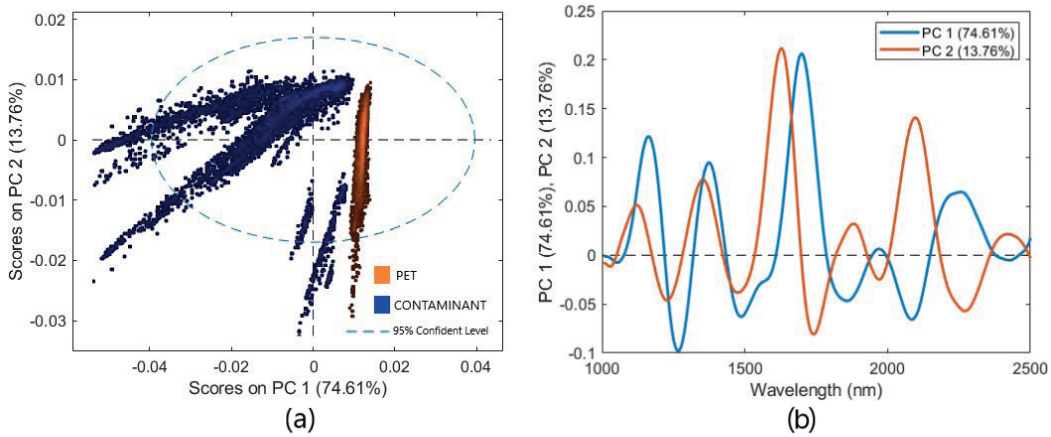

FIGURE 4: PCA score plot (PC1 - PC2) (a) and PCs loadings plot (b) of PET and contaminant classes.

taminant flakes (cf. Figure 1e and 5d).

The mean values of sensitivity and specificity, based on pixel detection, in calibration, cross-validation and prediction (Table 1) of validation, test 1, 2 and 3 datasets, showed the good performance of the model, with values of 1.00 for both classes.

Based on the application of i-PLSDA, the selected wavelengths were 1698-1754 nm corresponding to C-H of the second harmonic region, 1949-2005 nm and 2199-2255 nm corresponding to C-H stretching vibrations + C-H deformation of combination region of PET spectrum. Meanwhile the spectral bands selected using VIP scores method were 1138-1194 nm coinciding with C-H_2 and C-H of the third harmonic region, 1673-1729 nm corresponding to C-H of the second harmonic region and 2267-2324 nm correlated to C-H stretching vibrations + C-H deformation of combination region of PET spectrum. The spectral bands selected by i-PLSDA and VIP scores superimposed on the average spectra of the PET and contaminant classes are shown in Figure 6.

i-PLSDA classification model:. The results of i-PLSDA, in terms of prediction images, for the validation and test

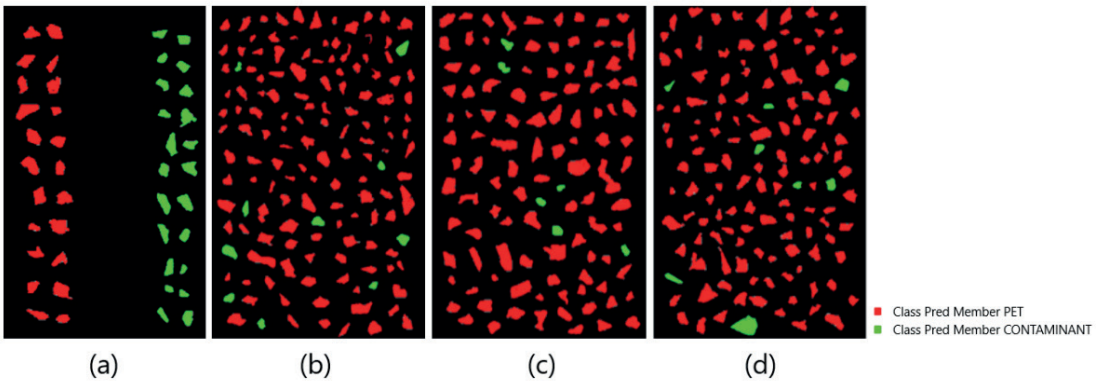

FIGURE 5: Full spectrum PLS-DA prediction maps for the validation (a), test 1 (b), test 2 (c) and test 3 (d) datasets.

TABLE 1: Mean performance values of full spectrum PLSDA classification for PET class in calibration, cross-validation and prediction phases. Selected LVs: 3.

	Sensitivity	Specificity
Calibration	1.00	1.00
Cross-validation	1.00	1.00
Prediction	1.00	1.00

datasets are shown in Figure 7.

PET and contaminant classes were correctly predicted, mainly in the validation dataset (cf. Figure 1a, 1b and 7a) and test 3 (cf. Figure 1e and 7d), except for some pixels due to border-effect (Figure 7b, 7c and 7d) and few samples attributed to the erroneous class (marked by yellow circles in Figure 7b and 7c), i.e., in the test 1: 4 badly assigned samples (cf. Figure 1c and 7b) and in the test 2: 2 badly assigned samples (cf. Figure 1d and 7c). The classification performances, based on pixel detection, obtained by i-PLSDA, shown in Table 2, revealed ranging values of sensitivity and specificity in calibration, cross-validation and prediction from 0.90 to 0.98.

VIP scores: The classification results obtained by the application VIP are shown in the prediction maps (Figure 8). PET and contaminant classes were correctly predicted, mostly in the validation dataset (cf. Figure 1a, 1b and 8a) and test 3 (cf. Figure 1e and 8d), except for some pixels due to border-effect (Figure 8b, 8c and 8d) and some whole samples assigned to the wrong class, marked by yellow circles in Figure 8b and 8c, i.e., test 1: 1 badly assigned sample (cf. Figure 1c and 8b) and test 2: 2 badly assigned samples (cf. Figure 1d and 8c). The classification performances, based on pixel detection, obtained by VIP (Table 2) revealed as sensitivity and specificity in calibration, cross-validation and prediction range from 0.97 to 0.99.

The classification performances, based on pixel detection, in term of efficiency in cross-validation and in prediction, were compared in Table 3. In more detail, good performances were obtained by both variable selection methods (i.e., i-PLSDA efficiency in prediction = 0.94 and VIP scores efficiency in prediction = 0.98), in fact the results were very close to the full spectrum PLS-DA model results (full spectrum PLS-DA efficiency in prediction = 1.00), considered as an ideal classification. In conclusion, the VIP scores method was the best variables reduction technique in terms of average values of sensitivity, specificity and efficiency.

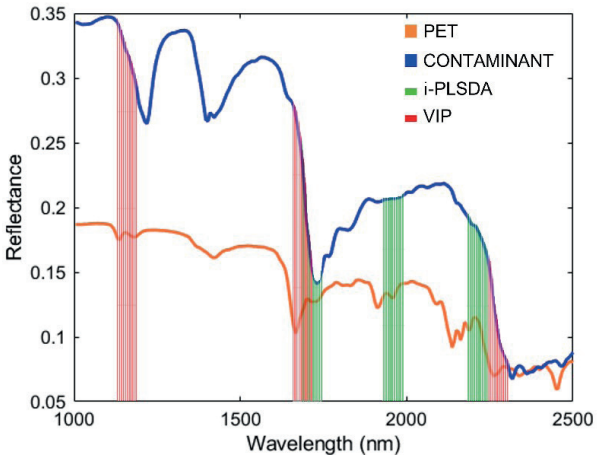

FIGURE 6: i-PLSDA prediction maps for the validation (a), test 1 (b), test 2 (c) and test 3 (d) datasets.

4. CONCLUSIONS

In the present study, SWIR hyperspectral imaging (1000 - 2500 nm) was applied to evaluate three different PLSDA-based classification models (i.e., full spectrum PLS-DA, i-PLSDA and VIP scores) in order to develop fast and robust strategies for sensor-based sorting of PET flow stream with reference to the presence of other plastics flakes considered as contaminant. The best prediction results were provided by VIP scores method, with sensitivity, specificity and efficiency average values close to the full spectrum PLS-DA, considered as an ideal prediction model. The results demonstrated how it was possible to obtain a good identification of contaminant in a PET stream, not only considering the full investigated spectral range, but also using a reduced number of wavelength bands from 240 to 30 obtained by variable selection methods, allowing the increase of processing speed and the construction of a simpler analytical logic with reduced costs, being both necessary requirements for industrial applications.

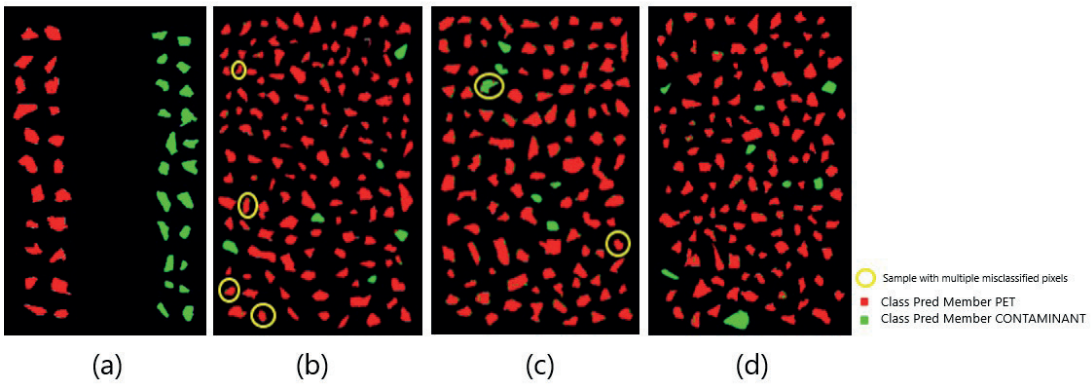

FIGURE 7: i-PLSDA prediction maps for the validation (a), test 1 (b), test 2 (c) and test 3 (d) datasets.

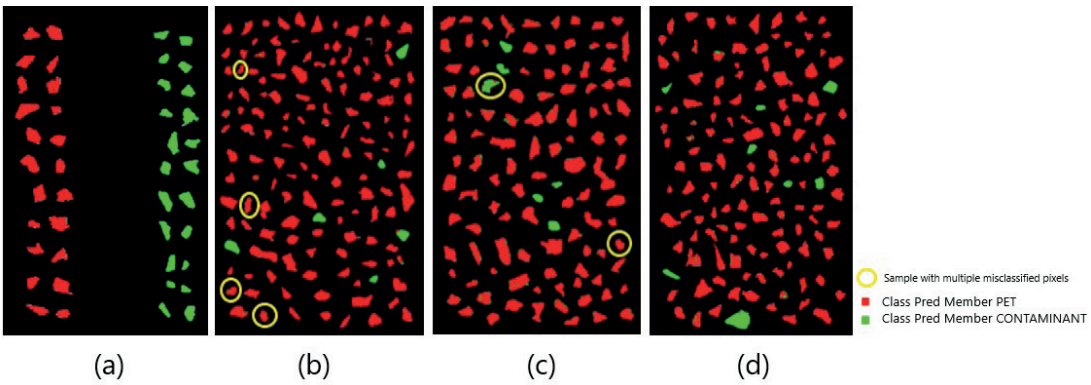

FIGURE 8: VIP prediction maps for the validation (a), test 1(b), test 2 (c) and test 3 (d) datasets.

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TABLE 2: Mean performance values of i-PLSDA and VIP classification for PET class in calibration, cross-validation and prediction phases. Used LVs: 3.

		Sensitivity	Specificity
i-PLSDA	Calibration	0.97	0.98
	Cross-validation	0.97	0.97
	Prediction	0.97	0.90
VIP	Calibration	0.99	0.98
	Cross-validation	0.99	0.98
	Prediction	0.99	0.97

TABLE 3: Classification performances in prediction and cross-validation phases in terms of mean efficiency values.

Models	Efficiency in cross-validation	Efficiency in prediction
Full spectrum PLS-DA	1.00	1.00
i-PLSDA	0.97	0.94
VIP scores	0.98	0.98

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A PLETHORA OF MICROPLASTIC POLLUTION STUDIES: THE NEED FOR A FORENSIC APPROACH

Alessandro Marrone * and Daniela Pellegrino

Department of Biology, Ecology and Earth Sciences, University of Calabria, 87036 Rende, Italy

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ABSTRACT

Microplastic pollution has been under the magnifying glass for several years now. Existing data relating to microplastics on surface waters suggest that they are globally widespread, but there are several gaps of knowledge in relation to understand how many there are in different locations, what is their composition, where do they come from and where they are going. What we need is a global collaborative effort to collect this information on a large scale. To date, standardized methodologies for the sampling and analysis of microplastics are still lacking, which therefore hinders the comparison of the reported data. This review summarizes the currently used methodologies for sampling and identifying microplastics in surface water, with the intention of contributing to the establishment of standardized and harmonized protocols. In addition, we focus our attention on the great potential that environmental forensic sciences have to face the delicate and insidious challenge of microplastic pollution, urging future research to go in this direction, in order to develop a rigorous and robust forensic method for microplastics study.

1. INTRODUCTION

Plastic pollution is undoubtedly one of the greatest global concerns of the 21st century. Nowadays, it is recognized as a complex, multidimensional and multi-sectorial problem with economic, environmental, public health, food safety and even cultural implications (Llorca et al., 2020). Complying with the ever-increasing demand, world plastic production has grown dramatically from year to year, reaching as much as 370 million tons in 2019 (Plastics Europe, 2019). This massive production of plastic materials seems destined not to stop, in fact this value is estimated to quadruple within the next 30 years, accounting for 20% of the global oil consumption and 15% of the annual carbon emissions by 2050 (MacArthur & Waughray, 2016). As if that weren't enough, such predictions will likely be aggravated by the excessive use and consumption of single-use plastics (including personal protective equipment such as masks and gloves) due to the outbreak of COVID-19 pandemic. In a business as-usual scenario, this projected increase in plastic production will be accompanied by the resulting mismanagement of waste, which often ends up in the environment through a variety of pathways. Currently, it is estimated that at least 8 million tons of plastic end up in the oceans every year, so without significant action and continuing to business as usual, by 2050 we will have more plastic than fish (by weight) in the world oceans (Jambeck et al., 2015). Plastics can remain in the ocean for hundreds of years in their original form and even longer in small particles (MacArthur & Waughray, 2016). Although many plastics are remarkably persistent, they are not immune to degradation (by photochemical reaction or mechanical actions), which can lead to the formation of plastic particles smaller than 5 mm generally known as microplastics (MPs). These small plastic particles may either result from the breakdown of larger objects, or they can intentionally produced in small sizes. At present, almost all of the world's oceans and seas are contaminated with MPs. Substantial quantities of MPs have been found in the global marine ecosystem (Shahul Hamid et al., 2018; Suaria, Achtypi, et al., 2020), from the tropics to the poles, including Arctic and Antarctic sea (Ross et al., 2021; Suaria, Perold, et al., 2020; Waller et al., 2017). The recognition of the magnitude of the problem has given rise to a series of initiatives by different institutions and the scientific community, which has shown an ever increasing interest in this problem and consequently, the number of published studies on surface MPs in the marine environment has significantly increased, but the result is a wide range of sampling, sample processing, sample analysis, data analysis, and reporting methodologies, which complicate cross-study comparability and larger scale synthesis. We currently have the awareness that MPs are everywhere, but knowledge about the polymeric composition, the spatial and temporal distribution of these

* Corresponding author:
Alessandro Marrone
email: alessandro.marrone@unical.it

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floating particles is still largely unknown. Environmental forensic approaches have the potential to tackle this ubiquitous challenge. Environmental forensics has emerged as an important growing area, which concerns the investigation of a diverse range of pollutants that have been, accidentally or deliberately, released into the environment (Philp, 2014). Environmental forensic analysis involves the application of defensible scientific methods to address questions related to understanding the extent, duration, and responsibility for environmental contamination sites in a regulatory and/or legal context. It generally involves the reconstruction of past environmental events, determining the timing, types, amounts and sources of chemical releases into the environment. Over the past decades, pollutants such as oil and heavy metals, have been the focus of investigation, however recently, emerging pollutants such as plastic waste have become of interest to environmental forensic scientists (S. K & Varghese, 2020). Although MPs are not a standard contaminant within the remit of an environmental forensic expert, the identification and characterization of pollutants and the consequent achievement of the pollution source is an integral part of any environmental forensic analysis. An effective forensic analysis involves the systematic and scientific evaluation of data obtained from field measurements or laboratory analysis, and historical information of the contaminated sites, in order to develop defensible scientific and legal conclusions regarding the release histories, age and source of a contaminant into the environment. In some cases, therefore, the forensic puzzle is resolved through such file review, while in others this guides the forensic strategy for testing and helps establish the most appropriate forensic tools. In the MPs case, for example, due to to the absence of standardized methodologies for the sampling and analysis of MPs, the comparison of the reported data may not provide any forensic answers. In order to manage environmental data and forensically interpret the results, specific approaches, commonly referred to as fingerprinting methods, should be carried out. "Fingerprinting" is a broad term that includes a variety of methods and techniques aimed to establish correlation and patterns of contamination that may be related to specific sources and/or time frames of contaminant release (I. Petrisor, 2005). Several main fingerprinting techniques are well established and their applicability proved (e.g., chemical fingerprinting, isotopic analysis, statistical methods). Methods and techniques for the study of MPs are continuously evolving with increased research in this field (Miller et al., 2021). Nevertheless, to date, the questions concerned with the level of MPs, the transport, eventual fate, and source identification are still to a large extent unanswered, mainly due to the fact that the forensic investigation of MPs is still in the infancy stages and the standards are not evolved enough.

The present review evaluates the current knowledge on the occurrence and abundance of floating MPs in the marine environment, providing a snapshot of the global MP contamination of surface waters and underlining the methodological differences of the various studies present in the literature. In addition, we focus our attention on the great potential that environmental forensic sciences have to face the delicate and insidious challenge of MP pollution, urging future research to go in this direction, in order to develop a rigorous and robust forensic method for MPs study.

2. ANALYSIS OF MICROPLASTICS IN SURFACE WATER

During the last years, several studies have evaluated the abundance, distribution and composition of floating MPs in marine environment. Table 1 summarizes some of the most recent works reporting MP concentrations found together with investigated areas, year of sampling, sam-

TABLE 1: Microplastics concentrations and methods used in some recent and representative works.

Study Area	Year of sampling	Sampling nets	Net mesh (µm)	Mean density	Analysis tool	Reference
Whole Mediterranean	2013	Neuston net	200	0.243 items/m²	Stereomicroscope	(Cózar et al., 2015)
Western Mediterranean	2013	Neuston net	200	0.40 ± 0.74 items/m²	Stereomicroscope/ FTIR	(Suaria et al., 2016)
Central-Western Mediterranean	2011-13	Manta trawl	333	0.147 items/m²	Optical microscope	(Ruiz-Orejón et al., 2016)
Central Mediterranen	2020	Manta trawl	333	0.13 ± 0.194 items/m²	Stereomicroscope/ FTIR	(Marrone, La Russa, et al., 2021)
Eastern Mediterranean	2018	Manta trawl	52	4.3 ± 2.2 items/m³	Stereomicroscope/ Raman	(Kazour et al., 2019)
Eastern Mediterranean	2013-15	Manta trawl	333	7.68 ± 2.38 items/m³	Stereomicroscope/ FTIR	(van der Hal et al., 2017)
Mid-west Pacific Ocean	2017	Manta trawl	333	34,04 ± 25,1 items/km²	Stereomicroscope/ µRaman	(S. Wang et al., 2020)
Eastern Indian Ocean	2019	Manta trawl	330	0.34 ± 0.80 items/m²	Stereomicroscope/ µFTIR	(C. Li et al., 2021)
Northwest Pacific Ocean	2017	Manta trawl	330	10^4 items/km²	Stereomicroscope/ µRaman/SEM	(Pan et al., 2019)
Southern Ocean	2016-17	Neuston net	200	188 ± 589 items/km²	µFTIR	(Suaria, Perold, et al., 2020)
Arctic Ocean	2016	/	63	40.5 ± 4.4 items/m³.	µFTIR	(Ross et al., 2021)

pling net and instrumental methods used for detection of MPs. Clearly the comparison between the different studies is very difficult due to the absence of a standardized sampling protocol and the lack of homogeneity both in the identification methods and in the expression of the results. In the following sections we summarize the sampling and analysis methods used so far aiming to promote homogeneous monitoring programs for MPs in aquatic environments.

2.1 Sample collection and preparation

The selection of sample collection methods is critical and will dramatically influence the study results (Miller et al., 2021). Most of the studies carried out so far used different versions of the Neuston and Manta trawl nets to sample sea surface MPs. Although either of these two trawling devices are recommended, a limiting factor is the net mesh sizes that can vary widely, strongly influencing the size spectrum and the abundance of collected particles (Gago et al., 2019; Lindeque et al., 2020). For instance, MP concentration using a 100 µm net is 10-fold greater than a 500 µm net. A nylon net (100 µm) revealed concentrations almost a hundred times higher than a manta net (333 µm) (Vermaire et al., 2017). Another study showed that an 80 µm mesh could retain up to 250 times higher concentration of plastic fibers than that of a 330 µm mesh (Dris et al., 2018). Despite these evidences, it should be noted that most of the currently used sampling techniques are only applicable to collection of MPs with certain size ranges. The Marine Strategy Framework Directive (MSFD) guidelines recommends a mesh size of 333 µm, and as can be seen from the table, the most usual mesh size ranging from 300 to 390 µm, which seems a reasonable cut-off to yield acceptable and meaningful samples under open net sampling conditions. However, the above examples suggest underestimation of smaller plastics based on traditional sampling, thus it remains of fundamental importance to adequately cover the lower MP size ranges in surveys that estimate current pollution levels. The quantity of MPs sampled has been expressed in different units, divided by the towed area (e.g., items/m^2) or volume of sampled water (items/m^3) or weight by sampled area (g dry weight/km^2). It is clear that having three different units of measurement to express the same quantity does nothing but complicate or sometimes make it impossible to compare the different studies. An interesting study showed that of the two most commonly used methods for calculating MP concentration (flowmeter and ship's log), ship's log provided consistently smaller abundances, with the exception of one sample, calling for a standardisation in the techniques and measurements used to quantify floating microplastics (Rivers et al., 2019). In addition, it has been proven that the concentration of MPs in the sea can be strongly affected by the presence of wind, therefore recent studies, taking into account this factor, corrected MPs concentration using a widely used theoretical model (Kukulka et al., 2012). Once collected, separation and extraction of MPs from samples are performed by sieving, density floatation and filtration, whose effectiveness depends on the particle size and MP typology (Martellini et al., 2018). Clearly it is important to adopt the most appropriate strategy based on the starting sample, also because the subtraction of even a single particular type of MP to the analysis can be costly, especially in investigations with forensic purpose (Kumar et al., 2021).

2.2 Microplastics identification and characterization

After field collection and laboratory preparation of the samples, MPs must be accurately identified from the remaining matrix and suitably characterized (W. Wang & Wang, 2018). Methods for characterizing MPs are rapidly evolving. Many older publications only visually identified likely plastic particles, the so called microparticles, while today the standard has shifted to a more accurate MPs identification (Miller et al., 2021). Particle analysis, or characterization, involves two steps. Morphological or physical categorization which take into account sizes, shape and color of potential MPs, followed by chemical characterization for definitive confirmation. This framework is based on the idea of characterizing samples initially using basic techniques and then progressively using more complex techniques in order to obtain a comprehensive picture of the composition of the basic material and its possible relationship to the origin source. In addition to identifying the basic material, tracing back the exact source requires rigorous efforts and the use of advanced technologies. Therefore a standalone method may not provide useful insights, and it is more useful to adopt several independent methods which would lead to identical conclusions (Cattle et al., 2010; Haddad, 2004; I. G. Petrisor, 2014). Analysis of MPs in environmental samples also requires an experienced laboratory due to the prevalence of background contamination sources.

2.2.1 Morphological characterization

In order to describe the morphological and physical properties that characterize MPs, the most common method involves the visual inspection of suspected MPs on optical microscope (typically a stereomicroscope). Magnified images using microscopy provide detailed surface texture and structural information of objects, which is essential for identifying ambiguous, plastic-like particles (Shim et al., 2017). To improve the accuracy of identification results, a series of previously established criteria must be taken into consideration during MPs visual inspection: absence of cellular or organic structures; fibers should have consistent thickness and color along the entire length and particles should be uniformly colored (Hidalgo-Ruz et al., 2012). Transparent and white particles should be further confirmed under a high-magnification microscope or a fluorescence microscope after Nile Red staining (Hidalgo-Ruz et al., 2012). Although high magnification optical microscopy, with optimized illumination methods, allows high resolution visual inspection, previous studies have shown that false identification of plastic-like particles using microscopy was often over 20%, and over 70% for transparent particles (Hidalgo-Ruz et al., 2012); highlighting the limits of visual characterization, which is subjective and prone to errors. In addition, this procedure, although it is the most widely used, is strongly influenced by several factors such as the sensitivity of the examiner, the particle shape and

size, the sample matrix and the microscope used, which could introduce potential bias affecting the final results (W. Wang & Wang, 2018). Moreover, visual inspection becomes more challenging as the size of the particles under consideration decreases, greatly increasing the possibility of misidentification and underestimation of these smaller elements, which are the most dangerous, since it has been suggested that smaller the particle size is, the higher are the chance of ingestion and retention rate by organisms (Gray & Weinstein, 2017; Kögel et al., 2020). For all these reasons, performing spectroscopic and chemical analysis to confirm the polymeric nature of the suspected MPs and to allow the specific identification of the different plastic types, avoiding MPs overestimation due to the presence of non-plastic items, isessential, especially for the smaller items (de Haan et al., 2019). Various techniques are feasible for MPs identification, such as scanning electron microscope (SEM) which allow to obtain high resolution images of a sample by firing a high-intensity electron beam at the sample surface and scanning it in a raster scan pattern (Crawford & Quinn, 2017). Surface details (<0.5 nm resolution) of the sample are imaged by the electrons at very high magnifications, thus differentiating the MPs from other organic or inorganic residues (Crawford & Quinn, 2017). Moreover, the combined use of SEM and energy dispersive X-ray spectroscopy (SEM-EDS) is able to provide detailed information about the MPs elemental composition and the inorganic additives they contain (Crawford & Quinn, 2017; Fries et al., 2013). SEM-EDS helps to further differentiate MPs from natural materials, but this technique requires considerable time and effort for sample preparation and therefore is hardly applicable for routine analysis of large numbers of samples.

2.2.2 Chemical characterization

Chemical characterizationis a final step to confirm the polymeric nature of MPs and distinguish them from other natural materials, when visual and microscopic observation is not enough to confirm particle nature. Additionally, this step allows for specific identification of different plastic types, which can be helpful in better understanding their parent materials, possible sources and input pathways, as well as the toxic chemicals associated with plastics with further instrumental analysis. The most common method in the chemical characterization of MP particles is spectroscopy, both Fourier-Transform Infrared (FTIR) and Raman. FTIR spectroscopy provides information on the specific chemical bonds and functional groups of each plastic polymer. The different chemical compositions of each materials produce unique infrared spectra, making it possible to identify an unknown substance by comparing its spectrum with the spectra of known materials. Raman spectroscopy, on the other hand, involves irradiating a suspected sample with a monochromatic laser beam, which results in a varying wave length of a backscattered light due to absorption, reflection, or scattering of the specific molecular structure and atomic composition (Crawford & Quinn, 2017). This so-called Raman shift can produce a unique spectrum for each polymer (Huppertsberg & Knepper, 2018). Thanks to their extreme efficacy and high degree of reliability, both of these are the most widely employed techniques in the chemical characterization of MPs from different environmental samples (Araujo et al., 2018; Shim et al., 2017; Silva et al., 2018). FTIR and Raman spectroscopy are both non-destructive methods that allow high throughput screening, requiring low sample quantities and respecting the environment (Araujo et al., 2018). In addition to the advantages, these two methods also share some disadvantages, in fact both require expensive instrumentation and are time-consuming when a large number of MPs need to be analyzed. FTIR, unlike Raman spectroscopy, can not only accurately identify the polymeric composition of MPs, but also provide further information about their physiochemical weathering by analyzing their oxidation intensity (Corcoran et al., 2009). Raman spectroscopy, on the other hand, is advantageous in terms of higher spatial resolution, wider spectral range, tighter spectral bonds and lower sensitivity to water interference than FTIR techniques (Käppler et al., 2016). At the same time, the main drawback of Raman spectroscopy is that it can be easily interfered by the presence of pigments, additives, or chemicals associated with MPs, which may adversely affect the accuracy of identification (Huppertsberg & Knepper, 2018). The application power of both of these methods is significantly increased in combination with microscopy. Micro-FTIR (μFTIR) and micro-Raman (μRaman) in fact allow the detection and identification of MPs with dimensions in the range between 10 and 20 μm (Lenz et al., 2015). All this is possible through the use of a single tool, by switching between the object lens and beam, whether it be IR or laser, thus allowing the chemical and physical characterization of the analyzed particles simultaneously (Elert et al., 2017).

2.3 Quality assurance and quality control (QA/QC)

It is standard practice in forensic investigations to apply strict anti-contamination protocols (Kumar et al., 2021). Forensic examinations are under scrutiny by the criminal justice system, therefore rigor and validity of approach are critical to their design (Woodall et al., 2015). The same principles should be applied when conducting monitoring programs on MPs, during which it is essential and crucial to adopt strict quality assurance and quality control (QA/QC) measures throughout the methodological process, in order to improve data quality (W. Wang & Wang, 2018). Background contamination can in fact cause a significant overestimation, negatively affecting the accurate assessment of MP abundance in the studied area. Despite the high potential for sample contamination, many studies still only report crude or limited procedures far less comprehensive than those that would be used in criminal investigations (Kumar et al., 2021). A recent study analyzed the problem of contamination in the analysis of MPs, proposing a protocol to be adopted during all analytical phases, from field sampling to the laboratory analysis (Prata et al., 2021). First of all, to check for background contamination, during sampling and laboratory handling process, a series of procedural blank tests should be conducted and processed in the same way as the real samples. During laboratory analyzes, as general control rules, some preventive measures

should be adopted, such as wearing 100% cotton laboratory coats (avoiding synthetic clothing) and nitrile gloves. In addition, all work surfaces should be thoroughly cleaned and all laboratory equipment (such as sieves, tweezers and glassware) should be rinsed with bi-distilled water. Besides, a special mention goes to the potential airborne contamination by fibers. The presence of high background levels of fibers in a working laboratory was demonstrated by Nuelle and coworkers (Nuelle et al., 2014) and confirmed by Woodall and coworkers (Woodall et al., 2015), which in their study developed a protocol based on the recommendations and procedures made for the forensic investigation of fibers, therefore it follows that are likely to be the most effective as they must stand up to the scrutiny of the courts. However, a very recent study has verified that, despite the application of the most rigid and severe anti-contamination protocols of a forensic nature, fiber contamination can be reduced (in this specific case by 36.9%), but cannot be completely avoided (Kumar et al., 2021). To overcome these problems, the authors therefore suggest protocols which, in addition to minimizing contamination, also allow monitoring it, for example outfitting the whole team in the same thin garments in unusual colors, ideally also with unusual fiber morphology. The authors therefore state that using forensic analysis techniques, which aim to completely profile a particle, including its morphological, optical and chemical characteristics, enable to obtain information that allows much more confident conclusions to be drawn as to whether it comes from the environment or procedural contamination.

2.4 Source identification

One of the biggest challenges in environmental forensic investigations is determining the source of the contaminant. Identifying the sources of pollutants and the extent of their contribution is one of the first steps in their management (Kumar et al., 2021). Before continuing, however, it is necessary to to keep in mind a concept: it is very important to make very clear that source refers to the point of release, not the manufacture of a particular product. This is very important since there were papers published many years ago that tried to use certain characteristics of products made by certain manufacturers and use those properties to determine whether a particular released product was produced by that particular company (Philp, 2014). Having made this important premise, we can continue by saying that establishing provenance is not easy when the materials are microscopic in nature. Fortunately, as we have seen previously, MPs have tell-tale chemical fingerprints of their origin that can be recognized using modern analytical chemistry techniques. The first step towards the identification of the origin of microplastics starts with their complete and detailed characterization. As in any forensic context, the complete labeling of the samples provides invaluable information. For instance, fibers may result from washings of textile products, whereas regular shapes like spheres, cylinders, etc., are indicative of specific sources (i.e. personal hygiene products) and the detailed labeling cannot be missed when the purpose of analysis is source identification (Farooq et al., 2022; Kumar et al., 2021). If the MP is secondarily sourced from a larger plastic product, the debris will be irregularly fragmented. Observing MPs degradation patterns under an optical microscope can provide a basic idea on the resident time of MPs in the environment (Kumar & Varghese, 2021). Such observation will help in answering the questions if the MPs are recently formed or are quite old. Sharp edges of a fragment indicate freshly formed MP when compared to a MP with blunt edges. Also, crack formation, loss of material from the surface, etc. are indications of longer residence time in the environment (Kumar et al., 2021). In aquatic environments MPs age can be a determining factor also in relation to their origin, for example, a smooth MP suggests a local source, while a worn-out MP with a biofilm may suggest a distant source (Farooq et al., 2022). Moreover, studies have also shown that there is a significant effect for the shape on the MPs transport in the environment (Harrison et al., 2018; Jahnke et al., 2017). Unfortunately, many MPs studies limit their observations to colour, size and classification of the sample set as a whole rather than fully characterizing each microplastic as seen in forensic examinations (C. M. B. Gwinnett et al., 2021). In this regard, much can be learnt from forensic fibre analysis, where polymer fibres are examined for their colour, width, cross-sectional shape, presence of inclusions and optical properties such as its birefringence and sign of elongation (Robertson et al., 2017). This is the direction taken by Gwinnet and coworkers, who in a recent study have proposed a new workflow for the recovery and analysis of MPs, particularly fibres, which allows greater differentiation between samples and aids in source identification (C. M. B. Gwinnett et al., 2021). Obviously, the increased information of spectral techniques allows polymers and sometimes additives to be clearly identified, which can be utilized for chemical identification and MPs characterization (Primpke et al., 2020). Moreover, in recent years the forensic analysis of polymers has been improved by the application of advanced statistical analysis techniques (Cowger et al., 2020; Fang et al., 2022). In fact, several studies have processed the large data sets produced by the various spectral imaging techniques used, in analysis and identification groups, thanks to principal component analysis (PCA) (Fang et al., 2022; Y. Li et al., 2020; Lorenz et al., 2019). PCA is a universal method of static data analysis which projects high-dimensional data onto a low-dimensional space, commonly two dimensions. The basic idea of PCA is to convert a set of correlated variables into a new set of uncorrelated variables called principal components (PCs), which are linear combinations of the raw variables that account for a large proportion of the total variance of raw data (Jollife & Cadima, 2016). Wanting to simplify, PCA allows to manage large datasets by reducing their dimensionality, increasing the interpretability but at the same time minimizing the loss of information (Jollife & Cadima, 2016). Over the past few years, PCA has been increasingly used to identify and differentiate particles, materials or cells in various fields of research, such as chemistry and biology, but also environmental and forensic science (Fang et al., 2022). Therefore, PCA is considered suitable for the analysis of microplastics by de-

coding their spectrum matrix. It allows differentiation between the spectra of synthetic and natural origin, resulting in the enhanced visual accessibility by creating a two-dimensional image of the MP (Farooq et al., 2022). Data of similar spectra are grouped and labelled accordingly by comparing it to the reference spectra. A lot of studies state the effectiveness of using PCA for the identification of polymers, nevertheless further research is still needed to develop the reference library, in order to ensure the automatic decoding of the spectrum matrix for mapping and imaging. Furthermore, advances in analytical and data exploration techniques in recent years have helped researchers to evaluate larger patterns of contamination or "footprints" in the environment. Statistical methods, including PCA, provide additional analytical tools to obtain fingerprints, as they aim to correlate contamination with sources (I. Petrisor, 2005). Increasing or decreasing contamination trends are established over time and space by widely available statistical techniques. Therefore, more research is required to collect forensic information regarding the frequency and distribution patterns for different shapes, sizes, colours and types of polymers and the possible entering pathways (Browne et al., 2011). Tracing the MPs source is in fact extremely challenging, due to the different use of a single type of polymer, multiple manufacturing techniques, use of different additives in the same type of polymer by different industries, etc. (Kumar & Varghese, 2021). Only the application of robust environmental forensic approaches and protocols and a correct interpretation of the information obtained in the previous phases, starting from those collected during the sampling (i.e. GPS coordinates, along with local details such as geographical features, proximity to harbor or wastewater treatment plants, influence of river, type of beach activities, etc.) up to the analyzed data, can allow to address this challenge (C. Gwinnett et al., 2021; Kumar et al., 2021). Kumar and Varghese (S. K & Varghese, 2020), applying a framework developed for forensic investigation, were able to reach some useful conclusions regarding the source of each type of MP they observed; in some cases it was possible to identify the exact source, whereas in other cases only the pathway through which the MP reached the marine environment could be identified. Clearly, the further away the source of pollution is, the more difficult it is to trace it. This, for example, is the case of the Antarctic continent, the southernmost part of the planet, which despite its geographical isolation, is not protected from the negative impact of human activities (Marrone, La Russa, Brunelli, et al., 2021). Several contaminants, such as heavy metals and MPs, have been detected in this area, even in significant amounts, despite the pollution sources being very distant (Cincinelli et al., 2017; Marrone, La Russa, Brunelli, et al., 2021; Suaria, Perold, et al., 2020). Particularly interesting is a study recently published by Leistenschneider and collaborators, which using a forensic approach were able to discriminate between environmental and vessel-induced MPs, and thus revealing that 45.5% of all MPs they have sampled in the Weddell Sea (Antarctica), it was actually due to ship-induced contamination (Leistenschneider et al., 2021).

3. CONCLUSIONS AND FUTURE PERSPECTIVES

Plastic pollution has become one of the most pressing environmental issues. Existing data relating to MPs on surface waters suggest that they are globally widespread, however, there are still some bias that do not allow for a reliable and comparable quantitative data analysis between different studies. Several analytical steps in the study of MPs have become critical bottlenecks that prevent a global collaborative effort for large-scale data analysis. Therefore, the establishment of standardized and harmonized protocols for sampling, identification and expression of the results, and so of all operating procedures involved in the cycle of assessing environmental MPs from field sampling to laboratory analysis, it is essential to improve the current knowledge on MPs phenomenon. Furthermore, to try to answer still unresolved questions concerned with the real extent, source and fate of MPs, the forensic approach applied to environmental studies represents an added value for the development of more complete strategies and robust methods, thus allowing to provide a real and more complete picture of MP pollution in the marine environment.

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MICROPLASTICS IDENTIFICATION IN LANDFILL LEACHATES BY DIFFERENT SPECTROSCOPIC TECHNIQUES

Camilla Simongini [1,*], Milda Pucetaite [2], Silvia Serranti [1], Martijn van Praagh [3,4], Edith Hammer [2,3] and Giuseppe Bonifazi [1]

[1] *Department of Chemical Engineering, Materials & Environment (DICMA), Sapienza University of Rome, Rome, Italy*
[2] *Department of Biology, Lund University, Lund, Sweden*
[3] *Centre for Environmental and Climate Science, Lund University, Lund, Sweden*
[4] *Ensucon, Stora Södergatan 8C, 222 23 Lund, Sweden*

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ABSTRACT

Discovered more than 40 years ago, microplastics have become a major environmental issue. With increasing global plastic production, microplastics are of growing concern. Landfills have been pinpointed as primary sources of microplastics to surface waters and they have, in fact, been identified and quantified as such. Due to their small size, different polymers and interfering non-plastic materials, microplastics are difficult to analyse in a complex matrix such as leachate. To elucidate the impact of pre-treatment on the performance of the most common microspectroscopical analytical methods employed, i.e., FT-IR and Raman, we re-examined previously pre-treated and analysed leachate samples. Additionally, we subjected duplicates of previously analysed samples to different concentrations of H_2O_2 with varied reaction times to digest and remove non-plastic organic matter. The pre-treated samples were subjected density separation and (re-)analysed by means of FT-IR and Raman microspectroscopy. Larger particles were also analysed by near-infrared (NIR) hyperspectral imaging. We found the concentration of H_2O_2 to impact the possibility of identifying and quantifying PET particles, with Raman scattering microspectroscopy enabling more particles to be counted than with FT-IR. This is likely due to the increased detectable particle size range, from around 50 µm for FT-IR to 1 µm for Raman scattering microspectroscopy. Optimized H_2O_2 concentration with subsequent density separation enabled to clearly identify numerous PE particles, but also PP, PS, and PET particles and carbon compounds with Raman scattering microspectroscopy. Hyperspectral imaging performed well for particles larger than 30 µm.

1. INTRODUCTION

Plastic pollution is one of the most pressing environmental issues. Plastic production has been increasing year by year and is projected to double in the next 20 years (World Economic Forum et al., 2016). It is estimated that at least 10% of plastic produced ends up in the environment; through storm water, wastewater treatment plants, waste management and littering, as well as by air deposition, it reaches the oceans. Microplastic particles (MP) are defined as plastic particles below 5 mm in size (Arthur, 2009; Thompson et al., 2004), of mixed shape, size, colour, and chemical composition that are present in air, soil, freshwater, seas, biota, and in several components of our diet (Science Advice for Policy by European Academics -SAPEA-, 2019). Microplastic pollution is estimated to account for 60–80% of marine litter (Derraik, 2002). Storm water from road run off and wastewater are regarded as the main transport routes for microplastics to surface waters (Bläsing and Amelung, 2018, Eriksen et al., 2013; Barnes et al., 2009; Horton et al., 2017). Landfilling and even leachate has been suspected to be a significant source of microplastics to surface waters as well (Sundt et al., 2014, Magnusson et al., 2016).

Leachate composition widely varies depending on the age of the landfill, the type of accepted waste, operational praxis, whether the landfill is capped, etc. Generally, landfill leachates contain nitrogen, salts, and inorganic and organic micropollutants such as metals and persistent organic substances (Kjeldsen et al., 2002; Haglund et al., 2015; Modin et al., 2011).

Comprehensive information or data on the amount of microplastic particles in leachate or their potential environmental impacts is still scarce. The Nordic Waste Group

* Corresponding author:
Camilla Simongini
email: camilla.simongini@gmail.com

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and the Marine Group under the Nordic Council of Ministers, therefore, commissioned the design and conduction of a study on the occurrence of microplastics in landfill leachates in Norway, Iceland and Finland, in order to elucidate whether landfill leachates are potentially significant sources of microplastics to surface waters (van Praagh et al., 2018).

Isolation of microplastic particles from the complex environmental matrix that constitutes landfill leachates is crucial. It typically includes sieving/filtration followed by chemical treatments to remove non-plastic organic materials that may obstruct further analysis (Zarfl, 2019). Identification of microplastics can be done by visual inspection of the isolates. It allows estimating the amount of the microplastic particles, but misses information on the specific polymers comprising them, which can be important for determining the microplastics source and environmental impact. Therefore, spectroscopy-based methods have been utilized to characterize microplastic particles in various environmental samples.

The most common methods include infrared absorption (IR) and Raman scattering microspectroscopy (Käppler et al., 2016), as well as near-infrared (NIR) hyperspectral imaging (Shan et al., 2018). IR spectroscopy and NIR hyperspectral imaging have been found to be suitable to characterize larger (>50 µm) particles, but spectral analysis can be hindered by contributions of contaminants on microplastic particles' surfaces. Furthermore, only thin (<10 µm) particles can be analysed in transmission mode of IR spectroscopy, and the reflection spectra can be affected by baseline artefacts resulting from scattering from wavelength-scale sized, irregular shaped particles (Rasskazov et al., 2019). Meanwhile, Raman microspectroscopy provides higher spatial resolution (down to 1 µm), but it is more sensitive to sample pre-treatment as organic contaminants can yield fluorescence masking the Raman signal. Therefore, further comprehensive studies are necessary to identify the most suitable sample pre-treatment and analytical techniques for microplastic identification and characterization in landfill leachates.

The work presented here aims at providing guidelines in support of the identification of microplastic particles in landfill leachate, paving the way for scalable applications aimed at better understanding the typology and size of microplastic particles emitted by landfill leachates. This is a fundamental aspect for dealing with plastic-waste management in any context, including the minimization of plastic-waste production at the source. This scope is pursued through the further analysis of samples collected and pre-treated in the aforementioned project (van Praagh et al., 2018), by comparing three different techniques for microplastic analysis while studying the effects of sample preparation on analytical results.

2. METHODS AND MATERIAL

2.1 Leachate samples

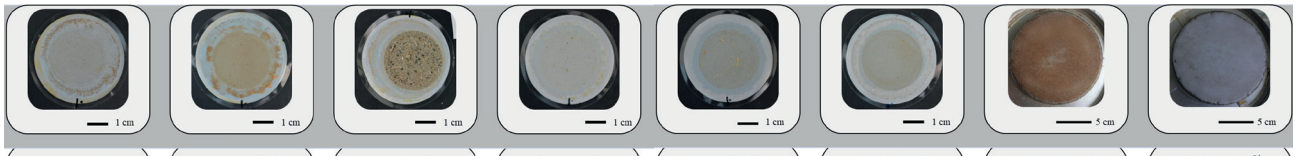
As part of the study commissioned by the Nordic Waste Group and the Marine Group under the Nordic Council of Ministers, leachate samples were collected by pumping leachate through three different stainless-steel filters of different mesh size (5000, 411, 47 µm). Subsequently, filters were rinsed with deionized water, re-filtered and subjected to a hydrogen peroxide solution (15% H_2O_2) in order to remove organic and non-organic materials. Screening of split samples (particles of >500 and >50 µm), showed no or few particles >500 µm (see van Praagh and Liebmann, 2019, for details).

For this study, we chose those samples available from the aforementioned investigation that exhibited the highest number of MP particles with relatively low particle density for Raman scattering microspectroscopy analysis (see Figure 1). All samples, except for u1 and u2, had been previously treated and analysed at the Austrian EPA's laboratory in Vienna by means of µ-FT-IR (Fourier transform infrared) microspectroscopy and imaging (see van Praagh and Liebmann, 2019).

2.2 Sample treatment

2.2.1 Hydrogen Peroxide Treatment

Selected samples were treated with 15 or 30% H_2O_2 solution, see Table 2. Sample 9, already treated with a 15% solution of H_2O_2 at the laboratory in Vienna, underwent treatment in 30% solution of H_2O_2 for 6 days. Nuelle et al.,



Sample 3	Sample 4 bis	Sample 5	Sample 7	Sample 8	Sample 9	Sample u1	Sample u2[3)]
• Iceland • Non-hazardous landfill • Raw leachate • 0 microplastic detected • SBR previously identified polymer[1)]	• Iceland • Non-hazardous landfill • Raw leachate • 60 microplastic detected • PE, PS, PET, PU previously identified polymer	• Finland • Non-hazardous landfill • Raw leachate • 0 microplastic detected • None previously identified polymer	• Finland • Non-hazardous landfill • Raw leachate • 88 microplastic detected • PE,PVC,PS,PET, PA,PU,PMMA previously identified polymer	• Finland • Non-hazardous landfill • Raw leachate • 138 microplastic detected • PE,PS previously identified polymer	• Finland • Hazardous landfill • Treated leachate • 60 microplastic detected • PE, PS, previously identified polymer	• Finland • Non-hazardous landfill • Raw leachate • - • -	• Norway • Non-hazardous landfill • Raw leachate • - • -

1) Plastic polymers included in the screening: Polyethylene (PE), Polypropylene (PP), Polyvinylchloride (PVC), Polystyrene (PS), Polyethylene terephthalate (PET), Polyamide (PA), Polyurethane (PU), Polycarbonate (PC), PMMA (Polymethylmethacrylate), POM (Polyoxymethylene), SBR (Styrene-Butadiene-Rubber (essentially the main component in tyre rubber, and PMB (Polymer-Modified Bitumen, an admixture in asphalt paving); 2) SBR identified in screening; 3) duplicate of 4bis

FIGURE 1: Samples background information: type and location of landfills covered in this study, microplastics (MP) count and polymers detected previously by FT-IR microspectroscopy (see van Praagh and Liebmann, 2019).

2013, found that this removes as much as 50% of non-plastic organic matter.

In order to test potential impact of H_2O_2 on microplastic particles, PET and PP particles from reference materials were treated with a 30% solution of H_2O_2 for 3, 8 and 15 days.

2.2.2 Density separation

Particles were separated by dispersion in a NaCl solution (35 g of NaCl in 100 ml of *milliQ* deionized water), see for example Quinn et al., 2017. The solution was mixed with a magnetic stirrer for at least 5 minutes, after which NaCl grains were undissolved on the container bottom, indicating saturation. The solution was left to rest, allowing density separation. To remove the floating particles (plastic particles, except for PET and PVC, exhibit a lower density than a saturated NaCl solution), two different methods were used, see Table 1. Subsequently, particles were deposited onto Anodisc© (Whatman) aluminium oxide filters with a polypropylene support ring (25 mm, pore size 0.2 µm)

2.3 Sample analysis

2.3.1 Raman microspectroscopy

Raman microspectroscopy measurements on all samples were performed using a LabRAM HR Evolution Raman system (Horiba Scientific), equipped with a front illuminated thermoelectrically deep cooled Charge-Coupled Device (CCD), called Syncerity (Horiba Scientific). Raman scattering spectra were recorded with a 50/0.5 LWD (Long Working Distance) objective and a diffraction grating of 600 gr/mm.

Microplastic identification in leachate samples requires the setting of specific optical measurement parameters to successfully apply Raman spectroscopy. Thus, initial analysis was carried out on single particles within the samples, chosen randomly and with a diameter larger than 10 µm. In addition, several spectral maps of multiple particles were recorded, showing areas with a size of 1 cm x 0.5 cm, easily discoverable for later analyses.

The defined measurement parameters used were as follows: excitation wavelength was 632.8 nm (He-Ne laser), with an acquisition time of 5-18 seconds; 5-8 scans were averaged for a single spectrum, a wavenumber range 1800 to 800 cm^{-1}; excitation power set to 5-10% of the total laser power (17 mW).

In case of fluorescence when using the 632.8 nm excitation, the spectra were recorded with 785 nm (diode solid-state laser) excitation wavelength; acquisition time of 60 seconds, 12 scans for a single spectrum and an excitation power set to 100% of the total laser power (100 mW). Spectral analysis was performed by comparing the recorded Raman spectra of particles in the samples with spectra of references (microplastics of PE, PP, PS, etc.).

2.3.2 FT-IR Microspectroscopy

FT-IR microspectroscopy measurements on samples 7 and 8 were performed with a Hyperion 3000 microscope connected to a Tensor 27 IR spectrometer *(Bruker)* in reflection mode. Either a single channel mercury cadmium telluride (MCT) detector was used to obtain a single spectrum, or a focal plane array (FPA) detector, with a 64×64 array size, was used to obtain an IR multispectral image. The field-of-view of the ×15/0.4 Cassegrain objective that was used in these measurements is 250×250 µm. The spectra were recorded with 4 cm^{-1} spectral resolution. 64 interferograms were averaged and the result was Fourier-transformed into a spectrum applying the Blackmann–Harris 3 apodization function and zero filling factor 2.

Additionally, a ×20 Attenuated Total Reflection (ATR) objective (field-of-view 100×100 µm) combined with the single channel MCT detector was used to record IR spectra of single particles. Spectral analysis was performed by comparing the recorded IR spectra of particles in the samples with spectra of microplastic (PE, PP, PS, etc.) references.

2.3.3 Hyperspectral Imaging

Hyperspectral imaging was performed on sample 8, by using the SISUChema XLTM Chemical Imaging Workstation (Specim, Finland), equipped with ImSpectrorTM N25E imaging spectrograph. It works in the short-wave infrared (SWIR) range (1000-2500 nm). The device has been equipped with a macro lens, that has a field-of-view of 1 cm, since the particles in these samples are very small. One pixel corresponds to about 30 µm. The spectral resolution was 6.3 nm.

TABLE 1: Sample and reference treatment type and duration prior to spectroscopic analyses.

ID code	Previous treatment Vienna	Treatment Solution	Duration	Density separation	Floating particles removal method	Comment
Unit	H_2O_2 (%)	H_2O_2 (%)	d	Yes/no	-	-
3	15	-	-	Yes	Vacuum pump	-
5	15	-	-	Yes	Syringe filter	Particles moved by tweezers
9	15	30	6	No	-	-
u1	-	30	6	Yes	Vacuum pump	-
u2	-	15	6	Yes	Vacuum pump	-
PET	-	30	3/8/15	No	-	Reference material
PP	-	30	3/8/15	No	-	Reference material
PP	-	30	3/8/15	No	-	Reference material

The analysis of environmental samples with hyperspectral imaging requires building a hierarchical model based on pre-defined plastic polymers. Six polymers were selected - PA, PET, PE, PP, PS, PVC – their raw spectra acquired and carefully analysed to observe and compare characteristics, due to the different absorption of light of molecules in the SWIR range. Applying the procedure described by Bonifazi et al. (2018) a hierarchical Partial Least-Squares Discriminant Analysis (PLS-DA) model was built and represented by a dendrogram.

PLS-DA is a supervised classification technique that requires a prior knowledge of the data. In order to provide a better discrimination of each variable (wavelength), samples are classified with PLS-DA into predefined groups, by forming discriminant functions from input variables (wavelengths) to yield a new set of transformed values providing a more accurate discrimination than any single variable (wavelength) (Ballabio and Consonni, 2013). A discriminant function is then built using reference samples to be later utilized to classify samples belonging to an unknown set. Once the model is obtained, it can be applied to an entire hypercube and for the classification of new hypercubes (Bonifazi et al., 2018).

To create a hierarchical model, objects are progressively divided into a first and successive levels of subsets, until each subset contains a single object (Monakhova et al., 2016), with the main objective of isolating the most different object, for each step.

3. RESULTS AND DISCUSSION

3.1 Raman Scattering and FT-IR microspectroscopy results

Raman scattering spectra of particles within randomly chosen areas (see example in Figure 2) of five samples were acquired. A total of 465 points were analysed within 2 to 3 areas per sample. Distribution and spectral analysis results are shown in Table 2.

From the results displayed in Table 2, the following can be derived:

- Many spectra identified as stemming from PET exhibited two unidentified bands at 1370-1399.3 cm-1 in the spectrum (see Figure 2), which are potentially due to external contamination, as they are not observed after treatment with 30% H_2O_2 and density separation (see Table 2 and Section 3.4 for more details).
- 26% of all detected particles are made of PET (“PET” and “PET + unidentified spectra”), 78% of which show the unidentified spectral bands at 1370-1399.3 cm-1.
- Sample 8 appears to have the highest number of PET particles (“PET” and “PET + unidentified spectra”) related to the total number of analysed particles within the sample itself (about 41% of all the detected particles of the sample).
- 36% of particles are made of undefined materials; for 37% of the particles’ spectra were too noisy or obscured by fluorescence to analyse.

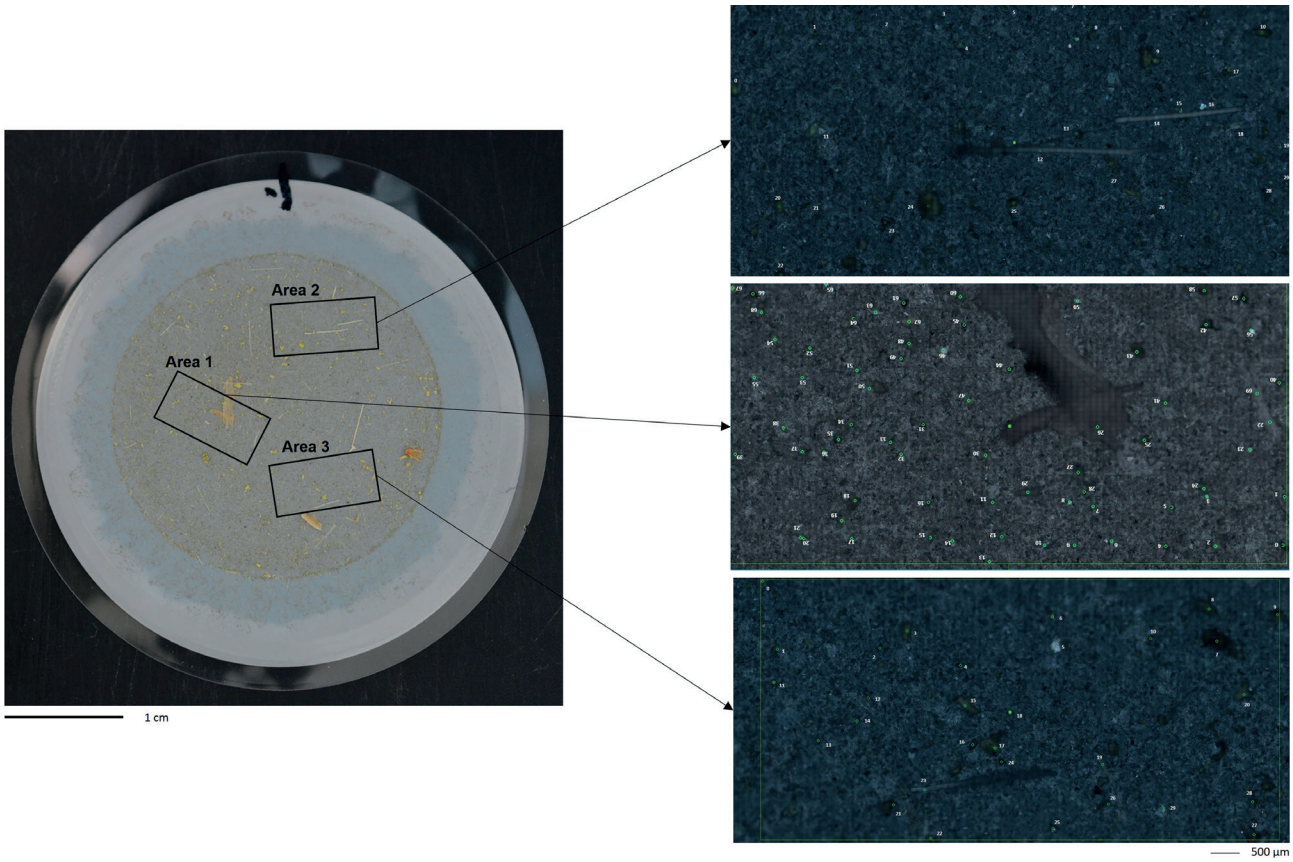


FIGURE 2: Example of mapping areas. Mapping areas within sample 8 with measurement points on randomly selected particles highlighted on the right (70 points in total).

TABLE 2: Type and number of particles detected with Raman scattering microspectroscopy within the mapped areas.

Sample	Area ID	No signal[1)]	PET	PET+ unident.[2)]	Unidentified spectra	Undefined materials[3)]	Particles analysed	Plastics ident. / Particles analysed (%)
3	1	20	7	16	3	19	65	35
	2	39	5	9	6	6	65	22
4bis	1[4)]	4	-	-	-	26	30	-
	2	11	-	-	4	15	30	-
7	1	16	3	1	5	5	30	13
	2	9	1	2	2	11	25	12
	3	9	1	4	1	14	25	20
	4[3)]	3	4	-	-	23	30	13
8	1	21	2	23	15	9	70	36
	2	5	0	12	6	7	30	40
	3	4	1	15	3	7	30	53
9	1[5)]	9	0	4	0	7	20	20
	2	11	1	6	3	9	30	23
	3[5)]	9	1	2	4	9	25	12
Sum	14	170	26	94	52	167	465	26

- No other plastic polymers have been detected. This result is unexpected, since the analysis carried out during the previous study by using FT-IR microspectroscopy (see Figure 1) showed the presence of several microplastic polymers.

In Figure 3, an example of identifying PET from Raman spectra is shown. Most of the spectral bands of the analysed particle in the sample ("PET sample") coincide with the ones observed in the spectrum from the "PET reference" particle. Two unidentified bands at 1370-1399.3 cm-1 in the spectrum of the particle do not correspond to any of other plastic materials; we tentatively associated the occurrence of these bands with contaminations resulting from sample treatment. This is discussed more in detail in section 3.4 of this work.

For comparison and clarification of Raman microspectroscopy analysis results, sample 8 was re-analysed via FT-IR microspectroscopy. The main results from this analysis are as follows.

- A visible particle in sample 8 shown in Figure 4 was clearly identified as PE (see Figure 5).
- Spectra from other particles were recorded; however, they were distorted by the effects such as refractive index dispersion (see for example Korte, 1990). This phenomenon distorts the shape of the absorption bands, thus complicating or hindering the identification of materials from smaller particles.
- For the aforementioned reasons, only the PE largest particle was clearly identified through FT-IR analysis.

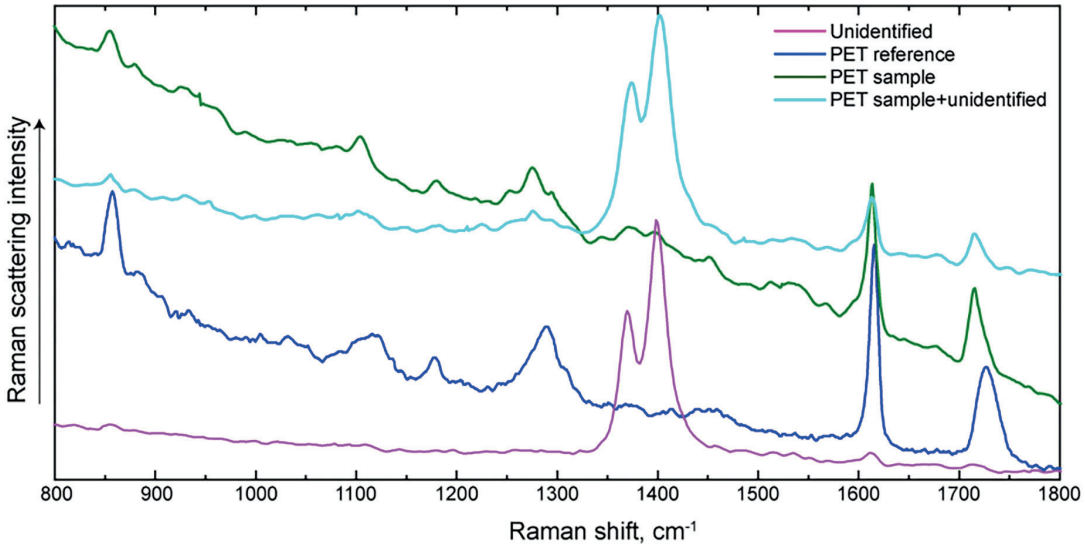


FIGURE 3: Raman scattering spectral analysis results. Results for PET reference material (blue); undefined spectrum (pink), PET particle in the sample (green), and PET with undefined spectra (cyan); spectra are shifted on the y-axis for clarity.

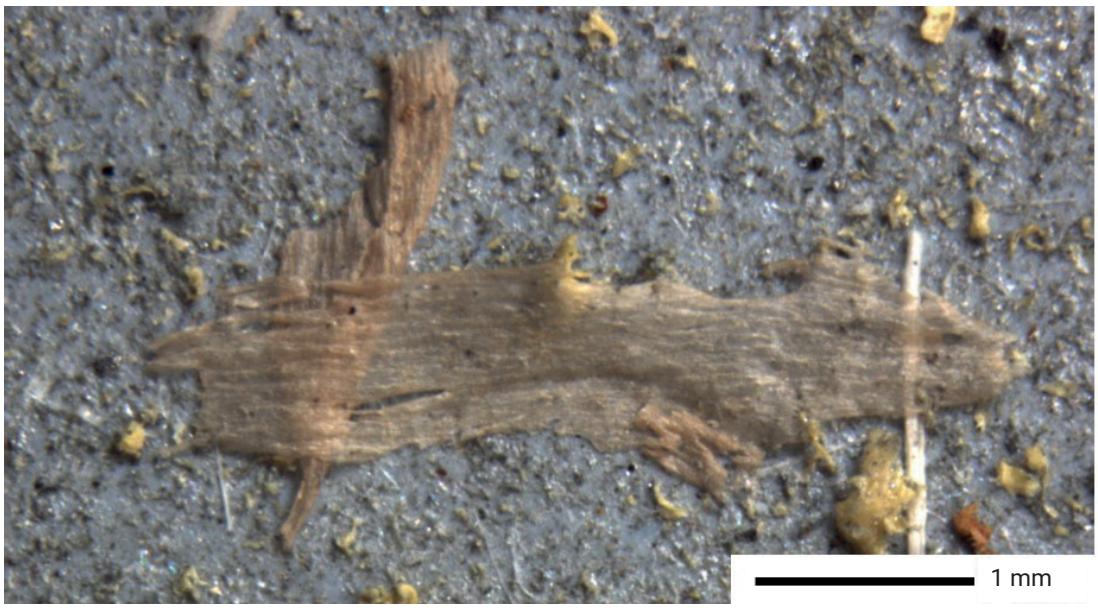


FIGURE 4: PE particle in sample 8. The PE particle image acquired with stereomicroscope Lecia M205 C with x1.25 magnification.

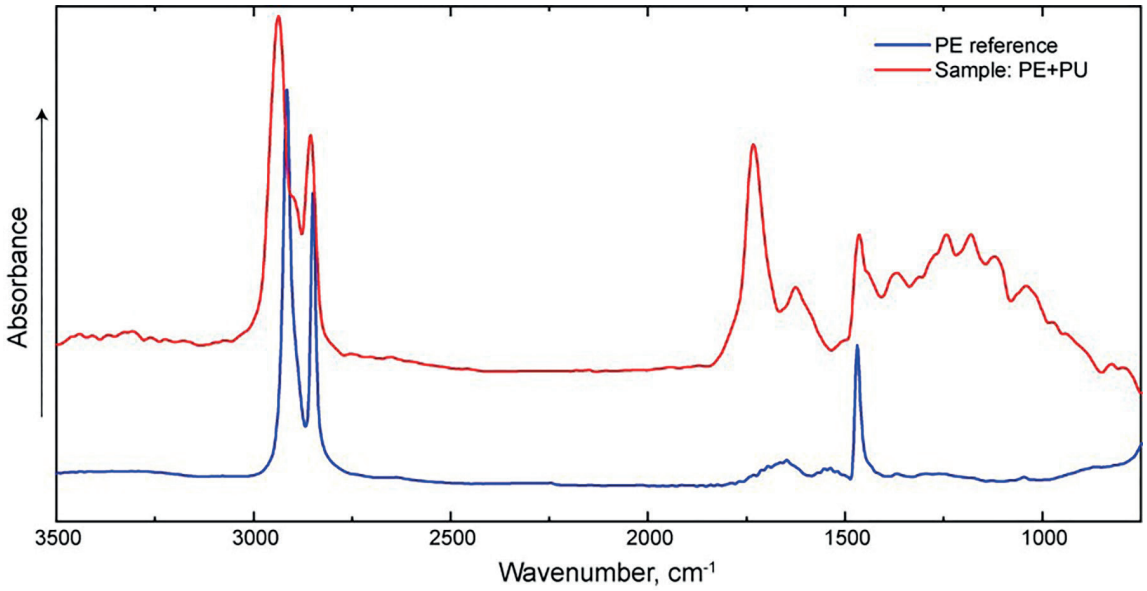


FIGURE 5: PE spectra. Spectrum of a reference material (blue) and PE particle spectrum acquired with FT-IR microspectrometer (red); spectra are shifted on the y axis for clarity.

After identifying the chemical composition of the large particle in sample 8 by using FTIR microspectroscopy, the same particle was re-analysed with the Raman scattering spectrometer and used to determine optimal parameters for recording its spectrum. The identified parameters were 785 mm excitation laser, acquisition time of 60 seconds, and 12 accumulations (see paragraph Materials and Methods). The newly identified spectral acquisition parameters were then used to collect spectra using Raman microspectroscopy from other particles on the sample. However, that signal was still overwhelmed by broad spectral bands of unidentified material(s) that we assign to contaminations that have not been removed by the initial treatment. Therefore, new samples (ID u1 and u2) were re-treated with higher concentration of H_2O_2 and density separation.

3.2 Hyperspectral Imaging results

The results of hierarchical PLS-DA applied to landfill leachate sample 8 are shown in Figure 6 as prediction maps. Sample 8 was selected for the larger size of some particles. In fact, particles larger than 30 µm in size are the key aspect for the correct implementation of hyperspectral imaging method, which includes also the removal of the sample background (i.e. the aluminium oxide filter) needed to highlight and better detect the particles.

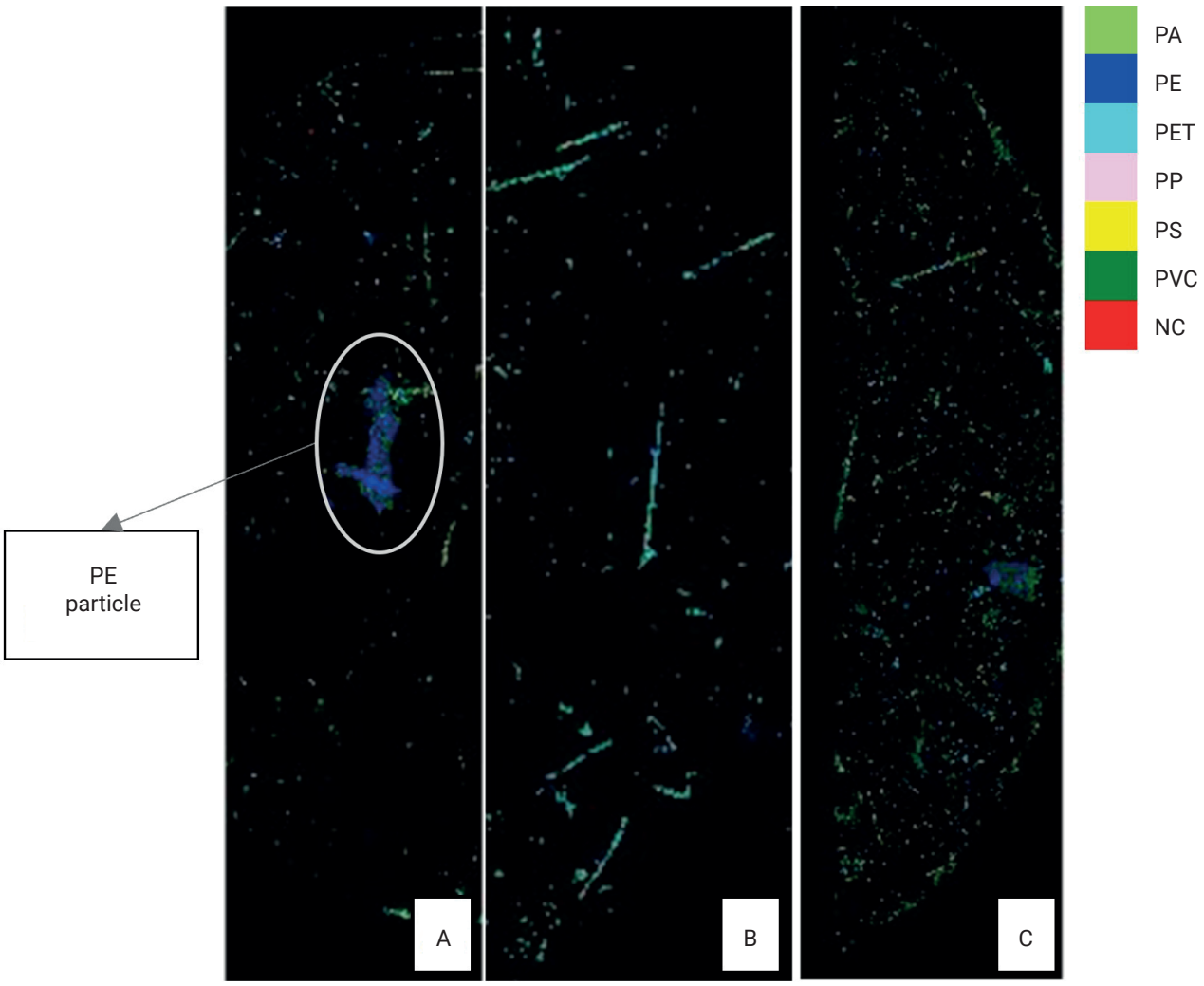


FIGURE 6: Hyperspectral imaging results. Results shown in terms of prediction maps for sample 8 with the largest particle highlighted.

The sample was divided into 3 areas (named A, B and C from left to right) for a better acquisition, as shown in Figure 6.

Results derived from this analysis show that the largest particle (in area A in Figure 6), was clearly identified as a PE particle (as with Raman and FT-IR microspectroscopy previously), confirming the validity of the technique and the possibility to obtain successful results also on smaller particles changing the optics of the hyperspectral device. Hyperspectral imaging results suggest that most of the particles in this sample should be made of PE. However, these results are not reliable because the particles are significantly smaller than 30 µm.

3.3 Effect of sample treatment on results and new treatment protocol

Results from the analyses with Raman scattering microspectroscopy of two retreated samples are reported in Table 3. As can be derived from Table 3, retreating samples does not have a clear, discernible positive effect on identifying PET with Raman scattering microspectroscopy, apart from that PS particles could be identified.

Thus, samples u1 and u2 were treated. They are shown in Figure 7 from which it can be derived that still a considerable amount of recalcitrant material is on the filter plates, indicating that digestion with H_2O_2 (respectively 30% and 15%) and density separation was not sufficient. A multi-step pre-treatment approach, as for example developed to analyse microplastics in sewage sludge and described by Simon et al., 2018, is at hand. After the treatments, both samples were analysed with Raman scattering microspectroscopy, and results are shown in Table 3.

The following can be derived from the results shown in Table 3:

- Unlike the results of the analyses on the previous samples, in sample u1 it was possible to identify PS, PP, PE and carbon particles and not only PET particles.
- The most abundant identified polymer was PE (23% of particles in sample u1) whereas not a single PE particle had been detected in all previous observations.
- Only the floating particles from sample u1 (top) contained microplastics, thus confirming the need of a density separation treatment.

TABLE 3: Type and count of particles detected with Raman microspectroscopy within the mapped areas, of samples 3 and 9 before and after the treatment and of samples u1 and u2 treated with the new protocol.

Sample	Area ID	Noise[1)]	PE	PP	PET	PS	PET + unident.[2)]	Unidentified spectrum	Undefined material[3)]	Carbon	Particles analysed	Plastics ident. / Particles analysed %
3 previous	2	59	-	-	12	-	25	9	25	-	130	28
3 retreated	1	9	-	-	2	0	10	10	14	-	45	27
	2	7	-	-	1	0	21	8	18	-	55	40
3 retreated Subtotal	2	16	0	0	3	0	31	18	32	0	100	34
9 previous	3	29	-	-	2	0	12	7	25	-	75	19
9 retreated	1	10	-	-	4	0	-	13	23	-	50	8
	2	17	-	-	2	2	2	16	11	-	50	12
9 retreated Subtotal	2	27	0	0	6	2	2	29	34	0	100	10
Samples with new treatment												
u1 (top)	1[4)]	6	16	-	-	1	-	-	5	2	30	57
	2[4)]	1	-	-	-	4	-	-	25	-	30	13
	3	22	24	-	-	-	-	-	11	-	57	42
	4	52	23	2	-	1	-	-	21	-	99	26
	5	86	19	-	1	-	-	-	32	-	138	14
u1 (bottom)	1	20	-	-	-	-	-	-	10	-	30	-
	2	2	-	-	-	-	-	-	28	-	30	-
u2	1	24	-	-	7	-	2	-	12	-	45	16
	2	30	-	-	5	-	4	1	30	-	70	7
Total	9	243	82	2	13	6	6	1	174	2	529	21

- Sample u1 did not show any kind of contamination in terms of the two bands in the spectra observed previously.
- Results from analysis of sample u2 showed the same result as for the samples pre-treated (i.d 7,8,9,3,4bis): only spectra of PET particles and unidentified contaminations could be recorded.

An example of identifying PP and PE with reference spectra is shown in Figures 8 and 9 for particles in sample u1. The PP spectrum of the sample was strictly matching with the reference materials, the PE spectrum exhibited a contribution from several unidentified spectral bands as compared to the reference.

3.4 Comparison of spectroscopic methods

The use of the three different methods for microplastic analysis in landfill leachate samples clearly showed that all of them are suitable to identify microplastics, but that they all have their limitations. When it comes to a direct com-

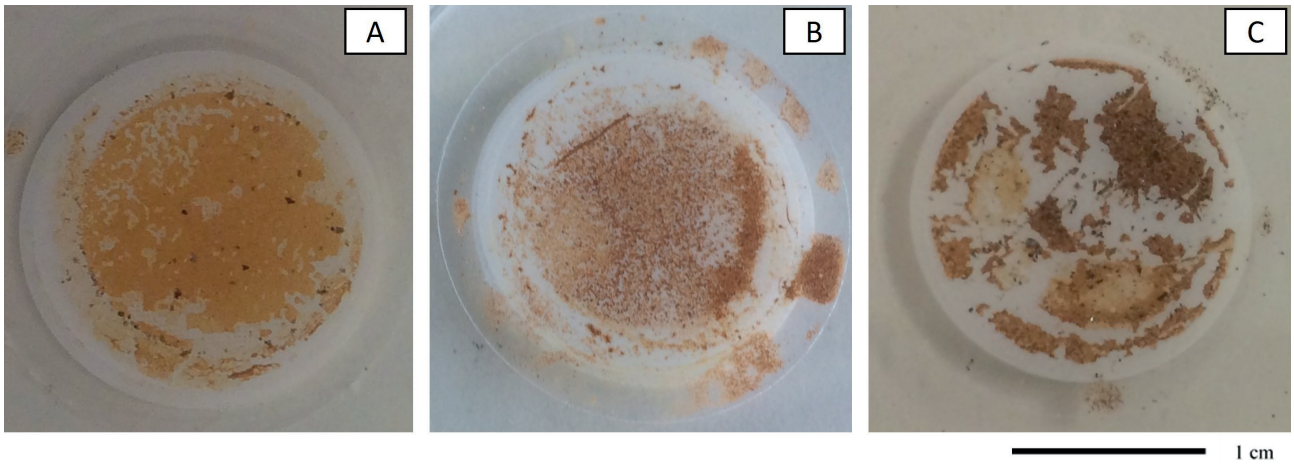


FIGURE 7: Samples u1 and u2. Samples after density separation treatment (A: u1 top, B: u1 bottom), and without treatment (C: u2).

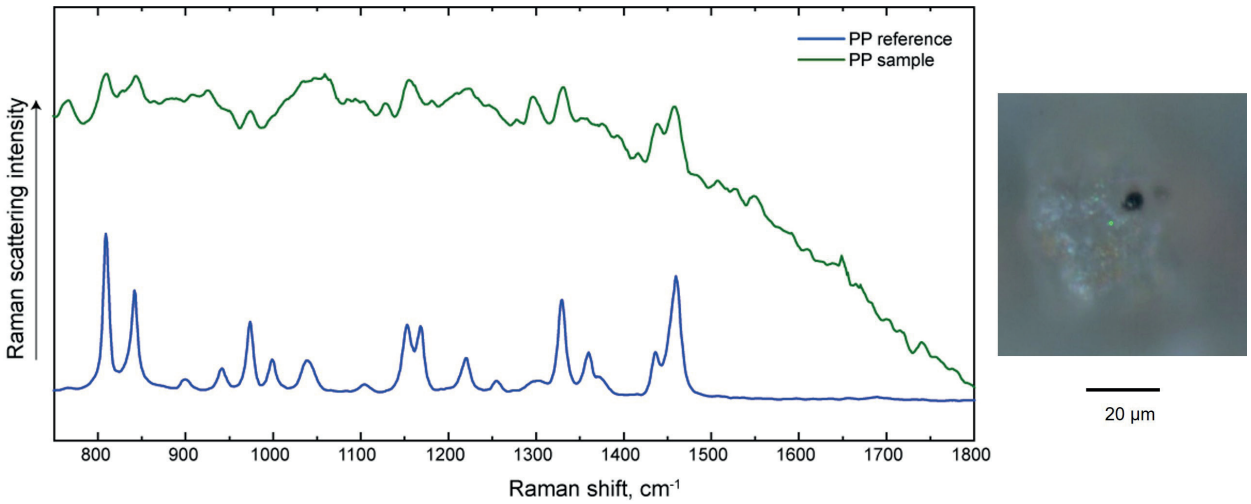


FIGURE 8: Example of a PP particle found in the sample u1 and its Raman spectrum. PP spectrum of a reference material (blue) and PP particle spectrum (green).

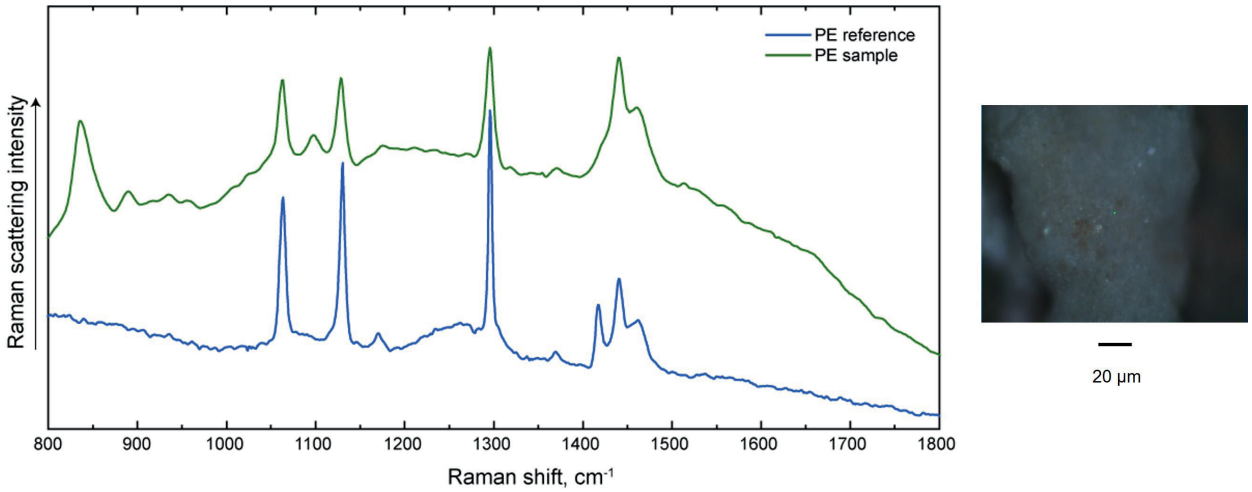


FIGURE 9: Example of PE particles found in the sample u1 and its Raman spectrum. PE spectrum of a reference material (pink) and PE particle spectrum (red).

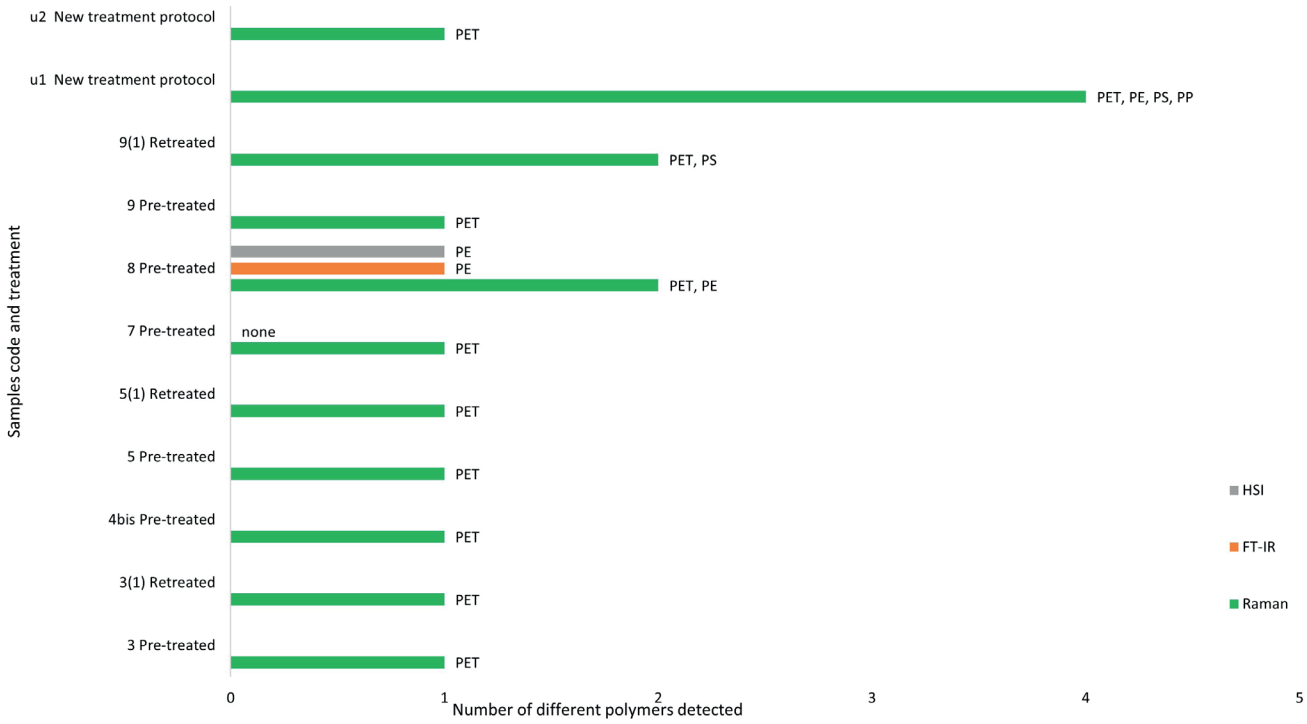
parison between analysing the same filtered landfill leachate samples with Raman microspectroscopy and FT-IR microspectroscopy, it appeared that, even though Raman microspectroscopy was clearly more effective for particles smaller than 20 µm, FT-IR was the more suitable solution to identify the spectra of some types of polymers (i.e. PE), affected by environmental or treatment distortion.

He et al., 2019, and Xu et al., 2020, found that FT-IR microspectroscopy worked well for analysing microplastics in landfill leachates with particles larger than 25 and 20 µm, respectively, after sample treatment with 30% H_2O_2 and Fe (II) followed by density separation, and treatment with 30% H_2O_2 (≥48h) and filtration, respectively. Su et al., 2021, applied Raman microspectroscopy on treated leachate samples (30% H_2O_2 for 72h, and NaCl density separation) to analyse microplastic particles down to a size of 20 µm. However, microplastics with much smaller sizes down to nanoscale have been observed in the environment (Gigault et al., 2016). In order to cover the full scale of microplastics in landfill leachates, particles below 20 µm have to be targeted, as well. Considering that, by using high magnification objectives, Raman microspectroscopy can work down to 1 µm, and it appears to be promising for identifying these smaller microplastic particles in landfill leachate.

Raman scattering microspectroscopy in our study enabled to identify more microplastic particles than FT-IR but appeared to be very sensitive to sample preparation. This evidence is clearly shown in Figure 10, in which a synthesis of samples, treatment procedure and spectroscopic methods applied is described, as well as the results of analysis related to the identification of plastic polymers.

3.5 Recommended procedure for sample preparation and microplastic analysis

During this study, samples from landfill leachate were analysed and, in some cases, treated. It has been evident that environmental samples, especially leachate ones, re-



(1) retreated samples with the same name as the pre-treated ones

FIGURE 10: Sample treatment, spectroscopic method applied to each sample and results in terms of detected polymers.

quire an accurate treatment to avoid any kind of contamination that can influence the spectra. Thus, recommendations for future studies are suggested below, only related to sample treatment and techniques for the analysis.

Firstly, it is strongly suggested to pay much attention for potential sources of plastic contamination during the samples management (e.g., clothes, plastic equipment, gloves etc) and especially during the samples treatment. Moreover, the following procedure for sample preparation is recommended:

- Treatment: Selected samples should be treated with 30% H_2O_2 solution.
- Density separation: Particles should be separated by dispersion using saturated salt solutions, e.g. NaCl (35 g of NaCl in 100 ml of *milliQ* deionized water). The solution should be mixed with a magnetic stirrer for at least 5 minutes. Saturation is indicated by NaCl grains undissolved on the container bottom. An adequate period of rest should be allowed for a correct density separation.
- Particle's collection: The most suitable method for the specific case should be selected to remove the majority of floating plastic particles. Both vacuum pump and syringe filter appeared to be effective for the collection. Eventually, particles should be properly deposited onto aluminium oxide filters with a polypropylene support ring, of adequate size and pore size.

Analysis of environmental samples often states challenges, especially if the analytical targets are of microscopic (or smaller) sizes. All three proposed methods are theoretically suitable for microplastic analysis in leachate or other effluents. However, due to the variable and unknown characteristics of the case-specific microplastics, a combination of techniques is recommended.

In addition, the following settings of instruments are recommended:

- Raman microspectroscopy: it is recommended to define the measurement parameters on a smaller section of the sample before starting the overall acquisition of the spectra. This allows to identify the most suitable and context-tailored set of parameters. However, this work highlighted that the following parameters are likely to be suitable for this kind of leachate sample studied:
  - excitation wavelength of 632.8 nm (He-Ne laser), with an acquisition time of 5-18 seconds; 5-8 scans in average for a single spectrum, a wavenumber range 1800 to 800 cm^{-1}; excitation power set to 5-10% of the total laser power (17 mW).
  - In case of fluorescence, excitation wavelength of 785 nm (diode solid-state laser); acquisition time of 60 seconds, 12 scans for a single spectrum and an excitation power set to 100% of the total laser power (100 mW).
- FT-IR microspectroscopy: Either a single channel mercury cadmium telluride (MCT) detector may be used to obtain a single spectrum, or a focal plane array (FPA) detector, with a 64×64 array size, to obtain an IR multispectral image. A good response has been experiences by using a 250×250 µm field-of-view of the

×15/0.4 Cassegrain objective. The spatial resolution for recording the spectra was 4 cm^{-1}, with 64 interferograms averaged. The result was Fourier-transformed into a spectrum applying the Blackmann–Harris 3 apodization function and zero filling factor 2. Furthermore, a ×20 Attenuated Total Reflection (ATR) objective (field-of-view 100×100 µm) combined with the single channel MCT detector showed to be suitable to record IR spectra of single particles but paying particular attention to the physical contact that could damage the sample.

- Hyperspectral Imaging: this analytical technique should be further explored in future studies. It is suggested to build a broader hierarchical model in order to detect a wider range of particles in the short-wave infrared (SWIR) range (1000-2500 nm). During this study, a satisfactory response has been experienced by equipping the device with a macro lens of a field-of-view of 1 cm, and with spectral resolution of 6.3 nm.

In Table 4, the advantages and disadvantages of samples treatment and analysis are listed, according and limited to the direct experience and findings of this study.

4. CONCLUSIONS

During this study, more than 1000 particles from landfill leachate samples were analysed with Raman microspectroscopy and partially re-analysed with FT-IR microspectroscopy and Hyperspectral Imaging, to determine the best approach for analysis. Results indicate that with the application of the three methods it was possible to identify microplastic particles of different polymers. However, the sample treatment is fundamental to avoid contamination that can influence the spectra, especially in leachate samples. Both digestion with H_2O_2 and density separation are invaluable sample treatments, but they should be optimized and complemented to remove more recalcitrant organic matter without impacting the plastic polymers. In fact, replicating a H_2O_2 treatment (with either the same or higher concentration) on a pre-treated sample did not improve at all the quality of results, supporting the hypothesis that the treatment itself could cause the undefined bands in the spectra.

In addition, the efficacy of pre-treatment has to be taken into regard for finding the optimal adjustment of key parameters for the FT-IR and Raman spectroscopic methods in order to avoid unwanted fluorescence or other spectral distortion phenomena. It is confirmed that microplastics in environmental samples are extremely difficult to detect since the spectra of particles are strongly affected by environment and treatments, which strengthen the need of a clear and efficient treatment protocol.

As a conclusion, the 30% H_2O_2 treatment with a density separation is the best one to identify plastic particles with an acceptable time of acquisition.

Eventually, hyperspectral imaging, a fast and promising analytical technique, should be developed for particles smaller than 30 µm, so that a direct comparison to FT-IR and Raman scattering microspectroscopy can be carried out.

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TABLE 4: Summary of advantages and disadvantages of the recommended sample preparation and analytical techniques, based on actual and direct findings of this study.

Method	Advantages	Disadvantages
Sample preparation		
H_2O_2 Treatment	Efficient removal of non-plastic organic materials	Risk of external contamination
Density separation	Efficient isolation of floating plastic particles	Risk of external contamination; risk of losing nano/micro particles
Analytical technique		
Raman microspectroscopy	Detection of particles up to 1 µm in size; possibility to detect particles in large areas of the sample; flexibility of measurement parameters; non-contact analysis	Sensitive to sample preparation; difficulties in identifying some types of polymers affected by environmental or treatment distortion
FT-IR microspectroscopy	More suitable solution to identify the spectra of some types of polymers (i.e. PE), affected by environmental or treatment distortion; flexibility of measurement parameters	Contact analysis (ATR); non suitable for particles smaller than 10-20 µm
Hyperspectral imaging	Extremely precise technique; context-tailored analysis technique	Non suitable for particles smaller than 30 µm; need to build the hierarchical model before the analysis; need to correctly remove the sample background for a better acquisition

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ON THE NEW HYDROLOGIC EVALUATION OF LANDFILL PERFORMANCE (HELP) MODEL VERSION 4 FOR THE WATER BALANCE SIMULATION OF LANDFILL LINER SYSTEMS

Klaus Berger *

Institute of Soil Science, University of Hamburg, Allende-Platz 2, 20146 Hamburg, Germany

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ABSTRACT

23 years after the last original US HELP version 3.07, in 2020 the US Environmental Protection Agency released a new version, called HELP 4. With this Excel-based version, the original HELP model has arrived in the modern Windows world. However, the model itself remains HELP 3.07. The paper deals with experiences of the author using HELP 4 and compares simulation results of four HELP versions (HELP 4.0.1, DOS HELP 3.07, and HELP 3.07 and HELP 3.95 D included in HELP 3.95 D) for two applications. First, the RCRA example of the original HELP version 3 in (US) customary units for 30 years of synthetically generated weather data for Nashville, TN. Second, the water balance test field F1 on the landfill Georgswerder in Hamburg, Germany, for 1988 to 1995 in metric units. The user interface is easy to use; however, it is more restrictive than necessary and not usable outside the USA without having weather data files of HELP 3.07 for import. The average annual totals of all tested HELP 3.07 model versions are close together. Differences occur probably due to computer numeric and because HELP 4.0.1 neglects the last day of leap years. The computing times of HELP 4.0.1 are for a factor of about 50 larger than for HELP 3.07 included in HELP 3.95 D. Despite reasonable criticism that may be made, the HELP model is a valuable tool for those who are aware of its limitations and merits further work on both the model and the Windows/Excel interface to match the current state of the art.

1. INTRODUCTION

Water balance calculations are an important tool for designing liner and top cover systems, particularly for developing sustainable landfilling (Grossule & Stegmann, 2020). The Hydrologic Evaluation of Landfill Performance (HELP) model, originally developed for the Environmental Protection Agency of the USA, presumably is the mostly applied model in the world for this purpose. The HELP model is a quasi-two-dimensional hydrologic model of water movement across, into, through and out of landfills and may be applied to open, partially closed, and fully closed sites. It calculates the water balance based upon meteorological, vegetation, soil and design data for periods of one up to one hundred calendar years.

The history of the HELP model comprises almost 40 years (Figure 1). Version 1 was released in 1984 with an extensive documentation (Schroeder et al., 1984a, 1984b) and version 2 in 1988, however, without a detailed documentation. HELP version 3, released in 1994 with the last update in late 1997 (HELP 3.07), was a major enhancement including an extensive documentation (Schroeder et al. 1994a, 1994b), the alternative use of internationally common metric units besides English units, and a user interface. Figure 2 depicts a schematic of a complete landfill profile illustrating typical layer sequences and features as well as the main hydrologic processes modelled by HELP 3. The versions 1 to 3 run in the operating system Microsoft DOS, which is completely out of date at least since the support end of Windows XP in April 2014.

Based upon HELP 3.07, in the late 1990's Waterloo Hydrogeologic Inc., Ontario, Canada, developed Visual HELP, a graphical user interface for Microsoft Windows 98/2000/XP including a database for the weather generator WGEN (Richardson & Wright, 1984), which is included in the HELP model. This database contains parameters for the weather generation for more than 2000 locations all over the world. Though Visual HELP is still available, the company no longer supports it.

The author performed an extensive validation study for HELP 3.07 (Berger, 1998, 2000; see also Berger, 2015) using especially measured water balance data of the test fields (large lysimeters) on the landfill Georgswerder in Hamburg, Germany (Melchior, 1993, Melchior et al. 2010). Further-

* Corresponding author:
Klaus Berger
email: klaus.berger@uni-hamburg.de

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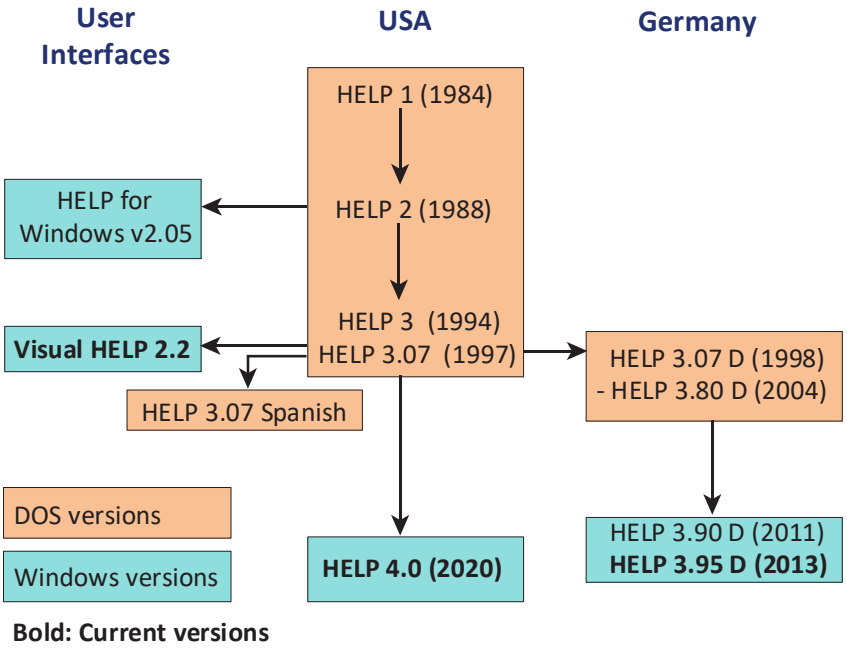

FIGURE 1: History and versions of the HELP model.

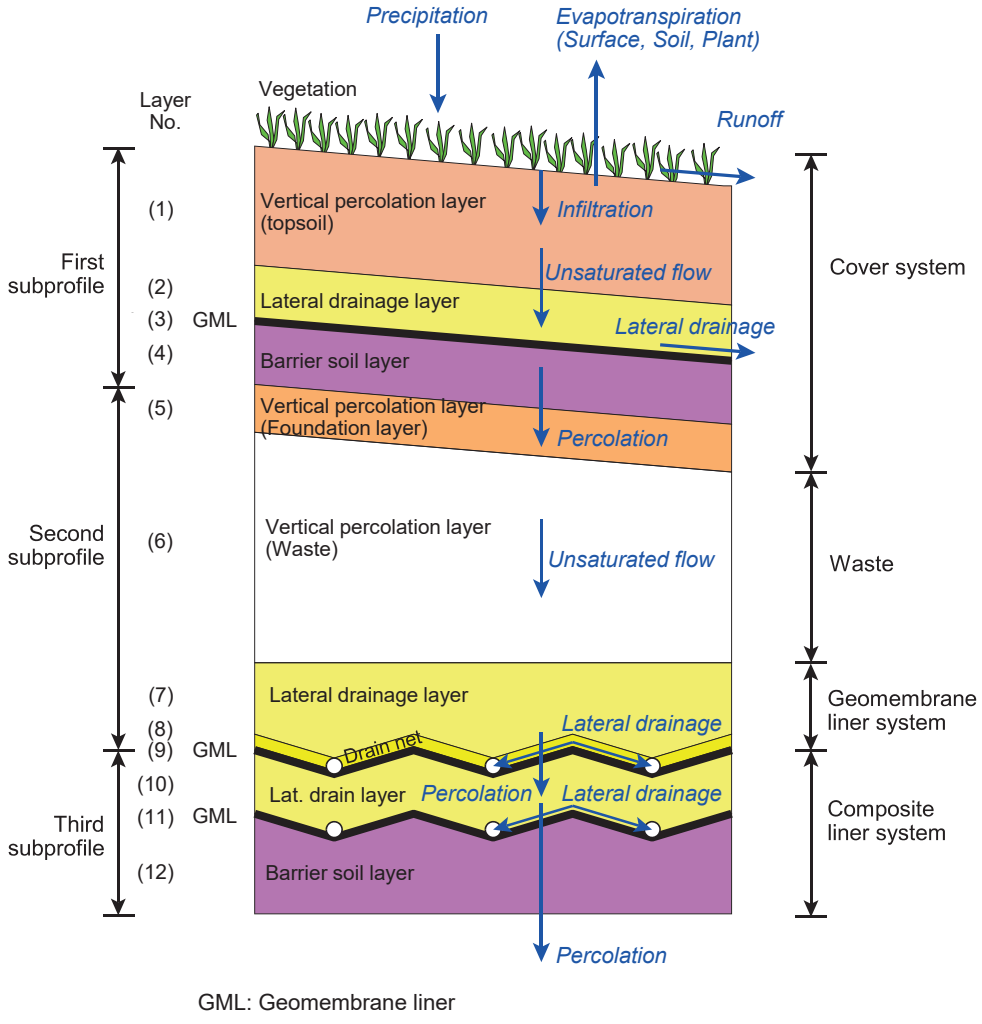

FIGURE 2: Schematic of a typical landfill profile including the main hydrologic processes modeled by the HELP model (modified and supplemented from Schroeder et al. 1994a, p. 7; RCRA example).

more, the author developed several enhancements, at the beginning for the Microsoft DOS operating system (HELP 3.07 D to 3.80 D). After Microsoft had announced the support end of 16-bit DOS programs in Windows, the author developed a user interface for modern Microsoft Windows versions. The latest is HELP 3.95 D from 2013, which runs in Windows (10/8/7) (Berger & Schroeder, 2013).

In late 2020, the US EPA released a new HELP version 4, which is Microsoft Excel-based and runs in modern Windows, too (Tolaymat & Krause, 2020).

The paper deals with the new HELP version 4 and its enhancements beyond the former original version HELP 3.07 and compares simulation results obtained with HELP 3.07, HELP 3.95 D and HELP 4.

2. MATERIAL AND METHODS

2.1 Brief characterization of HELP Version 4

HELP version 4.0 (Tolaymat & Krause 2020) was developed by the Center for Environmental Solutions and Emergency Management of the US EPA's Office of Research and Development. HELP 4.0 uses a Microsoft Excel workbook with embedded macros to support the user interface. It has been tested for use in Excel 2007 (Windows operating system) and higher and works on 64-bit processors.

Apparently, HELP version 4 includes the same model as the latest HELP version 3 (HELP 3.07, November 1997).

HELP 4 offers several options for data input (Tolaymat & Krause 2020), obviously developed for use in the United States. First, input files of HELP 3.07 can be imported. Second, data input of daily weather data has been updated. Precipitation and air temperature data from the National Oceanic and Atmospheric Administration (NOAA) and solar radiation data of the National Renewable Energy Laboratory (NREL) can be imported. Furthermore, synthetic generation of daily weather data based upon the weather generator WGEN (Richardson & Wright 1984) is included and updated. HELP 3 included a database with parameters for synthetic weather generation for more than 100 locations throughout the USA with differing numbers of locations for precipitation, air temperature and solar radiation. In contrast to HELP 3, HELP 4 includes a database with calculated weather generation parameters for more than 13,000 points located on a 0.25 x 0.25 degree grid across the continental USA (Tolaymat & Krause 2020, p. 14). Input weather data can be edited in the user's interface, which seems to be the only way for creating weather data of locations outside the USA (however, see section 3.1). Data for calculating evapotranspiration (wind speed, relative humidity, and vegetation data including evaporative zone depth), soil and design data including data for calculating the runoff curve number, and general information can also be input manually. The only parameter, which to the author's knowledge is new in HELP 4, is the longitude, which is used together with the latitude for synthetic weather generation. Consequently, longitude is obviously restricted to values for the continental USA.

2.2 Execution of simulations

The following HELP versions were applied in this study.

(1) HELP 4.0.1: Excel version, downloaded from the EPA website on 2020-12-09 (Tolaymat & Krause, 2020)
(2) HELP 3.07: DOS version from 1 November 1997 (Schroeder et al. 1994a, 1994b)
(3) HELP 3.95 D (version no. 3.95.1.7): Windows version including the model versions
(3a) HELP 3.07 (recompiled original version with a very few software-technical adjustments such as longer file names) and
(3b) HELP 3.95 D (Berger & Schroeder, 2013).

All model applications except for the DOS HELP 3.07 were run on a PC with an Intel Core i5-6500 CPU (3.2 GHz) and a usual hard disk drive in Windows 10 (64-bit) with German and English (USA) localization. HELP 4.0.1 was run in Microsoft Excel 2016 with the same localization as Windows. DOS HELP 3.07 was run approximately 10 years ago on a PC with Windows XP, which allowed DOS-programs to be executed without additional utilities such as DOS-boxes.

2.3 Simulated systems

Two applications were run with the models:

(1) The RCRA (Resource Conservation Recovery Act) example included in HELP 3 with 30 years of synthetically generated weather data for Nashville, TN in (US) customary units, and
(2) A simplified operational validation run of the water balance test field F1, which was constructed within the cover system of the landfill Georgswerder in Hamburg, Germany, for the 8 years from 1988 to 1995 (Melchior 1993, Melchior et al. 2010) in metric units. The validation run was simplified by using constant layer and vegetation properties, which actually were changing especially in the first two years after construction.

The RCRA example refers to a fully closed site. The layer sequence is depicted in Figure 2, comprising a cover with a composite liner, the waste body and a bottom liner system, which is designed as double liner system. Table 1 summarizes the main design properties used in the simulations.

The second application is the water balance test field F1 on the landfill Georgswerder in Hamburg, Germany (Melchior 1993, Melchior et al. 2010; see also Berger 1998, 2015). The landfill Georgswerder was operated from 1948 to 1979 for the disposal of municipal waste including bulky waste and construction waste. However, some hazardous waste was disposed, too. After detecting dioxin in the landfill leakage in 1983 the City of Hamburg decided to construct a cover system on the landfill. Due to lacking knowledge on efficiency and long-term performance of cover systems, a research project was initiated at the Institute of Soil Science of Universität Hamburg. For this project, six test fields (large lysimeters) with different cover systems were constructed within the cover system of the landfill in 1987 with the same materials and the same technology as the cover of the landfill to obtain representative measurement results. The test fields were operated extensively in the research phase from 1988 to 1995 and

TABLE 1: Main design properties of the RCRA example.

No	Layer and Layer type[1]	Thickness (inch)	Soil texture and HELP no.	Further main properties
1	Top soil, VPL	30	Silt loam, 9	
2	Mineral lateral drainage layer, LDL	12	Coarse sand, 1	Maximum drainage length: 200 ft. Drain slope: 4%
3	Geomembrane liner, GML	0.04	Low density polyethylene, 36	Placement quality: poor 1 pinhole/acre, 10 installation defects/ acre
4	Mineral barrier soil layer, BSL	36	Silty clay (moderately compacted), 28	
5	Waste, VPL	300	Municipal waste,18	
6	Mineral lateral drainage layer, LDL	12	Loamy fine sand, 5	Maximum drainage length: 100 ft. Drain slope: 3%
7	Drain net, LDL	0.2	Drainage net, 20	
8	Geomembrane liner, GML	0.06	High density polyethylene, 35	Placement quality: good 1 pinhole/acre, 10 installation defects/ acre
9	Mineral lateral drainage layer, LDL	12	Gravel, 21	Maximum drainage length: 100 ft. Drain slope: 3%
10	Geomembrane liner, GML	0.06	High density polyethylene, 35	Placement quality: good 1 pinhole/acre, 10 installation defects/ acre
11	Mineral barrier soil layer, BSL	36	Barrier soil, 16	
	Further properties	**Value**		
	SCS Curve number[2] (1)	82.2		
	Evaporative zone depth (inch)	21		
	Vegetation Maximum leaf area index (1)	fair grass 2.0		

[1] Layer types: VPL: vertical percolation layer, LDL: lateral drainage layer, GML: geomembrane liner, BSL: barrier soil layer; [2] Curve number of the curve number method of the US Soil Conservation Service (SCS) for calculating the surface runoff

to a lesser extent until 1998. Since 1999, the Environmental Protection Agency of Hamburg operates those test fields with the layer design of the landfill as part of the aftercare program.

Each of the six test fields is 50 m long in slope direction and 10 m wide, three having a slope of 4% (called test fields F1 to F3) and three having a slope of 20%, respectively; all test fields are exposed to the north. Test field F1 has a compacted soil liner, but no geomembrane. The major layer, design and vegetation data used in the simulations are as follows (layers listed from the top to the bottom):

1. Restoration layer (humous top soil), HELP layer type vertical percolation layer (VPL), 25.7 cm thick, constructed of a glacial marl, German soil texture loamy sand;
2. Restoration layer (non-humous top soil), VPL, 49.5 cm thick, glacial marl, loamy sand;
3. Mineral lateral drainage layer, layer type lateral drainage layer (LDL), 21.8 cm thick, constructed of a mixture of coarse sand and fine gravel, maximum drainage length 50 m, drain slope 3.5%
4. Compacted mineral soil liner, layer type barrier soil layer (BSL), 61.5 cm, constructed of a compacted glacial marl, sandy loam;
5. Curve number 55.0
6. Evaporative zone depth 75.2 cm (entire restoration layer)
7. Maximum leaf area index 3.5 (good grass)

3. RESULTS AND DISCUSSION

3.1 Applying the user interface of HELP Vs. 4

Briefly described, the major experiences of the author applying HELP 4 were as follows:

1) HELP 4 must be run with an English (or compatible) localization. In a German localization, input files of HELP 3.07 cannot be imported and simulations cannot be executed due to the different decimal separator (English: dot, German: comma).
2) Input files of the HELP 3.07 RCRA examples were imported fast and without error message.
3) The import of HELP 3.07 weather data files (daily values of precipitation, air temperature and solar radiation) is more restrictive than necessary. The number (1 to 37) at the end of each input line with ten daily values is required though these entries are ignored in the source code of the model HELP 3.07, subroutine READCD, and actually are unnecessary.
4) A least the import of HELP 3.07 solar radiation data (files .D13) in metric units (MJ/m^2) requires a blank character between two daily values and thus is more restrictive than the import routine of HELP 3.07 (subroutine READCD), which allows a numerical character instead of the blank character. (The author assumes that this also holds for precipitation and air temperature.) This is important insofar that the metric unit MJ/m^2 is for a factor of 23.89 larger than the US customary unit Langley (ly). Thus, the values are for this factor smaller

and instead of one decimal place, used for values in the unit ly, three instead of two decimal places are more appropriate for values in the unit MJ/m². This means that six instead of five numerical characters (including the decimal point) are required for the unit MJ/m².

5) Analogously to item 4) the import of HELP 3.07 evapotranspiration parameters (files .D11) is more restrictive than necessary due to required blank characters that are unnecessary according to the subroutine READIN of HELP 3.07. Furthermore, the error message of HELP 4 refers to an invalid .D10 (instead of .D11) file structure.
6) The import of HELP 3.07 soil and design data (files .D10) is also more restrictive than necessary. During the import of D10-files of the second application (landfill Georgswerder) layer descriptions that were accepted by the model's subroutine READIN led to an incomplete import in the HELP 4 user interface. Just two of four layers were imported; no error message was displayed, but an import confirmation. The incomplete import was caused by the second line of layer descriptions in the imported D10-files if these just contained blank characters.
7) When importing HELP 3.07 soil and design data files (.D10), for each vertical percolation layer the HELP 4 user interface asks for its type, i.e. soil layer or waste layer, obviously for internal purposes. The model HELP 3.07 does not require this information.
8) Usage of HELP 4.0.1 outside the USA without having HELP 3.07 input files for import is not reasonably possible at the present knowledge of the author based upon the HELP 4.0.1 version he was using. Though evapotranspiration parameters (.D11-files) and soil and design data (.D10-files) can easily be input manually, this is not a reasonable option for daily weather data due to curious restrictions of the editable data and the lacking recalculation of the monthly values. The first two years of precipitation and air temperature data and the first seven years of solar radiation data were locked and could not be edited. It was possible to enter or copy new data at the end of the existing data, but deleting e.g. a year of data somewhere in the middle (after the first locked years) led to the deletion of all subsequent years of data. The reasons for this behavior are unclear to the author. The author currently cannot exclude that the Windows and Excel localization and settings of his PC may play a role. However, he assumes the main reasons are in the Excel program of HELP 4.
9) Finally, the user interface of HELP 4 is easy to use.

3.2 Comparison of simulation results for the RCRA example

Average annual totals and computing times of the four HELP model versions for the RCRA example are summarized in Table 2. The average annual totals of the three model versions HELP 3.07 (1, 2, 3a) are not identical, but close together with deviations of usually less than one thousandth. The first assumption for explaining these small differences is computer numeric including maybe the operating system. Model versions (2) and (3a) have almost identical FORTRAN source codes, but were compiled with different compilers, which will have led to slightly different evaluation sequences including variable transformations from double and single precision FORTRAN variables to numerical representations of the numeric coprocessor and vice versa. Model (1) obviously uses Excel calculations and numerical representations of variables. For a second explanation, see section 3.3. Due to differences in the modeling approaches model (3b) should produce different results than models (1), (2) and (3a).

A striking result is the sum of computing and file saving time of the new HELP version 4 that is about 50 times as high as that of the two model versions 3.07 and 3.95 D of HELP 3.95 D. The Excel-based model (1) required 115 seconds for the complete execution compared to approximately 2 seconds of the compiled model (3a) (and 3b) on the same PC. Neglecting the file saving time reduces the execution (computing) time of model (1) for about a quarter. (Model (1) created a PDF and an Excel output file, whereas model (3a) just created a text output file.)

3.3 Comparison of simulation results for the test field F1 on the landfill Georgswerder

Average annual totals and computing times of three HELP model versions for the test field F1 are summarized in Table 3.

In this example the average annual totals calculated by HELP 4.0.1 and HELP 3.07 are close together, too; however, not as close as in the RCRA example in section 3.2. Curiously, the precipitation deviates for 0.15 mm per annum or in total for 1.2 mm in eight years that are missing in HELP 4.0.1. The daily results show that HELP 4.0.1 did not consider leap years, but neglected the last day (day 366) of leap years. The precipitation on 31 December 1988 was 1.2 mm and on 31 December 1992 0 mm. This is contradictory to the user manual (Tolaymat & Krause, 2020, p. 16). Thus, neglecting the last day of leap years should be the main reason for the deviations of model (1) and (3a), and not computer numeric (see section 3.2). In this case, computer numeric includes the special fact (for HELP 4 this is an assumption of the author) that both versions are calculating internally in US customary units and therefore are performing unit conversions from and to metric units in pre- and post-processing, respectively.

Similar to the RCRA example in section 3.2 the computing and total run time of HELP 4 in this example is about a factor 50 higher than for the two model versions of HELP 3.95 D.

An operational validation of the HELP model(s), i.e. the comparison of measured and simulated discharges is valuable and interesting. However, based on average annual totals it does not make sense due to the deterioration of the mineral liner of test field F1, which occurred in two stages. The deterioration of the mineral liner leads to an increasing leakage through the liner and consequently to a decreasing lateral drainage in the lateral drainage layer on the liner. The HELP model does not model the deterioration. Therefore, the simulated and measured average annual totals of the liner leakage and the lateral drainage cannot match. An operational validation of the model HELP 3.95 D based upon cumulative daily values from 1988 to 1995 is described in Berger (2015).

TABLE 2: Average annual totals and computing times of four HELP model versions for the RCRA example, simulated with 30 years of synthetically generated weather data for Nashville, TN, USA.

Model version	**1) HELP 4.0.1**	**2) HELP 3.07**	**HELP 3.95 D**	
Quantity / Variable		**(DOS, Win XP)**	**3a) HELP 3.07**	**3b) HELP 3.95 D**
Precipitation (inch)	47.49	47.49	47.49	47.49
Runoff (inch)	1.893	1.892	1.892	1.63
Actual evapotranspiration (inch)	31.779	31.781	31.783	29.81
Lateral drainage collected from layer 2 (inch)	13.7121	13.17156	13.71004	15.90518
Percolation through layer 4 (inch)	0.227766	0.22769	0.22764	0.26516
Average head on top of layer 3 (inch)	3.5168	3.533	3.533	4.142
Lateral drainage collected from layer 7 (inch)	0.0987	0.09869	0.09866	0.11936
Percolation through layer 8 (inch)	0.126056	0.12604	0.12601	0.1422
Average head on top of layer 8 (inch)	0.0001	0.000	0.000	0.000
Lateral drainage collected from layer 9 (inch)	0.1261	0.12604	0.12601	0.14219
Percolation through layer 11 (inch)	0.000005	0.00001	0.00001	0.00001
Average head on top of layer 10 (inch)	0.0007	0.0001	0.0001	0.0001
Change in water storage (inch)	-0.1148	-0.115	-0.115	-0.113
Computing time (sec)	88	n.d.	2	2
File saving time (sec)	27	n.d.	Included	Included
Total run time (sec)	115	n.d.	2	2

File saving time of model 1 for creating a PDF and an Excel output file; n.d.: not determined; Included: file saving time is included in computing time. Times determined on a PC with Intel i5-6500 (3.2 GHz) CPU

4. CONCLUSIONS AND OUTLOOK

23 years after the last US HELP model version 3.07 was released, the EPA published the new version HELP 4 in 2020. Already at the time of its release in 1994, the DOS user interface of HELP version 3.0x was not up-to-date. With the new version 4, the user interface of the original HELP model has arrived in the modern Windows world. However, the model itself is still HELP 3.07. Thus, model concept and approaches are almost 30 years old, some approaches are even older.

Despite reasonable criticism (for an overview see Berger 2015), the HELP model is a valuable tool for those users who are aware of its limitations. Therefore, in the author's opinion both the user interface and the model should be enhanced:

1. The restrictions of the user interface described in this paper should be eliminated.
2. An option for importing daily weather data from Excel files should be added to enable convenient usage of the model outside the USA and to enhance the usability within the USA.
3. The model requires and merits a substantial enhance-

TABLE 3: Average annual totals and computing times of three HELP model versions for the test field F1 on the landfill Georgswerder in Hamburg, Germany (years 1988-1995).

Model version	**(1) HELP 4.0.1**	**HELP 3.95 D**	
Quantity / Variable		**(3a) HELP 3.07**	**(3b) HELP 3.95 D**
Precipitation[1] (mm)	788.66	788.81	788.81
Runoff (mm)	6.046	5.841	1.483
Actual evapotranspiration (mm)	460.12	460.195	459.691
Lateral drainage collected from layer 3 (mm)	317.6173	317.73105	321.66617
Percolation through layer 4 (mm)	6.237859	6.21916	4.7924
Average head on top of layer 4 (mm)	5.826	5.835	5.905
Change in water storage (mm)	-1.359	-1.174	1.18
Computing time (sec)	45	1	1
File saving time (sec)	9	Included	Included
Total run time (sec)	54	1	1

[1] *Measured precipitation corrected for systematic measurement errors which were assumed for the standard rain gauge of the USA; File saving time of model (1) for creating a PDF and an Excel output file; Included: file saving time is included in computing time. Times determined on a PC with Intel i5-6500 (3.2 GHz) CPU.*

ment and update of the modeling approaches to the current state of knowledge and capability of PCs. Important enhancements are (see also Berger 2015):

a. The internal segmentation of layers and the evaporative zone should be made much finer. Currently layers are divided in up to three segments and the evaporative zone is divided into seven segments independently of their thickness. Thus, segments may become very thick and the vertical water movement may be modelled very course. A proposed maximum thickness of a segment of for example 10 cm (4 inches) would fix this problem.
b. The unit-gradient approach for calculating unsaturated flow should be replaced by an approach that includes the matric potential.
c. Besides grass and bare soil, different types of vegetation should be modelled, for examples shrubs and deciduous and coniferous trees. This requires revisions of the modelling approaches of vegetative growth and decay, potential and actual evapotranspiration.
d. The very simple frozen soil sub-model should be enhanced (for example the model HELP 3.95 D includes a pragmatic enhancement).

However, the already high computing and file saving times of the Excel calculations will further increase due to the enhancements, which users may find off-putting.

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ENVIRONMENTAL LAW ISSUES IN CONNECTION WITH LANDFILL MINING

Oskar Johansson * and Maria Pettersson

Division of Social Science, Luleå University of Technology, SE-971 87 Luleå, Sweden

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ABSTRACT

In Sweden, landfills are excavated on a relatively modest scale (mainly for the purpose of decontamination, to increase landfill capacity or to free up land for other uses). Lately however, aspirations for excavations aimed at recovering energy and materials have increased and an important goal according to the Mineral Strategy of Sweden is to increase the recycling rate of metals and minerals and reduce the amount of waste. The incidence of certain (critical) metals and minerals, including REE and phosphorus, is moreover assumed to be relatively large in Swedish landfills, and the interest in excavating landfills is therefore expected to increase. The legal situation as regards excavation of landfills in general and of mining waste in particular, is however unclear, not least regarding permit requirement according to the Swedish Environmental Code. Even though landfill recycling may entail numerous negative environmental effects, e.g., acidic and metallic leachate, release of gases, and destabilization of land the regulation of the activity is not clear. The aim of this paper is to describe and problematize the legal situation as regards landfill excavation in Sweden against the backdrop of, on the one hand, a potential increase in the demand for recycled metals and minerals, and on the other hand comprehensive requirements for a non-toxic and healthy environment.

1. INTRODUCTION

Throughout history, landfilling has been an effective method for the disposal of waste in Sweden, and it is still the primary approach to waste disposal in large parts of the world. Landfills, especially those established prior to the advent of modern environmental requirements, do however pose a risk for peoples' health and the environment e.g., in the form of pollution to soil, water and air (SEPA, 2021; Grossule and Stegmann, 2020; Hogland et al, 2018). In Sweden, landfilling of waste has gradually been reduced in favor of other treatment methods since the beginning of the 1990s. Currently, less than one percent of the municipal waste in Sweden is landfilled[1]; only waste that cannot be treated in any other way, such as contaminated masses, are landfilled. According to the Swedish Environmental Protection agency (SEPA) Sweden has two 'strategies' to reduce the environmental impact of landfilling: (1) to reduce the long-term impacts by designing more environmentally 'friendly' landfills; (2) to reduce the amount and the hazardousness of landfilled waste (SEPA, 2020). None of these strategies does however account for previously landfilled waste in older landfills.

Against the backdrop of an increasing awareness of the consequences of environmentally hazardous activities, particularly mining, and an increasing scarcity of virgin materials, most prominently metals or carbon-based materials such as wood or oil, the discourse of landfill mining gained momentum in the 1990s, after being more or less dormant since the first documented operation in the 1950s (Spencer, 1990; Dickinson, 1995; Krook et al, 2012; Burlakovs et al, 2017). In landfill mining, previously disposed of (landfilled) materials or other natural resources are excavated to extract valuable materials (e.g., Savage, 1993; Johansson et al., 2012; Krook et al. 2012; Hogland, 2018) and may thus constitute an alternative to the extraction of virgin materials (Särkkä et al., 2018), as well as a strategy to deal with negative impacts of landfills. This potential function of the landfills has also been pointed out in a number of official investigations and policies, both on EU level and by individual Member States (Laner et al. 2019; Jones et al. 2018).

In Sweden, landfills are excavated on a relatively modest scale, and mainly for the purpose of decontamination, to increase landfill capacity or to free up land for other uses (Johansson et al., 2012; SGU, 2014). Lately, however, plans for excavations aimed at recovering energy and materials have emerged. According to the Mineral Strategy of Sweden an important goal of this is to increase the recycling rate of metals and mineral and reduce the amount of

* Corresponding author:
Oskar Johansson
email: oskar.johansson@ltu.se

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waste. The incidence of certain (critical) metals and minerals, including REE and phosphorus, is moreover assumed to be relatively large in Swedish landfills (SGU, 2014).

As regards what quantities of different materials are currently stored in Swedish municipal landfills, Frändegård et al. assert that: "The total amount of deposited materials in Swedish municipal landfills as of 2012 is estimated to be 365 million tons" (Frändegård et al. 2013:10), and that "landfill mining could be seen as a supplementary resource strategy for meeting the growing domestic need for ferrous and non-ferrous metals […]" (ibid. p. 17). According to the authors, about 7 million tons of ferrous metal and 2 million tons of non-ferrous metals would be possible to extract, thus "enough to meet the demand of Swedish industry for ferrous and nonferrous metals for three and eight years, respectively" (ibid. p. 1).

There are however significant drawbacks associated with landfill mining and the scientific literature provides a fragmented impression of its pros and cons, as can be expected given the complexity of the issue. The excavation of landfills has consequences for both human health and the environment, and the very undertaking of the activity is governed by economic, social and legal prerequisites. What are considered pros and cons is largely a matter of perspective - from a global resource perspective, recovering materials from landfills can be seen as an opportunity, while the negative consequences might be in the foreground from a local perspective. Thus, while many authors argue that the problems outbalance the benefits, both from an environmental and an economic perspective, some see it as a solution to the overall resource problem (Esguerra et al., 2019).

There are considerable challenges in connection with landfill mining. Of these, methane emissions and local pollution as a result of disturbing and moving waste, and a lack of economic feasibility, in terms of e.g., waste treatment and disposal costs in connection with re-landfilling, are frequently mentioned (Laner et al. 2019; Esguerra et al., 2018; Johansson et al., 2017; Hogland et al., 2018; Frändegård et al., 2015; Van Passel, 2013). A different perspective is presented by Calderon Marquez et al., where landfill mining is outlined as a "strategic alternative" for sustainable development and "proper waste management" (Calderon Marquez et al. 2019:1102). In terms of positive economic factors, i.e., revenues from landfill mining, Laner et al., mention material sales, reclaimed void space and (future) avoidance of land landfill management costs etc. (Laner et al. 2019).

One of several significant gaps in the discourse of landfill mining appears to be the regulatory system. On EU level, De Römph refer to landfill mining as "…a promising but underexposed idea in EU policies, let alone in EU legislation" (De Römph, 2018:91). In Laner et al., the results from the study point to "the role of policy intervention" as an important factor to enhance the (economic) conditions for landfill mining not least as the economic performance of an individual activity will depend on the regulatory costs (Laner et al., 2019). Similar conclusions are made by Van Passel et al. who argue that "[enhanced landfill mining] projects have a clear private economic potential when adequate regulation and support policies are in place" (Van Passel et al., 2013:98). The consequences of "[u]nfavorable institutional conditions for landfill mining" are also highlighted by Johansson et al. (2017) that points to the importance of the design of the regulatory framework in supporting landfill mining and the current discrepancy between the basis for the landfill legislation (to permanently dispose of the material) and landfill mining (to excavate the material).

This paper aims to contribute to this research through increased knowledge of the function of the institutional framework – in particular the environmental legislation – in relation to landfill mining in Sweden. More specifically, the purpose of the paper is to describe and problematize the legal situation as regards the excavation of landfills in Sweden against the backdrop of; on the one hand, a potential increase in the demand for recycled metals and minerals, and on the other hand comprehensive requirements for a non-toxic and healthy environment.

1.1 Method

The analysis is conducted within the framework of EU and national level legislation on waste and landfill mining. Our intention is to contribute to the research in waste law in general, and to the discourse on landfill mining in particular. We do this by (a) exploring and analysing the legal framework governing waste and landfill mining in Sweden, and (b) providing insights on the manner in which this legislation corresponds to political ideas or ambitions of a circular economy and thereby an increased excavation of landfills. We use "constructive analytical jurisprudence" to analyse the concepts, rules and structures of the relevant laws. Constructive, as opposed to dogmatic, here means "problem oriented", which entails that the legal framework is analysed from the point of view of the factual situation rather than solely from the linguistic and logical elucidation of legal concepts (Westberg 1992, Agell 1997). The study of the legal material is qualitative, and in principle limited to legislation currently in force.

2. RESULTS

2.1 Concepts and definitions

A landfill is defined, as per the EU Landfill Directive, as a site where waste is stored either by the waste producer (internal landfills) or an independent landfill operator (article 2(g)). To classify as a landfill, the intended storage generally need to be of permanent nature, as the following is excluded from the scope of the Directive:

a. facilities where waste is unloaded in order to permit its preparation for further transport for recovery, treatment or disposal elsewhere, and
b. storage of waste prior to recovery or treatment for a period less than three years as a general rule, or
c. storage of waste prior to disposal for a period less than one year.

Storage of a more intermittent nature is not regarded as landfilling and landfill mining is thus legally restricted to 'mining operations' in long-term operational or closed disposal sites (landfills). Resource extraction from storag-

es sites of a temporary nature does not classify as landfill mining, at least not legally.

While there is no clear legal definition of operations that de facto constitute 'landfill mining' it is generally perceived as an activity where masses are extracted from an existing landfill for remediation or resource extraction purposes (Savage et al., 1993; Johansson et al., 2012). Landfill excavation for remediation purposes carries a lot less institutional uncertainty as remediation is an established activity with a clear objective to enhance environmental quality (by freeing up space for more waste, removing contamination or preparations for closure of the landfill). So far, most of the current successful landfill mining operations have also largely been deemed as remediation of contaminated areas where any resource extraction has been secondary (Hogland et al., 2018; Johansson et al., 2012).

With starting point in the objective of a circular economy some researchers argue for a clearer distinction between the old regime of landfill mining consisting of primarily remediation activities with resource extraction as a positive side effect, and the new regime, enhanced landfill mining, where resource extraction is the primary goal of the activity (e.g., Geysen et al., 2009; Jones et al., 2013). Enhanced landfill mining is defined by Jones et al as "the safe conditioning, excavation and integrated valorization of (historic and/or future) landfilled waste streams as both materials (Waste-to-Material, WtM) and energy (Waste-to-Energy, WtE), using innovative transformation technologies and respecting the most stringent social and ecological criteria" (Jones et al., 2013). Johansson summaries the difference between the (old) concept of landfill mining – primarily targeting remediation – and the emerging concept of 'enhanced landfill mining' and concludes that the new approach moves "towards a resource perspective with advanced technology for material process to reach higher quality outputs" (Johansson, 2016:21). As there is no explicit regulatory framework that covers neither landfill mining nor enhanced landfill mining, the European Parliament suggested, in the 2017 Waste Package (art. 5), that the Commission should further examine the possibility of a regulatory framework. The proposal was however rejected by the Council and the proposed amendments were not included in directive 2018/850 (OJ L 150, 14.6.2018, p. 100-108). A definition is however crucial as there is a major difference, not only on a principle level, between an activity that is undertaken with the primary purpose of remediation and one of resource extraction, not least in terms of the legal prerequisites for the activities.

2.2 Legal framework for landfill mining

It follows from the precautionary principle and previous CJEU case law, that the classification of waste should be extensive, and that any treatment of waste should either be categorized as (1) recovery or (2) disposal (i.e., landfilling) as shown by para 62-63 in the CJEU ruling Abfall Service AG (ASA) v Bundesminister für Umwelt, Jugend und Familie (Case C-6/00). The reasoning behind the 'one or the other' approach is that the legal prerequisites as well as the intentions of the legislation differ between disposal, on the one hand, and recovery on the other. As a waste treatment operation, landfill mining is in practice a combination of both recovery and disposal. According to article 3 of the waste framework Directive (WFD) 'recovery' means:

any operation the principal result of which is waste serving a useful purpose by replacing other materials which would otherwise have been used to fulfil a particular function, or waste being prepared to fulfil that function, in the plant or in the wider economy. […]

In the same article, the meaning of 'disposal' is outlined as:

any operation which is not recovery even where the operation has as a secondary consequence the reclamation of substances or energy […]

As far as we can tell, there is no legal source (legislative act or CJEU case law) that defines landfill mining in the way recovery and disposal is defined. Disposal is seen as the end of the life cycle of a product and the legislation is not designed with the excavation of waste in mind. However, in addition to generate resources, the process of excavating waste with the purpose of extracting resources will also give cause to new waste in the form of unwanted, and most likely contaminated, masses. Thus, while the extraction of resources would be considered a recovery operation, the disposal of unwanted masses would be considered a disposal operation. Whether or not the excavated masses should be considered as waste in the first place is also neither obvious nor previously determined by the CJEU. This highlights the need for a regulatory framework specifically designed for landfill mining, as it is important to keep in mind that the operator (i.e., the person/legal entity responsible for the excavation) does not have any interest of disposing of the material, at least not initially, but rather hope to assimilate resources[2].

According to article 13(c) of the landfill Directive the operator (as defined in the landfill directive) of a landfill is responsible for the aftercare of a landfill after its closure. This entails 'maintenance, monitoring and control in the after-care phase for as long as may be required by the competent authority.' In the recent preliminary ruling AMA – Azienda Municipale Ambiente SpA v Consorzio Laziale Rifuti – Co.La.Ri, the CJEU states that provisions on closure of landfills apply to all existing landfills, with the exception of those that were closed no later than two years after the Directives entry into force on the 16th of July 1999 (i.e. 16th of July 2001 at the latest) as per article 18(1) and 19 of the Directive (Case C-15/19, point 34-35). The court further clarifies that when the waste is deposited into the landfill is irrelevant. The responsibility of the operator is the same regardless of whether the waste was deposited before or after the date of transposition (Case C-15/19, point 48-49). The provisions in the Landfill Directive thus applies irrespective of when the landfill was made operational, on condition that it was not closed before July 16 2001. This is not unproblematic as the theoretical basis for the allocation of costs as formulated in article 10 of the Landfill Directive is the Polluter Pays Principle (PPP), i.e. 'the landfiller pays'. Accordingly, the costs for aftercare should be

considered already when holders (as previously defined in the landfill directive[3]) deposit waste into the landfill via taxes, fees, or 'price of admission'. In accordance with previous CJEU case law it is however up to the individual member states to allocate this as they see fit (Case C-254/08). In relation to this, Advocate general Kokott clarifies in an opinion delivered on 16 January 2020 that:

Articles 10 and 14 of Directive 1999/31, in the light of the principles of non-retroactivity, legal certainty and the protection of legitimate expectations, do not justify the collection of additional fees from previous holders who deposited waste in the landfill and who paid the fees required for that purpose if the duration of the maintenance of the landfill after closure is subsequently extended and that cost factor has not yet been taken into account in the initial fee.

It is thus not possible to retroactively impose fees to holders with the argument that the cost was not taken into account initially. This however gives rise to some concern: if the provisions apply 'retroactively' but with no capacity to allocate cost, it is not the original polluter who pays, it is the operator.

The question is thus who should pay for landfill mining in accordance with the polluter pays principle. Is it (1) the original holder (2) the operator, or (3) the 'miner'? Another question is if the costs for remediation activities, which has previously been the primary objective of landfill mining, should be considered when the waste is initially disposed by the holder. Based on the PPP, the answer would be yes. In accordance with article 10 of the landfill directive "…estimated costs of the closure and after-care of the site for a period of at least 30 years shall be covered by the price to be charged by the operator for the disposal of any type of waste in that site." As remediation activities such as freeing up space and contamination treatment certainly are included in 'costs of closure and after-care' this is a strong indication that the holder of the waste should bear the costs of such activities. Based on the same logic, the costs for primarily resource extraction activities are not likely to be considered in the same way, at least not in accordance with current regulation.

To conclude this section, (enhanced) landfill mining is not prohibited provided that the operation complies, as stated by the European Commission, with the main requirements in article 13 in the WFD (i.e., without risk to water, air, soil, plants or animals; without causing a nuisance through noise or odours; and without adversely affecting the countryside or places of special interest) and with a permit from the 'competent authority' in accordance with article 23. It is however the responsibility of the member states to transpose these requirements into national legislation.

2.3 Legal framework for landfill mining in Sweden

The EU waste legislation has primarily been transposed into Swedish law via the Swedish Environmental Code (SEC) (via Ch. 15), the Waste Ordinance, Ordinance on Landfilling of Waste (Landfill Ordinance) and the Environmental Assessment Regulation (MPF). As far as waste in general is considered, the primary rules in Sweden are found in Ch. 15 of the SEC, which was recently modified to better correspond with EU legislation (Government Bill, 2019/20:22). The definition of waste and waste management operations (such as recovery and disposal) is meant to match the corresponding definitions on union level. However, in recent rulings of the Land and Environmental Court of Appeal (M 7806-16 and M 1832-17), a more stringent approach to the waste definition is taken due to the Swedish transposition of the derogation regime in article 2(c)[4] of the WFD, which in turn has extended the scope of landfilling. The Swedish transposition of the Directive has thus resulted in that 'less' traditional landfilling, such as permanent storage of surplus masses in conjunction with road construction, also requires a permit for landfilling[5].

Overall, the basis for the Swedish legislation for landfilling of waste is the goal of reducing both the amount of landfilled waste and its hazardousness. The strategy for reducing the environmental effects is partly to reduce emissions from the landfills in the long term by controlling the design of the landfills, and partly to reduce the amount of and hazardousness of the landfilled waste. As mentioned above, operational landfills require a permit in accordance with the landfill directive (art. 6-9) and it is the individual member state's responsibility to guarantee that a permit process is in place. In Sweden, this is done via the SEC.

According to Ch. 9, s. 6(3) the SEC, the government can issue regulations requiring operators to apply for a permit to landfill waste. It thus follows from Ch. 29, s. 18-26, of the MPF that landfilling, as a main rule, requires a permit. Which type of permit depends on the waste - landfilling of certain specified amounts of non-hazardous, and non-inert waste does, for example, require a 'class A' permit from the Land- and environmental court, whereas landfilling of smaller volumes of the same type of waste can be permitted by the County Administrative Board (CAB) as a 'class B' permit (MPF, s. 20-21). The same logic is applied to hazardous waste (s. 23-24).

In keeping with the overarching objective to minimize the amount of landfilled waste, the Landfill Ordinance stipulates that only waste that has been treated may be landfilled (s. 14). With treatment is intended: "the use of physical, thermal, chemical or biological methods, including sorting, which modify the properties of the waste so that its quantity or hazard is reduced, its handling is facilitated or recycling is favored." The requirement for treatment does however not apply to inert waste, where treatment is not technically feasible, or other waste where treatment does not lead to reduced negative effects on human health or the environment. (s. 14, the Landfill Ordinance). In terms of substantive rules, the regulation requires that the operator has as good knowledge as possible about the composition of the waste, leachability, and other properties and effects both in general and in the long term (s. 16).

There is however no specific rule or regulation in the SEC, or in any other piece of legislation (such as the Minerals Act) that targets landfill mining[6]. While there are possibly regulations that can be applied analogously in this respect, the lack of specific rules for such a relatively new type of activity raises many legal questions, including who has the right to carry out the excavation and under what conditions;

who is responsible for the excess waste from the excavation (i.e., can excess waste be re-deposited and under what conditions?); and should excavation from all types of landfills be considered in the same way or do the differences in age, content, placement etc., call for special regulation?

These are important questions, not least considering that the responsibility of the operator of the landfill ceases 30 years after closure if the permit authorities have not taken future costs beyond those 30 years (economic or environmental) into account when issuing permits.

More specifically regarding the relationship between landfill mining and remediation of contaminated soil, there is moreover no clear-cut demarcation between the different activities. The question of under what conditions landfill mining can be considered – and thus may be authorized as – remediation depends on a number of factors.

Landfill mining – if that is the purpose of the planned activity – falls under the definition of environmentally hazardous activities under the SEC, as it entails risking spread of pollutants. Hence, the activity may be subjected to a permit requirement in accordance with Ch. 9, s. 6 in the SEC[7]. At the same time, landfill mining will often take place in areas classified as contaminated, which makes the rules regarding remediation applicable. The SEPA has investigated this issue and concluded that, in the current situation, the operator can "choose" which set of rules to follow when commencing a project. If the supervising authority subsequently assess that this was not appropriate, it can order the operator to change the approach (SEPA, 2015:70). The SEPA does not believe that this situation would change if landfill mining were to be subjected to a specific permit requirement, as the purpose of the activity would still be decisive (SEPA 2015:70).

The consequences of this legal situation is that an operator who commences a landfill-mining project might be held responsible also for existing contamination, as it has been established in case law that a new actor can become "polluter" and thus jointly and severally liable for the contamination (NJA 2012 s. 125). This joint liability entails that anyone of the polluters can be sought to answer for the entire remediation costs – a risk that is hardly mitigated by the fact that it is possible to subsequently demand refund by the other polluters as these may have gone bankrupt, or cannot be found. According to SEPA, this also does not constitute a reason to change the existing regulations for contaminated soil. The main reason for SEPA's assessment seems to be the small extent of landfill mining in Sweden. If the activity becomes relevant to a greater extent, SEPA believes that there may be reasons to reconsider this position. However, for landfill mining to become relevant, it might be necessary to address also the lack of specific regulations governing the activity. According to Krook et al. "Neglecting ELFM in EU policy and regulatory frameworks is, therefore, not a neutral act but rather an effective way to lock in conventional practices and lock out ELFM." (Krook et al., 2018:6).

All in all, there is a significant legal uncertainty in connection with landfill mining in Sweden that needs to be resolved before this type of activity can be pursued on a larger scale.

More in detail, excavated waste is furthermore subject to regulations in the form of bans and waste taxes. Redepositing excavated masses may be prohibited depending on the composition of the masses. This implies that the excavators are forced to deliver any excess (unwanted) waste for incineration or other 'recycling' at varying costs (Krook et al, 2012:518). In addition, any lawful landfilling of unwanted masses will be subject to an additional waste (landfilling) tax, depending on whether the excavated landfill contains waste that has already been taxed or not (Government Bill 2019/20:124 p. 18). In any case, taxation will constitute a detriment for potential landfill mining; even if the excavated waste was not taxed initially, the imposition of a tax liability for the 'excavator' in principle implies a transfer of the original polluters' responsibility upon the 'excavator', which is not consistent with the PPP. In the legislative preparatory works regarding changes in the Swedish law on Waste Tax, exemptions form taxes were amply discussed. Nine out of 14 referral bodies were against a general tax exemption for landfill mining, which was also in line with the Government Bill. Four referral bodies (Linköpings universitet; Stena Metall AB; Återvinningsindustrierna; Ragn-Sells AB) considered the investigation 'inadequate' inter alia because the scope of the proposed environmental assessment was limited, and there are "compelling reasons from an environmental, climate and resource efficiency point of view for promoting landfill mining [authors' translation]".

The amendments to the waste tax legislation entered into force on of January 1, 2021 and did not include any general exemptions from the waste tax. Instead, a possibility for a tax repayment was introduced[8]. Following this, the government has decided to further investigate the possibility of tax exemptions for excavated waste; the results of this investigation are still pending and shall be reported to the government at the latest on February 28, 2022.

In accordance with the PPP, taking into account future costs that may arise due to the landfill already at the time of disposal of the waste will promote a more 'efficient' resource use. There are two reasons for this. Firstly, if it is more expensive to landfill waste that could be subject to future resource extraction, holders are incentivized to choose a different recovery or disposal method, although it is very challenging (if not impossible) to determine what will be valuable in the future[9]. Secondly, if the costs of landfill mining are, at least in part, covered at the time of disposal the potential for economic benefit should be higher for the excavator, thus creating further incentives for landfill mining. Neither of this constitutes the basis for resource extraction from landfills made operational under current and older legislation (which is the vast majority of Swedish landfills). As previous case studies have shown the most 'benefits' are to be made from older, not newer landfills due to increasingly stringent landfill regulations (Johansson, 2012; Hogland et al. 2018).

In spite of investigations conducted on behalf of the government indicating that there is some political ambition for landfill mining (SEPA, 2013; SGU 2014; SEPA 2015) and also proposals for legislative changes (Government Bill 2019/20:124), landfill mining largely remains unregulated, and several regulatory barriers can be identified on national level.

3. DISCUSSION AND CONCLUSIONS

In this paper, we have discussed the legal situation regarding landfill mining. We have explored the different concepts associated with the excavation of landfills for different purposes – landfill mining and enhanced landfill mining – and the legal implications of this. We have mainly targeted Sweden, but as a member of the EU, EU law, especially in the area of waste, heavily influences Sweden and both Swedish legislation and relevant EU Directives are therefore accounted for. The aim of the paper has been to provide increased knowledge of the function of the institutional framework, in particular the role of environmental legislation, in relation to landfill mining in Sweden. The motive for the study is the potentially conflicting goals concerning, on the one hand, the increased demand for recycled materials, primarily metals and minerals, and on the other hand the comprehensive requirements for a non-toxic and healthy environment as expressed by the Swedish environmental quality goals.

3.1 The importance of a legal definition

Against this backdrop, we conclude that, from a legal perspective, it is important to be able to distinguish between different activities as the requirements that are to be set according to the legislation are applied differently depending on the circumstances of the individual case. More specifically, the lack of a clear legal definition of what constitutes (enhanced) landfill mining creates uncertainty regarding both which rules apply and how they should be applied. This in turn increases (the already high) costs of an activity that could possibly be part of a circular economy. On the other hand, legal uncertainty also means increased complexity in terms of what environmental requirements can and should be imposed on the activity; without a legal definition, it is difficult to make trade-offs between the pros and cons of the activity and thus to determine suitable conditions.

3.2 The question of permissibility

According to EU law, landfill mining is not prohibited, although it is also not promoted or directly regulated. As Einhäupl et al. concludes in their review of stakeholder needs, this does not mean that there are no legal barriers to (enhanced) landfill mining: "[d]espite the impression that no current legislation is hindering ELFM implementation, industrial and scientific actors, and regional institutions would appreciate a defining legal framework." Out of all interviewed stakeholders all nine mentioned the need for regulatory change (Einhäupl et al., 2019:118). The situation is the same in Sweden, where there is no specific requirement for a permit for the excavation of landfills to recover resources. An important question is therefore how the operation should be assessed – is it mining, "ordinary" environmentally hazardous activity, waste management or a combination of these?

It is important to remember that environmentally sound resource management is a relatively new notion. Sweden were for instance diligently landfilling up until the end of the last century when landfill taxes and bans on landfilling certain materials were introduced through the Swedish landfill ordinance and the Swedish law of waste taxation. Extracting these old and 'forgotten' resources is possibly one way of creating a higher grade of sustainable consumption. By re-introducing materials that have left circulation the need for virgin materials will decrease.

According to Johansson et al. Swedish authorities "seem unable to embrace the complexity of the concept [of landfill mining]." and argue that when the activity "is framed as a remediation activity the authorities are positive in support, but when it is framed as a mining activity the authorities are negative." (Johansson et al. 2017:46). Thus, regardless of whether excavation from landfills with the purpose of recycling resources is a "good" or "bad" idea – both research results and opinions seem to differ here – it can be concluded that as a concept, landfill mining would benefit from a clearer legal framework.

3.3 Concluding remarks

Landfill mining is a complicated process. In this paper, a review of some of the legislative challenges regarding landfill mining are presented. Amongst the identified potential legal barriers, the most problematic at this point seems to be the lack of a legal definition, as this carries with it a chain of "unregulated" issues. The uncertainty that this entails is probably a contributing reason as to why the economic conditions for landfill mining are not considered particularly favorable. While our study primarily covers Swedish legal conditions, there is much to suggest a similar situation is present in other European countries (Cossu et al., 2020). Similiar to the requirements regarding the designing of landfills (Cossu, 2016) current EU law displays no ambition to promote the institutionalization of landfill mining. Such a development can however be considered necessary for the individual Member States to be able to create favourable conditions for landfill mining as an integrated part of sustainable landfilling.

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[1] This can be compared with the EU totals: in 2018, 24% of all municipal waste generated in the EU was landfilled (https://ec.europa.eu/environment/topics/waste-and-recycling/landfill-waste_en).

[2] If the extraction is seen as a recovery operation it is possible that the waste will be subject to the 'end of waste' process, thus ceasing to be waste in accordance with the provisions in article 6 of the WFD. This is important for further use of the 'waste' but the application of end of waste is not unproblematic and, more importantly, unpredictable. As clarified in AS Tallinna Vesi v Keskkonnaamet, operators cannot demand a preliminary ruling regarding the status of the waste, and if operators cannot guarantee further use (i. e., the waste ceasing to be waste), it is challenging to calculate profitability in advance.

[3] Article 2(n) has since been cancelled through Directive (EU) 2018/850 of the European Parliament and of the Council of 30 May 2018 amending Directive 1999/31/EC on the landfill of waste.

[4] The reasoning behind the derogation regime in article 2(c) (uncontaminated soil and other naturally occurring material excavated in the course of construction activities where it is certain that the material will be used for the purposes of construction in its natural state on the site from which it was excavated) was that the waste management regime was deemed inappropriate for this kind of material even though the material de facto is discarded (Guidelines on the interpretation of key provisions of Directive 2008/98/EC on waste p. 42).

[5] Because of the Swedish transposition of the WFD, the regulatory conditions for handling such masses have been under review by the SEPA, commissioned by the government since 2018. However, at the time of writing, no legislative changes have been introduced. As of January 28, 2021 the regulatory framework for masses used for construction purposes in general is under review by the SEPA, commissioned by the government (https://www.regeringen.se/pressmeddelanden/2021/01/hantering-av-schaktmassor-ska-ses-over/).

[6] With regard to secondary extraction of minerals from mining waste, a study from 2017 concludes that while there are no formal hinders in the SEC regarding the possibility of assessing a permit application for secondary extraction, there is a need to investigate whether there are obstacles in the Minerals Act for such extraction, considering that for example the ownership of such minerals is unclear (SEPA and SGU, 2017).

[7] As described above there is no specific regulation targeting landfill mining in the SEC or related regulations.

[8] In accordance with general principles of 'repayment' the repayment cannot however exceed previous taxation, i.e., if the waste was not taxed initially the operator will not be eligible for repayment (prop. 2019/20:124 s. 26).

[9] This is why some researchers suggest a shift towards intermittent 'landfilling' in the future where traditional landfilling is replaced with temporary resource reservoirs (e.g., De Römph, 2016). Jones and Tielemans (2011) and Jones et al (2013) refers to this as enhanced landfill mining in combination with the concept of a 'temporary storage place' where waste is placed temporarily pending future extraction possibilities. To paraphrase Jones et al 2013 "[…] landfills become future mines for materials, which cannot yet be (economically) recycled with existing technologies or show a clear potential to be recycled in a more effective way in the near future." (Jones and Tielemans, 2011; Jones et al., 2013).

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CEDALION AND ORION: A TWO-STEP DECISION SUPPORT TOOL TO ALLOW SMART ELFM PROJECT PLANNING, PRIORITISATION AND SUSTAINABLE INTERIM USE (RAWFILL PROJECT)

Eddy Wille [1,*], Cuinera Isenborghs [1], Laura Lamair [2], Claudia Neculau [2], Renaud De Rijdt [3] and the RAWFILL team [4]

[1] *Public Waste Agency of Flanders (OVAM), Stationsstraat 110, 2800 Mechelen, Belgium*
[2] *Société publique d'aide à la qualité de l'environnement (SPAQuE), Boulevard d'Avroy 38, 4000 Liège, Belgium*
[3] *ATRASOL s.p.r.l., Rue Minique 37, 1450 Chastre, Belgium*
[4] *Marta Popova, , Sébastien Moreaux, David Caterina, Itzel Isunza Manrique, Fred Nguyen, Annick Vastiau, Pascal Beese-Vasbender, Jonathan Chambers, Ben Dashwood, Arnaud Watlet, Cornelia Inauen, Simon Loisel, Gaëtan Vivien, Alain Ducheyne*

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ABSTRACT

(Enhanced) landfill mining (ELFM) is a sustainable waste management strategy which supports the circular economy and reduces the environmental risks related to landfills. To facilitate and encourage stakeholders to launch (E)LFM-projects, RAWFILL has developed (1) an Enhanced Landfill Inventory Framework (ELIF), (2) an innovative landfill characterization methodology combining geophysical imaging and guided sampling (HADESS) and (3) a two-step Decision Support Tool (DST) to allow smart (E)LFM-project planning and prioritization. Based on the Interreg Europe COCOON experiences, the (E)LFM-concept was broadened to Dynamic Landfill Management (DLM), a sustainable and active long-term management of former landfills. DSTs improve decision-making by increasing the efficiency and lowering the uncertainty. The two-step approach offers an efficient and cost-effective solution. The DST 1 (Cedalion) requires limited data and provides guidance to the next step. The result is a ranking score on 4 scenario's: waste to materials, waste to energy, waste to land interim use. The DST 2 (Orion) provides an overview of relevant tools that can assist the user in the further project development, like estimations about the feasibility of a business case, simulating scenario's or finding sustainable interim solutions. The latter, interim use, is the novelty in this dual DST and should be seen as a loop in the roadmap. To summarize, the innovative approach of RAWFILL is the broadening of the resource scope at landfills and their comprehensive management, spanning the whole project cycle: from first screening to final redevelopment, including sustainable management and interim uses.

1. INTRODUCTION

The development of the circular economy has triggered the transition from traditional waste management in a linear economy to sustainable material management in a circular economy. Primary natural resources are finite and in the future, we will have to find another way to gather the resources that we need to sustain our economy and wellbeing (Heuss-Aßbichler et al., 2020). To achieve this, mining secondary resources will need to play a significant role. RAWFILL (Acronym for "Supporting a new circular economy for RAW materials recovered from landFILLs") therefore explored the potential of mining former landfills in order to recover raw materials. In that aspect, RAWFILL aims at including the end-point of a former linear economy back into the circular economy.

Besides a resource scarcity of materials, North-West Europe and many other regions across the world, are facing a scarcity of land and soil because of the growing hunger for space (EC, 2021). This puts an enormous pressure on the available land and its value. This is also endorsed by the EU Soil Strategy for 2030 that wants to achieve a limited land take and soil sealing with a circular use of land. In the strategy they emphasize the importance of land recycling: constructing in or rehabilitating already previously built-up or underused areas. This can spare more natural areas and will benefit biodiversity, green spaces, land for food, biomass, water and rainfall regulation (EC, 2021). Knowing that in Europe over 500 000 landfills are present, obstructing a big amount of land for important

* Corresponding author:
Eddy Wille
email: eddy.wille@ovam.be

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functions and services for nature and society. Estimates have revealed that 90% of these landfills are "non-sanitary" landfills, which predate the EU Landfill Directive and have limited environmental protection technologies (Jones et al., 2018). Land pressure is therefore a typical phenomenon in which landfills no longer count as a threat, but can also provide a solution. Landfills can play an important role within the second step of the hierarchy of land planning (Figure 1) by providing underutilised recycled land for redevelopment.

When the principal goal of landfill rehabilitation is land recycling, landfill mining is not a requirement as it will increase the costs of the rehabilitation project significantly, exceeding the benefits of rehabilitation. Thereby, it is important that a safe use of the site is guaranteed and it should be ensured that there are no human and environmental risks due to contamination. In the Netherlands, groundwater monitoring, conducted in the period 1999-2004, provided insights into the groundwater quality around old landfills. This indicated a minor influence of the landfill material on the groundwater quality and only small dispersion risks. Therefore, no follow-up measures were deemed necessary for most of the landfills (In 't Veld & Krol, 2005). The same is experienced in Flanders, where only 10% of the old landfills require remediation according to the Soil Remediation Decree. For these landfills, landfill mining can be a solution, or containment measures should be set in place. This means that for the other 90% of the landfills, no remediation is necessary and another (sustainable) management strategy should be installed (according to the concept of dynamic landfill management).

These current transitions oblige policy makers, landfill owners, environmental experts, etc. to look at landfills through another lens. We need to change our perspective on landfills in order to propose new and innovative solutions for the remnants of the linear economy.

2. FORMER LANDFILLS AND THEIR ROLE IN THE CIRCULAR ECONOMY

2.1 Dynamic Landfill Management

For a long time, landfills have been considered as static end points of the linear economy. These 'final' waste disposal sites were tended to remain in an eternal safe and controlled situation. That behaviour has resulted in a static concept of landfills, keeping them untouched for as long as possible. Taking the current policy challenges in the European Union (Circular economy) into account as well as the UN Sustainable Development Goals, landfills are to be considered as dynamic stocks of resources (materials, energy, land). As a result, the containment and monitoring model of landfills is becoming under pressure. Maintaining a static situation in a dynamic environment is not a sustainable answer and will come at some costs (COCOON, 2018).

Hence, there is a need for a new model for landfills. A model that can be integrated into the circular economy and the current challenges in view of sustainable development. A new comprehensive, long-term and multi-phased concept was developed within the COCOON project: Dynamic Landfill Management (DLM) (Figure 2).

The objective of DLM is to bring landfills in harmony with their environment by preventing or reducing negative effects as far as possible. Furthermore, it tends to maximise and optimise the positive effects that can be created by conducting a dynamic landfill management. Of course, this should be done with respect to the current Landfill Directive. Moreover, it should take into account the European policies and legislations in the broadest sense (waste and resource management, green deal, climate change, flooding (Wille, 2018), soil sealing, no net land take, land stewardship…). This concept of 'Land(fills) as a resource' is fully in line with EU-needs to restore degraded land and encourage land recycling, in particular by supporting the regeneration of brownfields such as landfill sites. With the DLM concept, a new framework integrates multiple goals ranging from pollution prevention, land reclamation and restoration, reclaiming void space and setting up sustainable interim uses to the recovery of materials and energy resources (Jones et al., 2018).

2.2 Enhanced Landfill Mining as optimal DLM strategy

As a result of the 2nd ELFM European Parliament Seminar (Jones et al., 2018), there was a consensus that the way forward is to prioritise the incorporation of the more comprehensive, multi-phased concept of Dynamic Landfill Management into European legislation rather than focussing only on its most ambitious part, i.e. Enhanced Landfill Mining. It was agreed that Enhanced Landfill Mining (ELFM) remains a highly valuable concept, albeit as one specific, more advanced component within the broader DLM concept. Within the concept of ELFM, the valorisation and recycling of materials and energy is maximized and performed as sustainable as possible (Hogland et al., 2010). This concept aims at maximizing four different aspects:

- Recycling of materials
- Generation of energy
- Reclamation of space and land
- Safeguarding drinking water supplies

ELFM projects tend to generate opportunities for economic development by creating new (local) jobs, all within the context of a EU-wide transition to a resilient, low-carbon, circular economy (COCOON, 2018).

Unfortunately, it is not yet feasible to start up ELFM projects on a large scale. In a study of Laner et al. (2019) only a minor share of the landfill mining projects are deemed profitable. This profitability mainly depends on the system conditions (markets for materials and energy, value of reclaimed land,…) which can not be controlled within the project implementation. Within these system conditions, it also appears that revenues from recovered materials are relatively insignificant to revenues from reclaimed land when determining profitability (Laner et al., 2019). Hence, material valorisation cannot be the mere driver of an ELFM project. However, there are already promising cases of ELFM projects but most of the time,

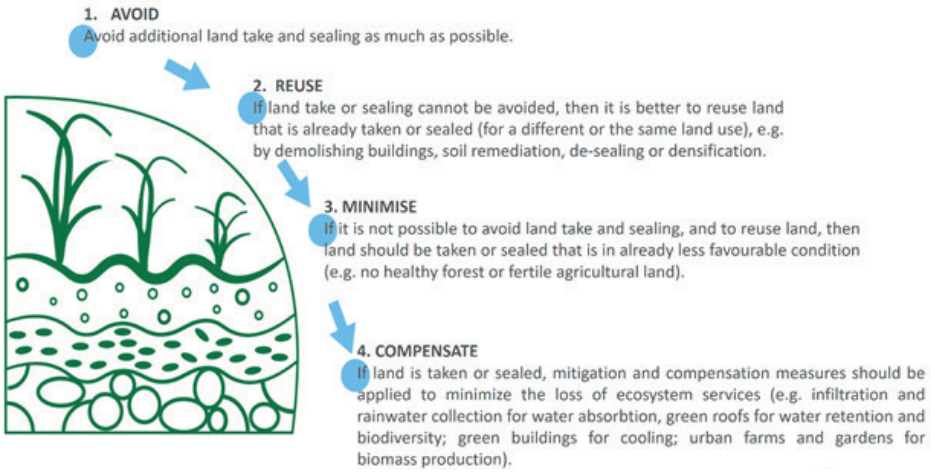

FIGURE 1: Land take hierarchy. Source: EU Soil Strategy for 2030, 2021.

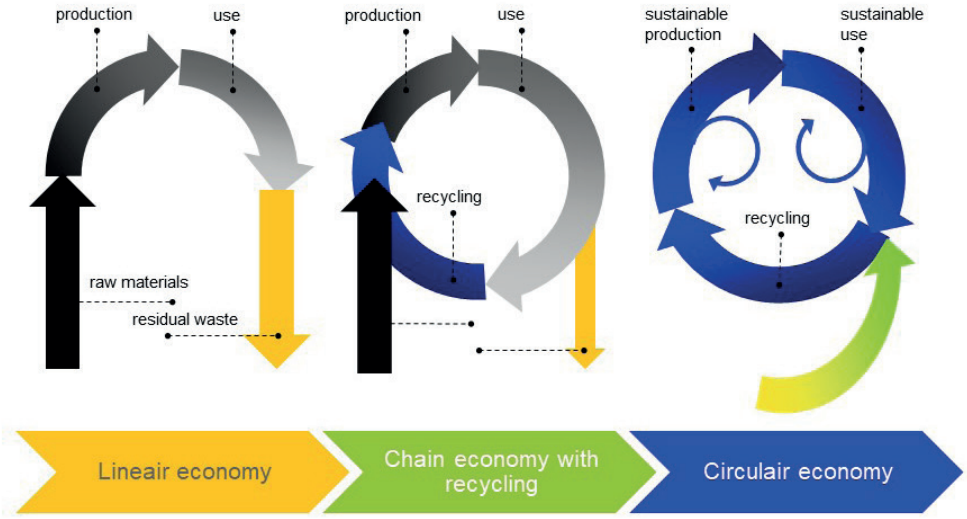

FIGURE 2: The transition of landfills in a circular economy: from waste to resources. Source: COCOON project.

these concern the landfill mining of homogenous, easy to process materials in mono landfills (Jones et al., 2013; Blengini et al., 2019).

2.3 The DLM warehouse

In order to bring the Dynamic Landfill Management concept into practice, the Public Waste Agency of Flanders (OVAM) proposed the need for interaction between three main system components for a first time in through MINEA (Mining the European Anthropocene), the pan-European expert network on assessment of anthropogenic resources in view of secondary raw material production. These three components are also seen as crucial in protecting health through urban redevelopment of contaminated sites by the WHO regional office for Europe (2021):

- "Orgware – represents how a process is organized, coordinated and regulated, and whether there are political and technical frameworks supporting remediation and redevelopment projects (e.g. enabling policies, such as grants or specific (financial) programmes; regulations and legal mandates; communication and engagement activities);
- Hardware – including equipment and techniques as well as procedures for risk assessment and site cleaning (e.g. machinery and tools for remediation, and sampling techniques);
- Software – assuring adequate evaluation procedures and calculation instruments (e.g. data collection, risk modelling and decision support tools)".

Together, these components are called the DLM Warehouse. To reach a sustainable and health-enhancing redevelopment of contaminated sites, a combination of all three components is needed. In case of landfill mining and dynamic landfill management, there has been a lot of focus on developing hardware and software. However, without a proper development of the orgware, the hardware and software will not be sufficient to promote landfill rehabilitation projects in the field. This is also illustrated by Laner et al. (2019), where policy intervention (orgware) is deemed crucial to launch profitable ELFM projects. Therefore, we want

to stress that using the developed decision support tools will not be sufficient to realize landfill mining or rehabilitation projects in the field. Instead, their use should be supported through the orgware.

3. THE IMPORTANCE OF DECISION SUPPORT TOOLS

Within the RAWFILL project, a lot of effort was put into developing specific software to support the implementation of Dynamic Landfill Management and to detect smart Enhanced Landfill Mining projects. For the landfill stock of 500 000 landfills in Europe, the available data of the landfill features and its waste content will be very diverse. A quick survey of all these landfills will result in a huge financial effort (500.000 sites, 10.000 euro/site: approximately 5 billion euro) and a short execution period will also pose capacity problems on available experts. Therefore, RAWFILL developed an integrated method to collect and analyse large datasets of landfill data.

Based on this dataset, policy makers, landfill owners, spatial developers, etc. need to be able to identify and rank the most promising landfills in terms of valorisation potential and project feasibility. Making decisions is part of life and humans do not continuously rely on instincts to make them. In that way, Decision Support Tools (DST) can improve decision-making by increasing the efficiency and lowering the uncertainty of the decision-making process.

3.1 The two-step decision support tool within the RAWFILL methodology

Data collection and analysis are part of economic and operational processes that have their limits. Therefore, the question rises on how to proceed with minor data supply but still make informed and intelligent decisions. A stepwise approach offers an efficient and cost-effective solution, limiting the efforts in the early stage of characterization and evaluation. In that view, Interreg RAWFILL developed a Decision Support Tool build on a two-step approach that aims at building up data capacity based on:

- the accessibility of the data (data mining); and
- the relevance for further investigation and planning.

In Figure 3, the role of the decision support tools within the RAWFILL methodology is illustrated. The two-step approach is realized by a combined DST named after Cedalion (DST 1) and Orion (DST 2). The DSTs take into account data on the characteristics of the (i) content of the landfill (e.g. grade, waste type, stability) and (ii) context of the landfill (e.g. accessibility, land pressure, climate change, vulnerability). This kind of data is collected and stored in the Enhanced Landfill Inventory Framework (ELIF) and can be easily exported to Cedalion. A first screening of the ELIF database with the Cedalion tool, allows to select the most promising landfills that require additional information for further analysis with Orion. This additional information can be gathered by using innovative landfill content characterization methods through geophysics and guided waste

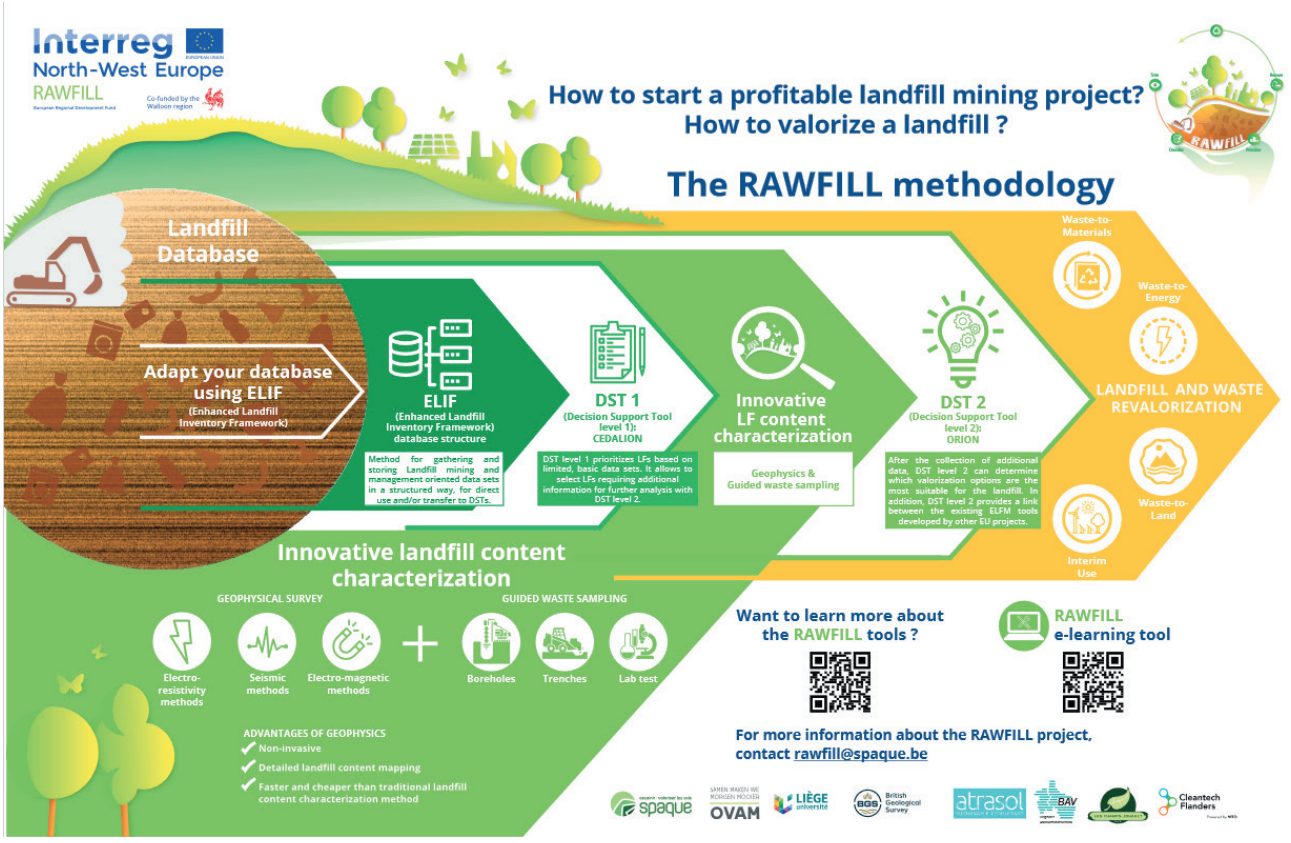

FIGURE 3: Infographic of the RAWFILL methodology. Source: RAWFILL project.

sampling (HADESS). With the detailed information gathered by HADESS, the Orion tool can be used to determine the most suitable DLM strategy for the valorisation of the landfill (and the waste if ELFM is profitable).

3.1.1 Enhanced Landfill Inventory Framework – ELIF

Conventional inventories merely contain administrative and environmental data. However, to get a view on the landfill resource potential, the feasibility of a possible landfill mining project or another sustainable management method, the RAWFILL project designed an enhanced landfill inventory framework. Within this framework, the emphasis is on the available resources in terms of materials, energy carriers and land. The framework also includes economic, technical, social and environmental threats and opportunities regarding landfill mining or other project developments. In that sense, it should be stressed that it is not only a question of "mining". Namely, all the information present in the ELIF is suitable for the evaluation of various DLM strategies, including interim use. The inventory structure is Excel based and serves as input for the first decision support tool Cedalion.

3.1.2 Decision Support Tool 1 - Cedalion

In the first step of the DST, Cedalion, a low investment in exploration cost will be sufficient, as the data can be exported from the ELIF into the DST. In order to get other stakeholders involved, a user-friendly application supports the use of the DST by allowing non-experts to update or add information (Figure 4). This application also enables local employees to evaluate and promote opportunities for DLM. The DST 1 performs an initial screening of the landfill database and guides the user to the next level. The output is not simplified to a yes/no decision, but the result will be a ranking for different possible pathways:

- waste to materials;
- waste to energy;
- waste to land; and
- interim use.

This ranking is based on a selection of simple parameters from the ELIF database: the type of waste within the landfill, the age of the landfill, the volume of the landfill, the design/use of the landfill, the accesibility and the surroundings of the landfill. At this level, a first overview of the opportunities is generated. It is not the goal to provide a detailed cost-benefit analysis. This will be done in the next step of the DST as a cost-benefit estimation requires more thorough data collection.

In the first place, RAWFILL introduced this method in view of large scale prospection campaigns. However, if you're not evaluating a database with that many landfill sites, the Cedalion tool will give you also results for an individual landfill. Furthermore, landfills can obtain a 'quick response' that indicates the start of setting up a long term management plan wherein ELFM might be an option. This approach is in line with the concept of Dynamic Landfill Management which aims at a long term active management of landfill, going beyond containment measures.

By means of this prioritization and classification, Cedalion can identify the landfills for which it is worth to invest in more detailed characterization by means of geophysical estimations (HADESS).

3.1.3 High-performing Acquisition of landfill Data by using a geophysical Exploration and Surveying Strategy - HADESS

When correctly applied, geophysical surveying methods can help to better understand the content of landfills (Isunza Manrique et al., 2019; Lamair et al., 2021). In that aspect, geophysical methods should be used in combi-

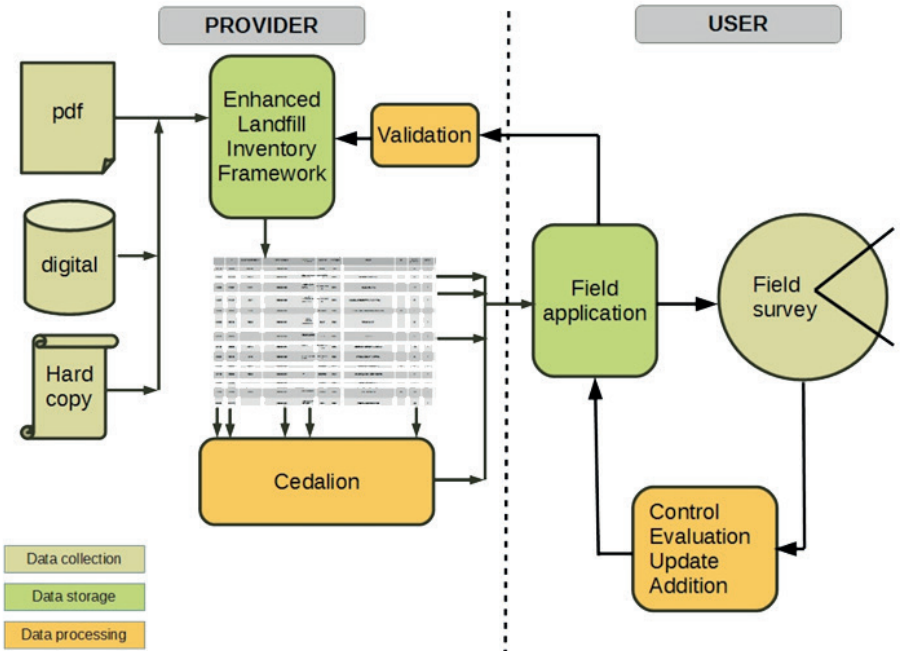

FIGURE 4: Scheme on the data collection, data storage and data processing within the Cedalion DST 1. Source: RAWFILL project.

nation with a priori data collection (see Section 3.1.1 on the ELIF) and targeted sampling (e.g. through boreholes, trenches). Geophysical prospection methods have a lot of advantages compared to conventional sampling: they are rapid, non-invasive, surface-based and they can be used to measure bulk ground properties such as electrical conductivity, density or stiffness. Due to these properties, relatively large areas can be investigated and areas with contrasting material properties can be delineated through mapping. The final step in the workflow of HADESS is the building of a Resource Distribution Model (RDM) that contains the spatial and volumetric distribution of indicative parameters of the landfill materials. For more information, we refer to the Landfill Miner Guide developed in the RAWFILL project (RAWFILL, 2021). The collected data can be used as input for the second step of the two-step DST: Orion.

3.1.4 Decision Support Tool 2 - Orion

Landfills selected by Cedalion as having a high potential for redevelopment are referred to the DST 2. Orion is an interactive tool that can assist the user in analysing the most suitable strategy for DLM on a specific landfill site. RAWFILL has identified several decision support systems in order to integrate them in an overarching DST. Each model or tool has its own strengths and weaknesses. Hence, the best decisions would be made by using them in combination.

When using the Orion tool, the user should start by going through the roadmap. This roadmap includes a sequence of straightforward but more in-depth questions about the characteristics of the landfill like the heterogeneity of the waste, the hazardousness of the waste, the geometry of the landfill, economic feasibility… The answers to these questions will lead to a possible outcome for a landfill in terms of valorisation or rehabilitation potential (Figure 5). However, to answer these questions, the user will need to invest more in data collection. Methods of geophysical explorations (cfr. HADES method developed in the RAWFILL project) are perfectly fit to gather the right information. The possible outcomes of the roadmap are the following suggestions:

- Develop a remedial action plan;
- Develop an enhanced landfill mining project;
- Develop a business case; and
- Set up an interim use.

When arriving at these end-points, Orion will redirect the user to the dashboard (Figure 6) and the relevant tools which can assist the user in the further progress, will be lightened up. From there on, the user can discover and explore the different tools that are indicated for further use. The central part with the steering wheel is symbolizing the landfill. The features inside are useful to evaluate the characteristics and fate of the landfilled waste. The Biogas button links you with a model designed to predict landfill gas production. SMART GROUND offers a tool to choose the best available techniques to process the landfilled waste (Pastre et al., 2018). OnToL (Online tool for the economic and ecologic evaluation of landfill mining) developed by TU Wien, was given a central position because of its relation with the United Nations Framework Classification for Anthropogenic Resources. Out of the inner circle of the steering wheel, the instruments are more related to effects and impacts coming from outside the landfill (the context). Floodrisks and erosion are typical phenomena, which could cause harmful situations and damage to the landfill. Land pressure is often a driver to undertake action on landfill redevelopment and specific regional models can provide prognosis on future land use and pressure. The period between the present and the rehabilitation might be relatively long e.g. sometimes decades. Interim use can be considered and green energy production might be an option in the meantime. For the latter, the US EPA model on renewable energy might support the user's choices. The redevelopment of the landfill is comparable with the process of brownfield revitalization. The Brownfield opportunity matrix is therefore also a relevant tool. When the redevelopment starts, quite often large quantities of waste or recycled materials must be transported to treatment facilities. Many countries have specific tools to choose the most sustainable option. More information on these models and tools can be found on the web pages behind the dashboard buttons.

Using the Orion tool will help the user with estimations about the feasibility of a business case, simulating certain scenario's or finding sustainable interim solutions. The latter, interim use, is the novelty in this dual DST and it should be seen as a loop in the programme. The landfill will be given a function that is beneficial for nature and/or society while bridging time until a better valorisation might be profitable. Interim use can go from one year up to several decades.

3.2 Practical implementation of the DST in frame of nature development

In Flanders, a large scale application of the DST was set up, to support the project "Landfills and nature redevelopment opportunities on landfills". This project is related to the ambition of the Flemish Minister of Environmental Affairs to achieve 4.000 ha of additional forest by 2024. In Flanders, open space is scarce and hence, it is not easy to find space for nature. As landfills are often abandoned areas that have low societal value, OVAM explored the possibilities of afforestation or nature development on landfills as a mid- or long term interim use with a high value for the society. To do so, OVAM implemented the knowledge and tools that were created within the RAWFILL project.

3.2.1 Exploration phase

In a first step, we used our Flemish Cedalion database with 3318 records to explore the theoretical possibilities of afforestation and nature development on landfills by doing a large scale prospection. This prospection resulted in the identification of the high potentials for afforestation or nature development (Figure 7).

Furthermore, we used the Orion Dashboard to further analyse these high potentials. Therefore, for the Flanders region, the RuimteModel Vlaanderen from VITO is present behind the land pressure button in the dashboard. With this model, the external drivers and limitations were analysed to see if afforestation or nature development would match

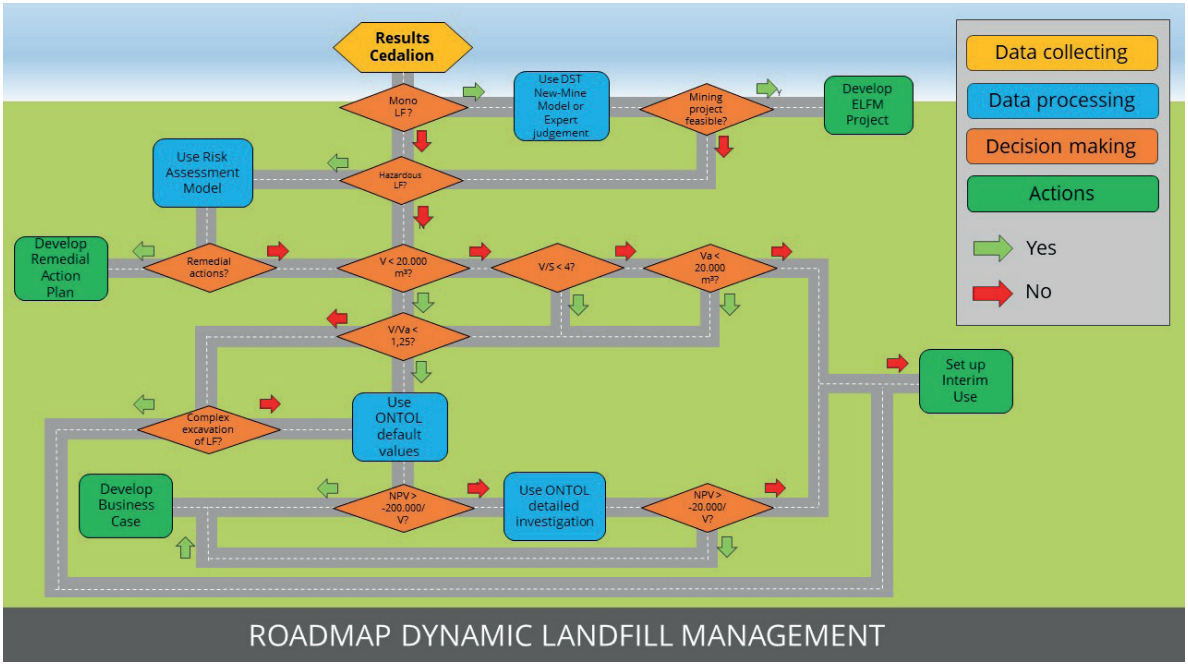

FIGURE 5: The Orion Roadmap. Source: RAWFILL project.

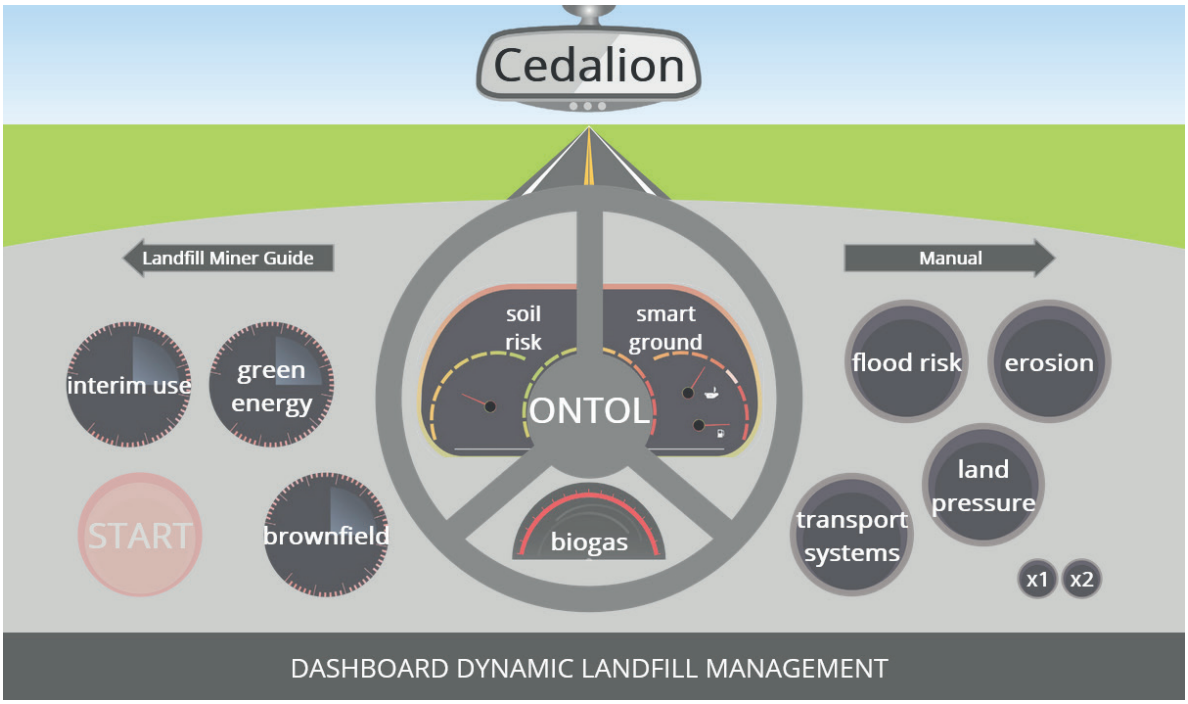

FIGURE 6: The Orion Dashboard. Source: RAWFILL project.

with the needs of the surrounding environment at these specific locations. Also the land pressure was taken into account: when the land pressure is lower, the land value will also be lower and the potential for afforestation or nature development increases.

3.2.2 Implementation phase

Based on the results of the first exploration with the RAWFILL tools, OVAM developed an implementation plan in cooperation with the governmental Agency for Nature and Forest to realize additional forest on landfills in Flanders. The approach was mainly oriented at the local authorities, as they have the best view on the actual possibilities on site. An on-site check with owners and stakeholders is always necessary to affirm the actual potential.

In practice, we send a letter to all local authorities for which OVAM documented old landfills in the Cedalion da-

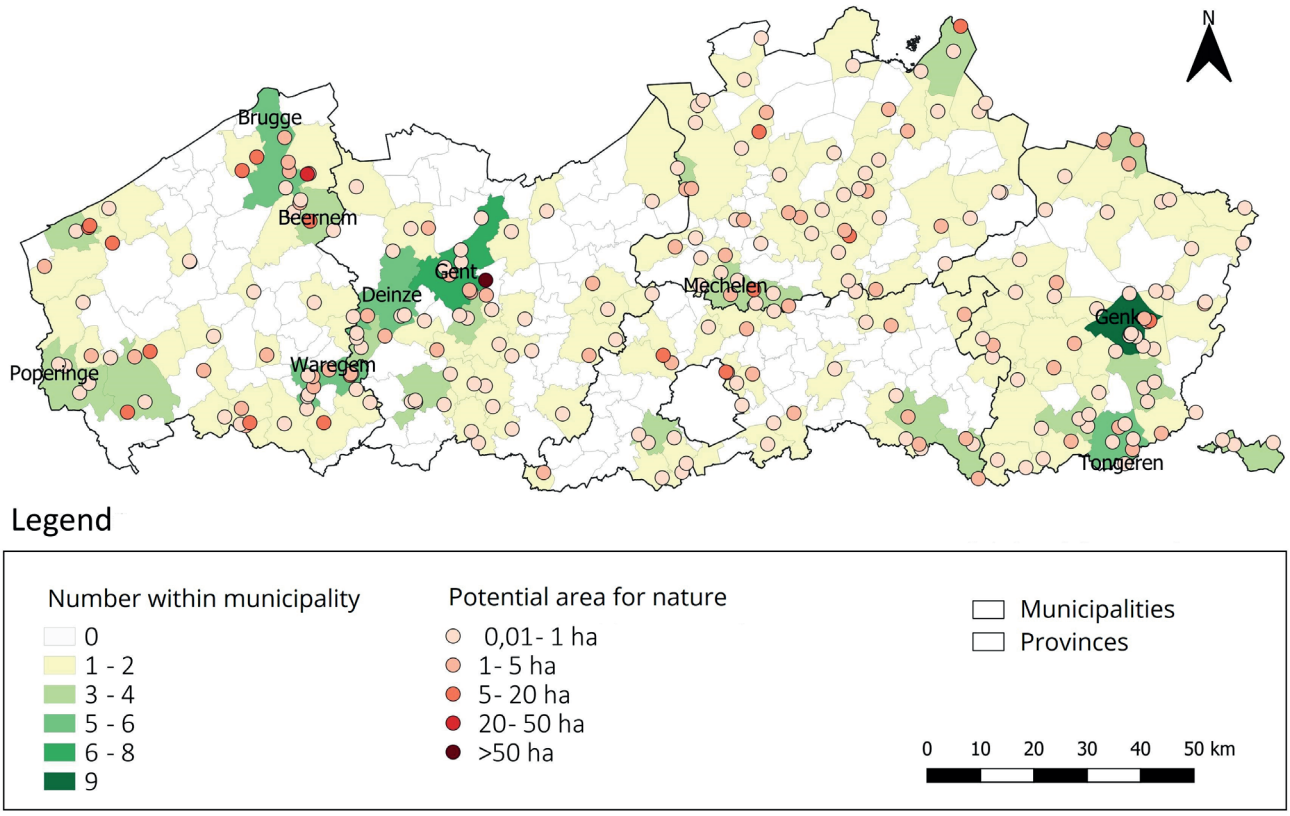

FIGURE 7: Map of landfills in Flanders with a high potential for afforestation or nature development resulted from a large scale prospection campaign. Source: OVAM.

tabase (296). Each local authority received (1) a letter send from the office of the Minister of Environmental Affairs, stating the purpose, conditions and benefits of the project and (2) a map with the identified landfills present in the Cedalion database.

On the map, the QR code of the Cedalion field application was included. In that way, the local civil servants are able to digitally share information on the landfills with OVAM by means of a simple smartphone device. This sort of civil servant science provides OVAM information on the interest of municipalities to set up nature conservation and/or forestation projects. Furthermore, the Cedalion database is validated and updated based on the local knowledge of the local authorities.

If the local authorities intend to upgrade a landfill to a forest or other natural landscape, and a Preliminary Soil Investigation is not performed yet, OVAM will perform the investigation at its expense. During that investigation, OVAM will also analyse the afforestation potential from an environmental technical point-of-view. To determine this potential, a flow chart was developed in order to determine that (1) afforestation is possible, (2) afforestation is possible under certain conditions or (3) afforestation is not possible. Thereby, also specific advice is given on measures that should be taken when you afforest a specific landfill and which prevention measures should be taken to guarantee the safety of the users. This scheme will be included in the DST 2.

4. RESULTS AND DISCUSSION

Although Circular Economy is the new paradigm, former landfills will remain as remnants of the Linear Economy. Estimates have revealed that 90% of Europe's 500,000+ landfills are "non-sanitary" landfills, which predate the EU Landfill Directive. These landfills 'claim' an estimated one million hectares of space (60 times the Brussels agglomeration) in the EU. On the other hand, natural primary resources and land are becoming scarce in Europe. These 500.000+ landfills doesn't only pose risks but could also be regarded as potential zones for secondary resources (Winterstetter et al., 2016; UNECE, 2019).

The variety of landfills (size, composition,...) and its surroundings (vulnerability, demands,...) necessitates structural support to evaluate the potential valorisation and long-term monitoring. The decision support tools developed by RAWFILL process the data provided by the geophysical prospection (HADESS) and which were uploaded in the landfill inventory (ELIF). The dual system was chosen to allow assessments on landfills with limited datasets (Cedalion) and more detailed analyses (Orion).

Cedalion extracts data from the ELIF and a field application makes it possible to verify, adapt and add data to the database. Although the number of data is limited, it acts as a driver to visit landfills, pay attention to the current situation and initiate new initiatives. The interest of public and private actors in former landfills increases if data is provided and more sustainable use options are put in place.

Traditionally, EU-policies refer to 3Rs or more Rs (refuse, reduce, reuse, repurpose, recycle,…) but in the particular case of landfills, maybe 'rethinking the long term management' is the most crucial element.

The DSTs are applicable on a large number of landfills and can be used as prioritization tool to select the most promising landfills for further investigation and appropriate actions. The Orion dashboard is easy to customize to local conditions and demands. It also puts the landfill sites in the broader perspective of the surrounding systems (ecological, economics). The DSTs take into account both the content and context of the landfill. These system conditions might trigger the management actions in case of threats (flooding risks, health risks) and/or opportunities (redevelopment, mining).

The DSTs use basic concepts from traditional mining to estimate the mining potential: characteristics of the deposited waste: grade (distribution, homogeneity, concentration) and accessibility of the landfill (depth, stability, transport, weather conditions). Although similarities exist between the geogenic mining and the mining of anthropogenic stocks, their differences require an appropriate approach (contamination, spatial pressure, liability, long term effects, …) and this was taken into account in the development of the DSTs. By looking in 4D, the most appropriate management can be chosen and combined with an interim use of the landfill site.

5. CONCLUSIONS

Management of non-operational landfills was often limited to containment and monitoring. If actions were undertaken, the driving forces were related to the negative impact on the environment. By introducing the concepts of Dynamic Landfill Management and Enhanced Landfill Mining, a new and broader focus was put on landfills. The RAWFILL-project provided several tools to inventorise, investigate and evaluate landfills in view of a sustainable long-term management and valorisation. This long-term management will be important in the frame of the EU Soil Strategy that emphasizes the need for land planning according to the land take hierarchy. In that view, landfills no longer count as a threat, but can also provide a solution.

The decision support tools Cedalion and Orion allow site-ranking, smart (E)LFM-project planning, prioritization and interim use options. The capacity-tests pointed out that thousands of landfills can be evaluated and Cedalion is suitable as a prospection tool in order to select the best suited landfill sites for mining, land redevelopment, forestation, etc. The Orion-dashboard offers the option to add region-specific models and tools, a customization which is crucial with regard to the variety of landfills and regional demands/threats.

The availability of the RAWFILL-products shows already effect in the mind of policy makers and environmental companies. Attention is paid to former landfills and programmes were set up to rehabilitate landfill sites.

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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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CISA

Environmental Forensic

REMOTE SENSING TECHNOLOGY FOR ENVIRONMENTAL FORENSIC

George Varghese [1], Claire Gwinnett [2], Massimiliano Lega [3] and Alberto Pivato [4]

[1] *NIT Calicut, Kozhikode, India*
[2] *Staffordshire University, United Kingdom*
[3] *Department of Engineering, University of Naples Parthenope, Italy*
[4] *Department of Civil, Environmental and Architectural Engineering (ICEA), University of Padova, Italy*

Introduction: definition and applications

Remote sensing, in its broad sense, involves acquiring information from a distance. But, in practice, it often refers to the 'process of detecting and monitoring the physical characteristics of an area by measuring its reflected and emitted radiation at a distance, typically from satellite or aircraft using specially designed sensors' (USGS). The sensors are either passive or active. Passive sensors record the natural energy reflected or emitted from a surface. Reflected sunlight is perhaps the most common source of radiation detected by passive sensors. Active sensors, on the other hand, detect the reflected portion of the radiation emitted by the remote sensing system itself. For example, in a microwave remote sensing system, a microwave is transmitted towards the target and the backscattered portion of the signal is detected by the sensor. Remote sensing has a wide range of applications including mapping, weather forecasting, agriculture, forestry, environmental monitoring, etc.

Remote sensing for environmental monitoring

Challenges to the quality and integrity of natural environments due to human interactions are diverse, but include oil spills, violation of land and wildlife habitat, water pollution, illegal waste dumping and wildlife crimes, such as illegal poaching and disruption of habitat and breeding areas. Environmental monitoring of the air, soil and water for pollutant presence is globally utilized to continuously assess the quality of the physical environment.

Traditional monitoring for the presence of pollutants involves field surveys, sampling and instrumental analysis. These monitoring techniques are important to identify and quantify the pollutant, but they are time consuming, expensive and, often, not in real-time. A method that provides an earlier indicator of a pollutant or other unwanted human interaction with a habitat or species, that can be easily accessed and interpreted by individuals whose job it is to monitor/prevent such activity, yet do not have access to analytical techniques, is desired. Remote sensing for environmental monitoring assumes significance in this context.

The use of remote sensing (RS) technology for environmental monitoring has a number of benefits including automated processing, wide coverage, good revisit capability and a vast range of identifiable features (Sizov et al, 2014; Gomez, 2019). High resolution satellite data has been used previously for environmental monitoring of oil fields (Sizov et al, 2014), wetlands (Jie et al, 2021), forests (Gomez, 2019), landfills (Lacoboaea and Petrescu, 2013), etc.

There are a range of sources of images (both optical and radar) that have been used for remote sensing of the environment including; ALOS PRISM, RapidEye, WorldView-2 and Quickbird imagery (Sizov et al, 2014), those taken using Enhanced Thematic Mapper Plus (ETM+), Landsat 8 Operational Land Imager (OLI) (Jie et al, 2021) and European Copernicus sentinel satellites and MODIS (Gomez, 2019). Many of these are available online and include their processing standards. Landsat (ETM+, OLI), Sentinel 1(SAR), Sentinel-2 (MSI), Terra and Aqua (MODIS) are all free to use whilst ALOS-2 (PALSAR), Radarsat-2 and TanDEM-X are available under a research license. It has been noted that there are unparalleled opportunities being offered by the availability of diverse RS data like those provided by the European Copernicus programme and recent satellite LiDAR launches for environmental monitoring work (Gomez, 2019). Specific reporting requirements, for example when monitoring forests, requires frequent data acquisition (Diaz-Balteiro & Romero, 2008). Although the use of satellite data has proved useful, the best results are obtained using data from multiple types of aerial platforms and sensors, placed at different altitudes, integrated in a GIS and analyzed with specialized software (Errico, 2014) - see Figure 1.

Remote sensing for environmental forensic applications

Brilis et al. (2000) have discussed the application of remote sensing and photogrammetry in environmental forensics, as back as in 2000. A major advantage of using aerial photogrammetry (perhaps the oldest form of remote sensing), according to the authors, is its ability to provide

Managing editor:
Alberto Pivato
email: alberto.pivato@unipd.it

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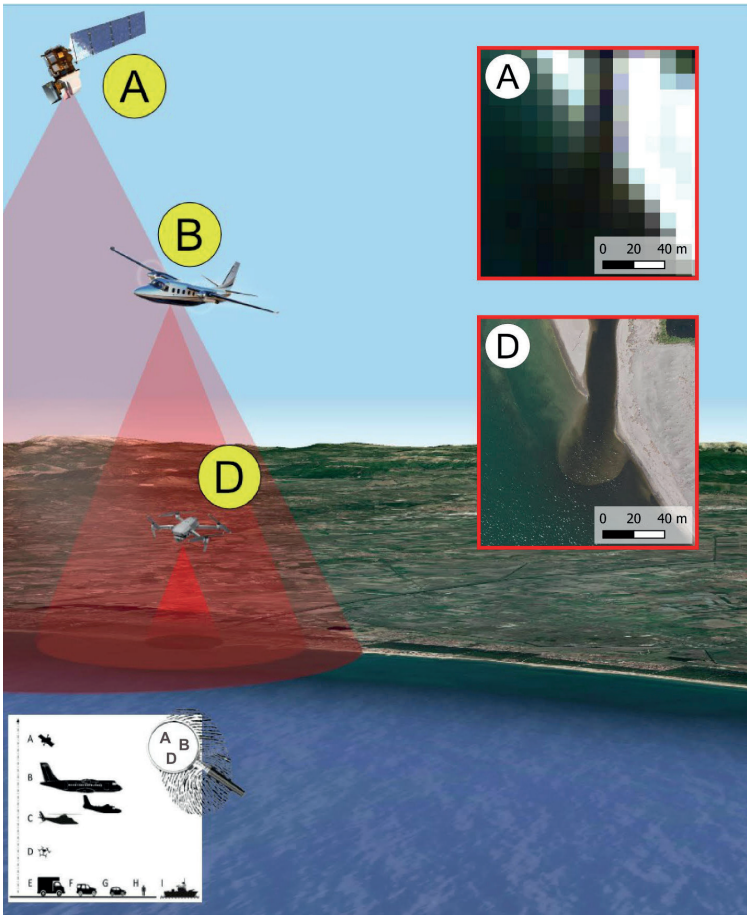

FIGURE 1: Hierarchical monitoring: multiple types of aerial platforms and sensors, placed at different altitudes and an example of different data acquired by satellite (A) and drone (D) targeted to the same area.

objective, detailed documentation of surface conditions at a specific time even in cases where access on the ground is denied to investigators. Where ever records are available, aerial photography can give valuable information concerning a site's waste handling practices which in turn can help in age dating of contaminant releases. Aerial photographs can be analyzed and interpreted to locate past barrel storage areas, open drainage ditches, stains on the ground, standing liquids, landfills, etc. that are often 'hotspots' as far as historical contamination episodes are concerned. In rare cases, aerial photographs, as forensic evidence, may capture fugitive emissions from industrial units or surface release of contaminants, which would help in fixing the responsibility in an otherwise difficult situation (Morrison, 2000).

Satellite remote sensing, though has the disadvantage of lower image resolution, can be extremely useful in environmental forensics, at times. One big advantage with the satellite remote sensing data is its use in tracking changes over a period of time. A series of images spanning over a period of time, of the site under investigation will reveal the changes in the handling pattern of the site and may offer valuable information in resolving the mystery regarding the timing of a contaminant release. Remotely sensed data regarding a site and its surroundings, like topography, land use, etc. may find use in the mathematical models used in forensic investigations. Investigations may lead to unjustifiable results if the changes that the topography of a site has undergone after the contamination episode, are not considered in arriving at a conclusion. Information obtained from satellite images assumes great importance in this context. An experienced image interpreter will be able to gather valuable information regarding the extent of contamination at a site from the variations in colours/ hues observed in the images of the place over a period of time.

The value of remote data is augmented by the correlation to the proximal and the in situ measurements.

A challenge that an environmental forensic expert would face during the in-situ monitoring of contaminated landscapes is the risk to his health due to the volatilization of pollutants. Maio et al. (2017) had demonstrated, on a laboratory scale, that thermal infrared (IR) remote sensing can discriminate between areas with volatilizing chemicals and differentiate between pollutant types and concentrations based on volatilization. Recent technologies of sensors, such as multi and hyperspectral cameras or gas-sensitive IR thermal imaging cameras, have introduced new potential in this field overcoming the limitations of the previous approaches. Lega et al. (2014) reported the use of a range of aerial platforms and an innovative application of thermal infrared remote sensing to detect several illegal activities like, illegal sanitary sewer and storm-drain connections, illicit wastewater discharges, etc.

The remotely sensed data detected at different altitude and that collected in situ, can benefit from their integration; indeed, a Multi-level and Multi-parametric monitoring framework, named MUM3 (Lega, 2018), outperforms the current routine monitoring programs because it combines and integrates multilevel and multiparametric data and information, creating a multi-layer dataset and allowing a complete overview of the phenomenon in a specific scenario. There are examples of the effectiveness of an integrated system both in the study of illegal landfills (Di Fiore, 2017) and coastal discharges (Ferrara, 2017).

By combining remote / proximal sensing (using drones) techniques with analytical / bioinformatic tools, it is possible to use environmental indicators that overcome the limitations of the individual parameters detectable in each acquisition layer. For example, it is possible to use bioindicators such as the cyanobacteria, detectable by remote, proximal and in situ monitoring, both to define the quality of the water and as tracers to define the relationships between the source of contamination and the target area (Teta, 2017; Esposito, 2019).

The range of applications of remote sensing in environmental forensics is wide. It is a useful tool in oil spill forensics to identify the spills and document the time and location of spill observations (Stout and Wang, 2016). It also finds application in the detection of unregistered cattle-breeding facilities, potentially responsible for hazardous littering (Gargiulo et al. 2016).

Concluding remarks

For the enforcement authorities, remote sensing provides a method capable of analyzing multiple variables on both spatial and temporal scales to indicate patterns of activity which warrant investigation and intervention. With the growing use of Unmanned Aerial Vehicles (UAVs), today often called drones, it is possible to have observations from low altitudes that improves the quality of data available to the enforcement agencies. This, coupled with the significantly enhanced data analysis capabilities of Artificial Intelligence (AI) and 'deep learning' techniques, is expected to drive the future of remote sensing in environmental forensics.

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Research to Industry and Industry to Research

LESSONS FROM A LARGE DATASET OF AQUATIC ECOTOXICOLOGICAL TEST RESULTS FOR ROUTINE HP 14 CLASSIFICATION OF WASTES: THE CASE OF BOTTOM AND FLY ASHES IN THE ITALIAN FRAMEWORK

Lorenzo Maggi [1], Giovanni Beggio [2,*], Claudia Mensi [3], Domenico Marchesini [4], Paola Grenni [5], Erica Tediosi [1], Stefano Ceriati [1] and Alberto Pivato [2]

[1] *Chemservice S.r.l. - Lab Analysis Group, Via F.lli Beltrami, 15, 20026, Novate Milanese, Milano, Italy*
[2] *Department of Civil, Environmental and Architectural Engineering (ICEA), University of Padova, Via Marzolo 9, 35131, Padova, Italy*
[3] *A2A Ambiente S.p.A., Località C.na Maggiore, 27010, Giussago, Pavia, Italy*
[4] *ARPA Lombardia, Via I. Rosellini 17, 20124, Milano, Italy*
[5] *Water Research Institute, National Research Council, Via Salaria km 29.300, 00015, Monterotondo Scalo, Roma, Italy*

* *email: giovanni.beggio@unipd.it*

INTRODUCTION

According to the European Waste Framework Directive (WFD), waste materials classified as hazardous are not suitable for recycling. In this context, an efficient and scientifically sound system for waste classification is crucial to achieve the ambitious goals of the European circular economy (European Parliament and European Council, 2018).

Wastes classified as "mirror entries" (i.e., wastes potentially classified as hazardous if containing hazardous substances above a specific level) on the European List of Waste (LoW, European Commission, 2000) require assessment of their specific Hazard Properties (HP). In this context, "Ecotoxicity" (i.e., HP 14) is acknowledged as the HP most frequently resulting from wastes classified as hazardous.

Current regulation states that HP 14 shall be used to classify wastes that can present or may present immediate or delayed risks for ecosystems (European Council, 2017). In practice, HP 14 can be assigned by an "indirect" approach, based on the total content of hazardous substances (selected according to "expert judgement"), or a "direct" approach, which relies on data from a battery of ecotoxicological laboratory tests. Considering toxic effects due to the speciation of hazardous substances in addition to possible mixture effects, the direct approach can provide more reliable assessments. For this reason, when performed, outcomes from bioassays will prevail over the results of chemical composition analyses.

The EU regulation does not indicate a detailed procedure for the direct test approach. Rather, it suggests that the methods indicated in Regulation 2008/440/EC (European Council, 2008) are compliant when used within the scope of the regulation on Classification Labelling and Packaging of products and substances, (CLP) (European Parliament and European Council, 2008), together with "other internationally recognized guidelines" (European Council, 2017). Among these latter, validated methods developed ad hoc for waste materials may vary from those used for assessing the ecotoxicity of products (i.e., CLP-related methods). These discrepancies, together with the lack of detailed instructions, fostered the development of an unharmonized analytical context within Member States, thus far hindering the use of the direct approach and the creation of a well-defined classification of mirror entries.

In Italy, the institutional/regulatory guideline for the performance of the direct approach is consistent with the Reg. 2008/440/EC and thus the CLP (SNPA, 2021).

The Italian Guideline allows only aquatic bioassays to be used with specific classification limits, as indicated in Table 1. Solid wastes require suitable leaching tests (ECHA, 2017) in which the solid waste sample preparation (i.e., particle size reduction and leaching conditions) is crucial to obtaining reproducible and reliable results. However, no specifications are provided for the treatment of materials containing substances and mixtures that are difficult to extract in aqueous solution, as is frequently the case for solid waste materials. These aspects are a source of variability in the HP14 classification, regardless of the total quantity and speciation of the solid phase chemicals in a waste (Stiernström et al., 2016).

Adopting product-related regulations, the Italian approach relies on the following technical guidelines for waste preparation and leaching test performance:

- OECD N.23 - Guidance document on aqueous-phase aquatic toxicity-testing of difficult test chemicals (OECD, 2019).
- OECD N.29 - Guidance document on transformation/dissolution of metals and metal compounds in aqueous media (OECD, 2001).

Managing editor:
Alberto Pivato
email: alberto.pivato@unipd.it

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TABLE 1: Battery of biotests and concentration limits used within the testing strategy complying with the CLP Regulation and SNPA (2021) (derived and modified from Beggio et al., 2021).

Organism	Type	Standard	Classification Criteria (waste is hazardous for HP 14 if)
Algae	Acute-Chronic *	OECD 201/2011 (Freshwater Alga and Cyanobacteria, Growth Inhibition Test)	Acute LC50 ≤ 100 mg/L
	Chronic	OECD 221/2006 (Lemna sp. Growth Inhibition Test)	Chronic NOEC ≤ 1 mg/L
Crustacean	Acute	OECD 202/2004 (Daphnia magna, Acute Toxicity Test)	Acute LC50 ≤ 100 mg/L
	Chronic	OECD 211/2012 (Daphnia magna, Chronic Toxicity Test)	Chronic NOEC ≤ 1 mg/L
Fish	Acute	OECD 203/1992 (Fish, Acute Toxicity Test)	Acute LC50 ≤ 100 mg/L
		OECD 236/2013 (Fish, Acute Toxicity Test)	Acute LC50 ≤ 100 mg/L
	Chronic	OECD 210/2013** (Fish, Early-Life Stage Toxicity Test)	Chronic NOEC ≤ 1 mg/L

** According to ECHA, (2017) "The algal growth inhibition test is a short-term test that provides both acute and chronic endpoints. However, EC50 is treated as an acute value for classification purposes."*
*** Test not reported within European Council, (2008) and SNPA, (2020), but present in ECHA, (2017).*

Alternative, internationally recognized guidelines are available, including similar aquatic tests, but with different leaching methods and, consequently, different limits (CEN, 2005; Moser and Römbke, 2009; Pandard and Römbke, 2013). Many authors (Bandarra et al., 2020; Tsiridis et al., 2012) have developed experimental designs that are more consistent with this approach than the CLP design. However, this comparison is beyond the scope of the current report (Beggio et al., 2021).

Two additional critical issues should be considered in the Italian framework. First, several methods are suggested by the guideline regarding the application of CLP criteria to obtain chronic endpoints (ECHA, 2017) but are not explicitly included in the list of methods validated for CLP or the Italian guideline for waste classification (European Parliament and European Council, 2008; SNPA, 2021). This fact still represents a limit because, from the definition of ecotoxicity, the assessment of delayed risks for ecosystems, in other words chronic effects, are needed.

Second, the OECD 236:2013 "Fish Embryo Acute Toxicity test" is suggested as an alternative test to the OECD 203/1992 without any comments on the validity of the method to replace the latter. Sobanska et al. (2018) explicitly affirm that OECD 236:2013 cannot be used as a direct "one-to-one" replacement for the AFT and thus cannot be used alone to meet the information requirement for short-term toxicity testing on fish (REACH Regulation, Annex VIII, 9.1.3). ECHA reached the same conclusions in 2016 (ECHA, 2016).

Among designated mirror wastes, those generated by the incineration of municipal solid waste (MSW), i.e., bottom ash (BA) and fly ash (FA), are of particular interest due to the large quantity of these materials generated yearly. In fact, European MSW production accounts for approximately 492 kg/year/inhabitant (7-10% of the total waste generated in 2018), and 60% of this waste is incinerated (Eurostat, 2020), in line with the recommended MSW management (Dri et al., 2018). Municipal solid waste incineration substantially reduces its volume by 90% (Cheng et al., 2010) by producing bottom ash (BA, approximately 200-300 kg/t of waste) and fly ash (FA, approximately 30-60 kg/t waste) (EU, 2015).

BA and FA can be classified as mirror entries according to the European LoW. Depending on their specific content, they could be classified with the specific entry codes: hazardous BA: 19 01 11* (hazardous) or 19 01 12 (not hazardous); FA: 19 01 13* (hazardous) or 19 01 14 (not hazardous).

Moreover, HP14 classification also has practical consequences regarding incineration plant authorization under the framework of the Seveso Directive (European Parliament, European Council, 2012). In fact, ashes are commonly stored in large quantities and for a long period in incinerator deposits, and if they are classified as dangerous, requirements for the Seveso Directive must be fulfilled. In accordance with the Seveso Directive, waste must be included in the calculation of the quantities of hazardous substances/mixtures for the purposes of verifying the applicability of the directive. In fact, Note 5 of Annex Directive 2012/18/EU states: "In the case of dangerous substances which are not covered by Regulation (EC) No 1272/2008, including waste, but which nevertheless are present, or are likely to be present, in an establishment and which possess or are likely to possess, under the conditions found at the establishment, equivalent properties in terms of major-accident potential, these shall be provisionally assigned to the most analogous category or named dangerous substance falling within the scope of this Directive". Table 2 reports the correspondence between CLP and Seveso classification.

The aim of the current paper was to report the results of routine classification outcomes from a large sample size of BA and FA derived from the results of both indirect and direct testing approaches and performed in compliance with the current Italian regulation. These data can be useful to a) define specific suggestions for laboratory procedures, b) provide a reference dataset for comparison to future data, and c) promote the use of bioassays for a more realistic HP14 classification of wastes.

TABLE 2: Comparison of Environment hazardous codes in CLP and Seveso regulations.

CLP Classification	Seveso Category
Aquatic Acute 1 H400	E1. Hazardous to the Aquatic Environment in Category Acute 1 or Chronic 1
Aquatic Chronic 1 H410	E1. Hazardous to the Aquatic Environment in Category Acute 1 or Chronic 1
Aquatic Chronic 2 H411	E2. Hazardous to the Aquatic Environment in Category Chronic 2
Aquatic Chronic 3 H412	-
Aquatic Chronic 4 H413	-

MATERIAL AND METHODS

179 samples of bottom ash (BA) and fly ash (FA) were collected from 20 different plants and assessed for routine HP14 classification by the "indirect" and "direct" approaches.

The indirect approach relied on the chemical characterization of collected samples. Total concentration data were used as input in the classification criteria laid down in the regulation 2017/997/EU (European Council, 2017). For the speciation of inorganic element concentrations a "worst case with information" approach was used.

For ecotest performance, sample preparation and leaching procedures followed the methods suggested by CLP regulations and Italian guidelines for waste classification (SNPA, 2021). Only acute ecotoxicological tests were performed on the eluates (see Table 1). Wastes showing an EC50 higher than 100 mg/L for each tested organism were evaluated as not hazardous. Conversely, wastes resulting in at least one EC50 lower than 100 mg/L among the performed bioassays were evaluated as ecotoxic and thus classified as hazardous for HP 14.

All analytical procedures were carried out at the "LabAnalysis" and ChemService laboratories (Italy).

RESULTS

According to the "indirect" approach, based on the measured total content of elements and substances already classified as ecotoxic in the CLP, approximately 81% (i.e., 130 of 161) and 89% (i.e., 16 of 18) samples of BA and FA, respectively, were classified as hazardous for HP 14.

Interesting considerations can be drawn from the outcomes of bioassays performed on samples already classified as hazardous by indirect approaches, which are graphically summarized in Figure 1.

Remarkably, all ecotests performed on fish resulted in EC50 values above 100 mg/L.

Among BA samples, the hazard classification by HP 14 was confirmed only for 15.4% (20 of 130) of the samples by the direct test approach. Among the results of single bioassays (Figure 1), the most sensitive test was the Daphnia magna acute toxicity test, with 13.1% (17 of 130) of the samples resulting in an EC50 lower than 100 mg/L, followed by the freshwater algae growth inhibition test, with 3.8% (5 of 130) of the samples showing an EC50 lower than 100 mg/L. There were 2 samples classified as toxic both for algae and daphnia.

In the case of FA, ecotoxicity was confirmed for 56.3% (9 of 16) of the samples by the performed bioassays, resulting in a waste stream with a higher probability of being classified as HP14 when compared to BA. Algae was the most sensitive organism, with 56.3% (9 of 16) of the samples having an EC50 lower than 100 mg/L, followed by the test on Daphnia magna, with 6.3% (1 of 16) of the samples having an EC50 lower than 100 mg/L. There was just 1 sample classified as toxic both for algae and daphnia.

No specific correlations were found among the different ecotoxicological tests.

Finally, a further issue could arise when controversial outcomes result from the performance of ecotests, which can classify a waste sample as hazardous when the same material was already classified as nonhazardous by the

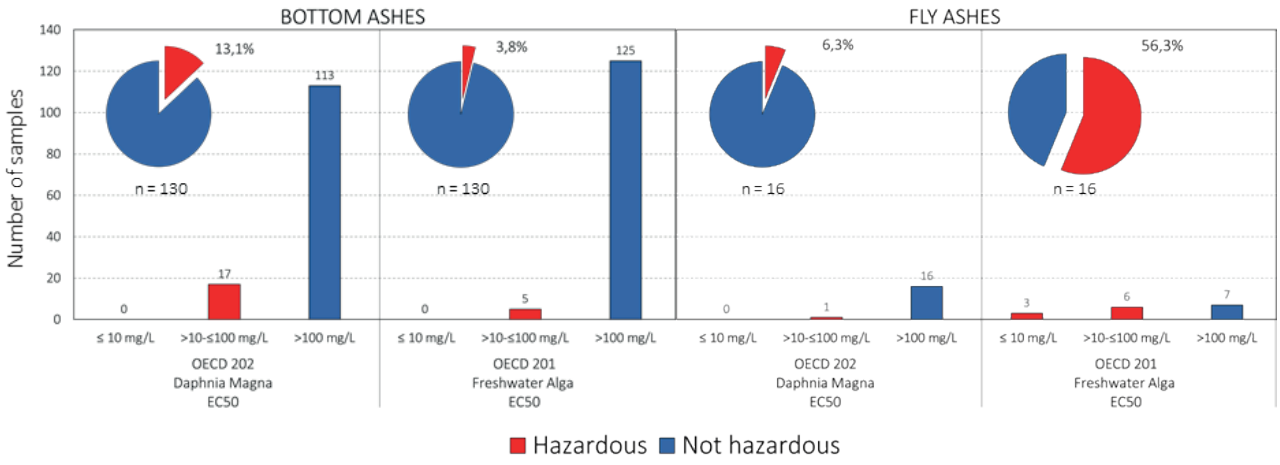

FIGURE 1: Results from the ecotoxicological tests (i.e., the "direct" approach) applied to samples of BA (n = 130 samples) and FA (n = 16 samples), already classified as hazardous for HP 14 by measured substances concentration (i.e., by the "indirect" approach).

indirect approach. In this case, outcomes from bioassays should prevail on the classification. In routine analysis, eco-tests are not usually performed on samples classified as nonhazardous, representing a further possibility to refine the classification designation. Therefore, this issue should be considered only from the perspective of establishing the mandatory performance of ecotoxicological tests.

Considering what has been reported here, a decision tree is proposed (see Figure 2) for HP 14 classification of waste. It is based on a sequence of ecotoxicological tests from the most sensitive to the least sensitive to optimize time and costs in the waste classification process. According to the results obtained, the most sensitive test is represented by the Daphnia magna acute toxicity test and the freshwater algae growth inhibition test for bottom ashes and fly ashes, respectively.

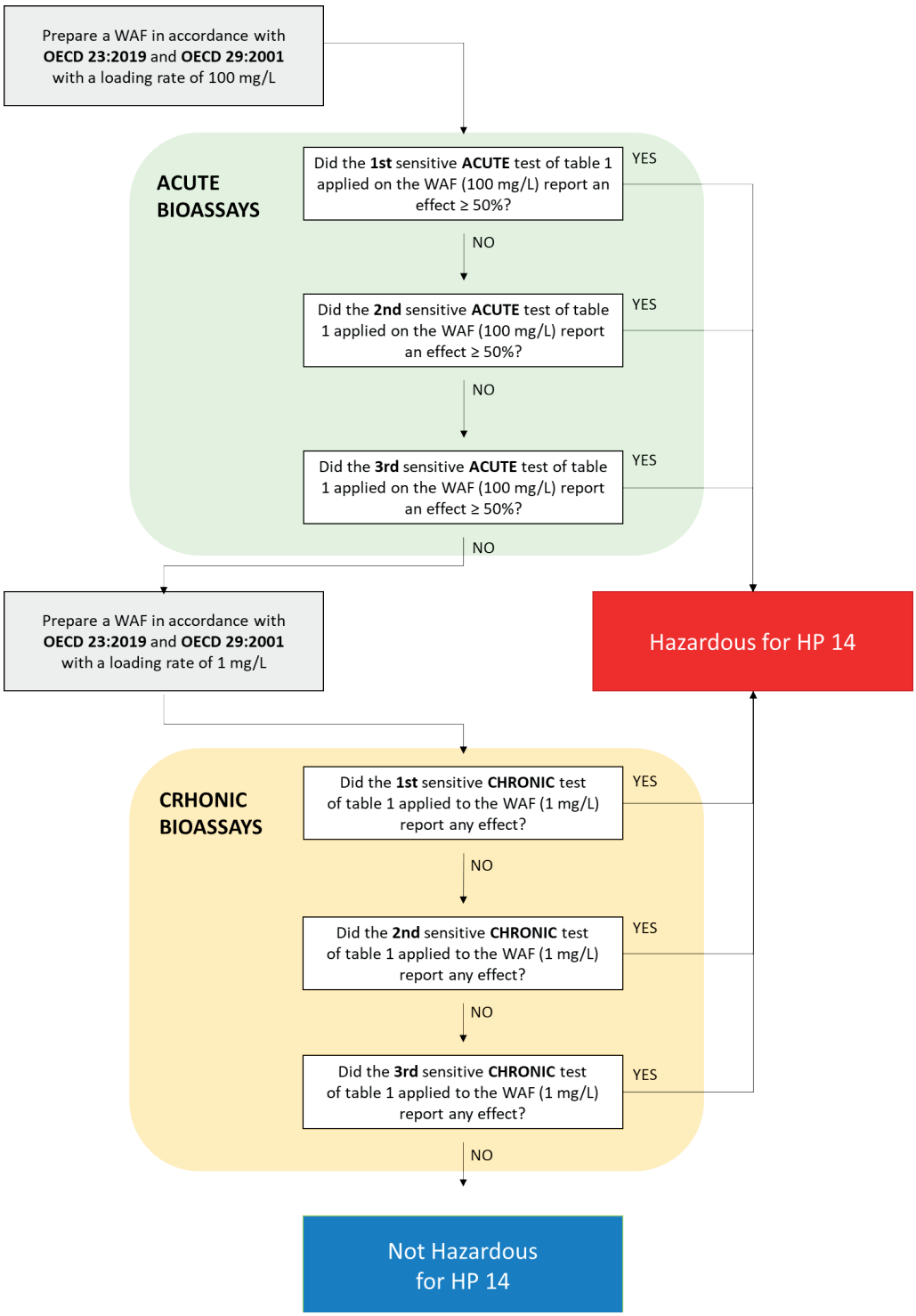

FIGURE 2: Proposed decision tree for HP 14 classification of waste with methods validated for CLP. WAF: Water Accommodated Fractions (derived and modified from Beggio et al., 2021).

CONCLUSIONS

Direct ecotoxicological tests for HP 14 assessment are useful to refine waste ecotoxicity assessments based only on chemical analysis, since variables such as bioavailability of the substances, their interactions, and their ecotoxicological effects on live organisms are immediately evaluated in the results of bioassays.

This work reports findings derived from a large dataset of results from bioassays applied on BA and FA samples that were already classified as hazardous according to their chemical composition. In particular, both water extract preparation and biotest batteries were completely compliant with Italian regulations. Based on the ecotest outcomes, the majority of samples could be reclassified as nonhazardous for HP 14. In addition to being used for future comparison analysis, with the correct awareness, this contribution could help to identify outlier results.

Moreover, the decision tree proposed here for HP 14 classification of wastes can be adopted for the classification of similar materials and optimizing the validity of the classification process. To optimize both time and costs, the decision tree recommends performing ecotoxicological tests from the most sensitive to the less sensitive and including both acute and chronic biotests.

This short communication contributes scientific data to the discussion around the topic of hazardous waste classification and promotes the use of direct ecotoxicological bioassays for the purpose of waste classification within the waste community.

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DETRITUS & ART / Waste to Fashion

by Rainer Stegmann

Fashion has a long tradition in all cultures; it shall protect, warm and enjoy. Fashion emphasizes beauty, reflects culture and tradition and mirrors epochs. Today, garments have increasingly shorter life time. Another trend is the cheap mass production of dresses with a frequently changing design that supports short-term use: Fast Fashion. A short period of use produces a lot of wasted dresses. The numbers are frightening, showing that 62 Million t of apparel were consumed worldwide in 2019 with increasing tendency. The fashion industry produces about 10% of the total annual carbon emissions; 20% of the wastewater comes from fabric dyeing and treatment. The fashion contributes to the discharge of massive amounts of plastic micro-fibers - https://www.worldbank.org/en/news/feature/2019/09/23/costo-moda-medio-ambien.

All produced garments one day become waste often with a detour via developing countries with the laudable intention to help poor people but with the negative effect of partly destroying local fashion industries, e.g., in Kenia, Ghana. Since only part of the clothes originating from the US and Europe is reused, many of them are dumped in the landscape or on waste dumps. On the other hand, more second-hand shops are created, and clothes are also supplied to people in need, but most of the used fashion is thrown away; dresses are burned and landfilled. This situation is one of today's severe waste problems, and not everybody is aware of this situation; waste science has to focus more on this subject. One way of reducing this problem is to make it visible to the users and producers and convince them to change their behaviour; producers need to change their strategy to create sustainable fashion. A very good example of reacting to fast fashion comes from fashion schools that use discarded clothes in their education programs. In addition, remains from designing new dresses and other wasted materials (e.g., plastic) are used to show the value in discarded materials.

About 40% fast fashion sent to Ghana ends up on landfills
https://www.abc.net.au/news/2021-08-12/fast-fashion-turning-parts-ghana-into-toxic-landfill/100358702

Many start-ups often founded by graduates from fashion academies and privately organized initiatives produce fashion designed from used dresses. The reasons are manifold: setting up own business, learning creativity in fashion and making aware of the fast-fashion problem. In addition, the large clothing companies and well-known brands - although to a low extent - offer clothes from recycled fabrics. I show some beautiful, very creative examples of Waste to Fashion, enjoy and get thoughtful...

Mumbai-based brand, Ka-Sha by Karishma Shahani Khan
http://www.doonething.in/content-hub-archive/2016/7/4/eight-indian-fashion-start-ups-committed-to-upcycling

Katell Gelebart, (a)
https://katellgelebart.com/
JAK Academy Hamburg, (b, c) - https://www. jak.de

Managing editor:
Rainer Stegmann
email: stegmann@tuhh.de

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The next edition will introduce unique art mosaics from scraps of plastic and fabrics from the fantastic Turkish artist Deniz Sagdic.

She was born in 1982 in Mersin, Turkey, and began her art education in Mersin University's Faculty of Fine Arts in 1999, where she graduated at the top of her class in 2003.

Her work was celebrated by critics, collectors, architects and interior designers and installed in various architectural spaces and design products.

Let me surprise you...

DENIS SAGDIC / Turkish artist.

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INTRODUCING THE 25+ YEARS OLD ENVIRONMENTAL POLLUTION AND TREATMENT RESEARCH GROUP AT UNIVERSITY OF UDINE, ITALY

Daniele Goi *

The Environmental pollution and treatment research group belongs to the Polytechnic Department of Engineering and Architecture (DPIA) at University of Udine (Italy), and was founded in 1995 by prof. Daniele Goi, who is currently Associate professor of Environmental Sanitary Engineering, and other colleagues and technicians working in the environmental field within Friuli Venezia Giulia region. University of Udine was founded in 1978 thanks to a popular initiative following the 1976's earthquake that severely struck the area. University of Udine is currently structured in 8 Departments and at present involves about 15,000 students, 700 professors, 500 technical and administrative personnel.

More specifically, the Environmental pollution and treatment research group is active in the broad field of **water, wastewater and waste characterization and treatment**. A large number of collaborations has been established throughout time at **local, national and international level**, including both public authorities, water utilities, private companies, universities. The group involved in this large timeframe a wide number of students, researchers, and technicians: in 25 years of activities, more than 100 bachelor's and master's degree thesis were produced in the water, wastewater and waste treatment field, together with 20 Ph.D. programs, belonging to the course of "Environmental and Energy Engineering Sciences" at University of Udine. A spin-off company was founded by the researchers employed in the group in 2008, which performed experimental and research activity in connection with the group itself until 2016.

The activities carried out during the most recent years included:

- Energy recovery from anaerobic digestion (AD) of liquid and solid substrates, both in mono-digestion and co-digestion mode, aimed at exploiting local circular economies with an increase in renewable energy generation in biogas form. In particular, recent research activities were aimed at assessing the energy potential of seagrass from the High-Adriatic coast, either alone or in co-digestion with sewage sludge. In addition, different pre-treatments were investigated on sewage sludge AD, with the overall aim of improving energy generation, reducing environmental emissions and leading to a positive economic balance;
- Characterization of municipal and industrial sludge from different scale wastewater treatment plants

University of Udine: location.

A phD student working on a wastewater treatment pilot plant.

Contact:
Daniele Goi
email: goi@uniud.it

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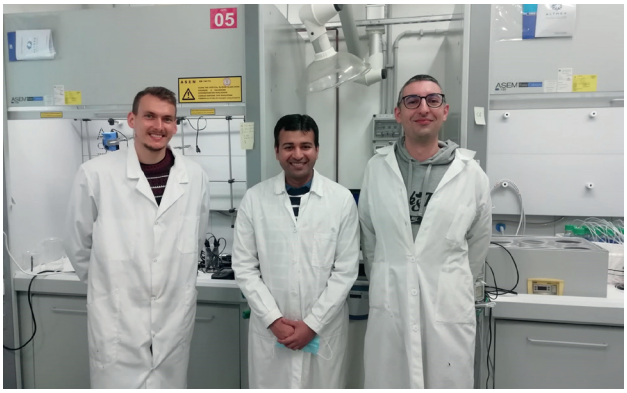
(WWTPs) aimed at assessing its properties for a safe agricultural reuse, enhancing the knowledge about substrate's composition (including macro- and micronutrients, heavy metals, emerging pollutants) before agricultural reutilization;

- Advanced oxidation processes (AOPs), including ozonation and sonication, for wastewater remediation and reuse, considering the required legislative standards and the peculiar effluent characteristics. Water recovery and reuse through fertigation practices can lead to a virtuous paradigm where both nutrients and water present in wastewater are exploited in a safe manner;
- Life cycle assessment modelling, aimed at evaluating the environmental impacts of alternative waste management strategies (e.g., AD, composting, landfill), considering meaningful impact categories such as global warming potential, eutrophication, ozone depletion;
- Respirometric tests, as a useful technique to characterize biomass and wastewater streams from WWTPs. This assay can help in obtaining a detailed influent and sludge characterization in view of the application of mathematical modelling, but also give insights in toxic or inhibitory effects to the biomass. More recently, respirometry has been proposed also to evaluate the activity of microalgae technologies for wastewater remediation;
- Mathematical modelling of processes and multi-parameter techno-economic optimization, with the purpose of improving WWTP operations and proposing innovative solutions to exploit and connect renewable energy generations within WWTPs, leading to an energy and economic saving.

The Group is recently proposing a new paradigm-project considering a partnership, as suggested by the 2030 Agenda for Sustainable Development, adopted by all United Nations Member States (Sustainable Development Goals 6, 12, 17), with water&waste management companies and Friuli Venezia Giulia Regional Authority for water and waste services (AUSIR). The target is to organize a place in which students, scholars and people together are sharing, teaching and learning water&waste awareness within their own territory. A Technical Scientific Committee was instituted to reach in next years the objective to translate theories to practices and common understanding.

Contacts:
Environmental pollution and treatment group - Polytechnic Department of Engineering and Architecture | University of Udine, Italy.
Daniele Goi: goi@uniud.it / webgoi.uniud.it

A bench top pilot plant to study wastewater biological treatment.



Some phD students and postdoctoral researcher in chemistry laboratory.

A Christmas lab meeting.

Friuli Venezia Giulia water&waste management companies, AUSIR and University of Udine join a partnership.

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