

The biogenic content of process streams from mechanical-biological treatment plants producing solid recovered fuel. Do the manual sorting and selective dissolution determination methods correlate?

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ABSTRACT

The carbon emissions trading market has created a need for standard methods for the determination of biogenic content (χ_B) in solid recovered fuels (SRF). We compare the manual sorting (MSM) and selective dissolution methods (SDM), as amended by recent research, for a range of process streams from a mechanical-biological treatment (MBT) plant. The two methods provide statistically different biogenic content values, as expressed on a dry mass basis, uncorrected for ash content. However, they correlate well ($r^2 > 0.9$) and the relative difference between them was $< 5\%$ for χ_B between $21\% \text{ }^w/w_d$ and $72\% \text{ }^w/w_d$. This range includes the average SRF biogenic content of ca $68\% \text{ }^w/w_d$. Methodological improvements are discussed in light of recent studies. The repeatability of the SDM is characterised by relative standard deviations on triplicates of $< 2.5\%$ for the studied population.

Key words: solid recovered fuel, biomass, selective dissolution, manual sorting, mechanical-biological treatment

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1. Introduction

Mechanical biological treatment (MBT) is widely adopted in mainland Europe for treating residual municipal solid waste (MSW), (Juniper, 2005; Velis et al., in press) under EU Landfill Directive (Council of the European Union, 1999) requirements. MBT that employs biodrying is also used to produce solid recovered fuel (SRF) (Velis et al., 2009), a renewable alternative to fossil fuel, incorporating a high fraction of biogenic matter, rendering SRF carbon-neutral, in part. Biogenic matter, denoted χ_B , is defined as material “*produced in natural processes by living organisms but not fossilised, or derived from fossil resources*” (European Committee for Standardisation, 2006a). An accurate, quality assured, measurement of χ_B in waste streams processed as SRF is important because the thermal recovery of biogenic matter is renewable and carbon-neutral, qualifying for subsidies such as: (i) renewable energy certificates (ROCs) in the UK, and (ii) emissions trading schemes (e.g., the European emission trading scheme EU-ETS) respectively (Garg et al., 2007; Ofgem, 2009; Velis et al., in press).

The requirements of these policy instruments have prompted a growing interest in analytical methods for the determination of biogenic content (Fellner et al., 2007; Fellner and Rechberger, 2009; Mohn et al., 2008; Staber et al., 2008) in wastes. The research efforts of the European Committee for Standardisation (CEN) have progressed through the stages of: (i) pre-normative research on standard development (Cuperus and van Dijk, 2002; Cuperus et al., 2005); (ii) the issue of a ‘draft standard for development’ (DD) (European Committee for Standardisation, 2006a; 2007); and (iii) validation of the DD methods through the QUOVADIS initiative (Gawlik et al., 2007; QUOVADIS, 2007). In the US, a simplistic methodology using waste composition data has been proposed (Energy Information Administration, 2007), and a ^{14}C method has been recently standardised (ASTM, 2008).

Draft European standard CEN/TS 15440:2006 on the determination of χ_B in SRF (European Committee for Standardisation, 2006a) offers analytical methods for the characterisation of waste tradable attributes. Many methods were considered for the determination of χ_B in SRF (Cuperus and van Dijk, 2002). The manual sorting method (MSM) and the selective dissolution method (SDM) were selected for development. The selective dissolution method relies on a feature of most biogenic materials: they dissolve and are oxidised more readily in acid mixtures; whereas non-biogenic matter remains intact and can be recovered gravimetrically. By contrast, the manual sorting method relies on the accurate sorting of components of biogenic origin from the waste stream. The method estimates χ_B by assigning a fixed (deemed) value in each of 14 material categories ($\chi_{B,i}$, i : category index) categories considering them ‘homogenous’ from a χ_B perspective (European Committee for Standardisation, 2006a).

Unsurprisingly, despite both methods offering surrogate estimates for χ_B , the SDM is considered the most accurate (Cuperus and van Dijk, 2002; Cuperus et al., 2005; Staber et al., 2008) and is used in several SRF production plants and/or prior to thermal recovery. Though simple, the MSM is time consuming (QUOVADIS, 2007) and labour-intensive (Fellner et al., 2007), and it embodies high levels of method uncertainty (Table 1). Nevertheless, manual sorting data could prove valuable to the optimisation of SRF-producing MBT plants, and may be a cost-effective means of allocating the biogenic content of certain SRF end-uses, as required for regulatory oversight of carbon trading mechanisms (Ofgem, 2009).

<insert Table 1. A qualitative comparison of SDM and MSM methods>

The QVOVADIS initiative undertook inter-laboratory comparisons of the MSM and SDM methods and delivered important suggestions for modifying the draft standard (QUOVADIS,

2007). Similar limited results were reported by Flamme (2006) – it is unclear if it is the same or different dataset. However, there remains scope for clarification on key aspects of the SDM and MSM, hence this research. For instance, the fines category introduces high levels of uncertainty into the estimation of χ_B by the MSM because of its variable composition, and substantial mass contribution to samples. This is evident for SRF, as most end-use specifications demand its size reduction at <30-40 mm (Velis et al., in press). This was recognised by QUOVADIS through its proposed amendment of the fixed value of $\chi_{B \text{ fines}}$ from 0% $^{w/w_d}$ in the draft standard (European Committee for Standardisation, 2006a) to 50% $^{w/w_d}$ (QUOVADIS, 2007). So far, no detailed scientifically robust data have been reported on how the SDM and MSM correlate. Could a more detailed sorting into material categories secure a better correlation? And how does the choice for estimating or ‘deeming’ the value of $\chi_{B \text{ fines}}$ impact on this correlation?

Our study set out to: (i) critically examine the assumed, but non-quantified, correlation between these two methods; (ii) in doing so, evaluate the required degree of detail in the sorting categories for the MSM; (iii) examine the effect of assigning a fixed value of χ_B for the fines fraction, as opposed to its direct measurement by the SDM; and (iv) investigate the application of these methods beyond SRF to a wider range of waste fractions encountered within MBT plants. Methodological complexities pertaining to the computation formulas proposed by CEN for the determination of biogenic content as ‘pure biomass’ are elaborated upon.

2. Materials and methods

An overview of the methodological steps followed in this research, intended to help readers conceptualise the sequence of steps and equipment used, is presented in Fig 1.

<insert Fig. 1. Overview of methodological steps>

2.1 Sampling

Samples were collected from an SRF- producing MBT plant processing residual MSW. From the process flowsheet (Fig. 2), fifteen sampling points (SP) were identified, including inputs to the mechanical processing of MSW, all outputs, and intermediate process streams (Fig. 2). Sampling followed the theory of sampling (ToS) for heterogeneous solids (Gy, 2004; Petersen et al., 2005) and the CEN requirements for SRF (European Committee for Standardisation, 2006b). Three increments (INC) (i.e., three series of fifteen process stream samples) were used. The first two increments (INC1 and INC2) were fully analysed; with an additional increment (INCad) used to quantify the moisture content (M) by material category, and the biogenic content of the fines fraction (χ_{B_fines}) at each process stream. These sampling choices enabled coverage for a range of MBT-related materials, including all pre-processing stages of the SRF output.

Samples were stored in plastic bags in a refrigerated container ($2\pm 2^\circ\text{C}$) until the entire on-site sampling effort was completed (up to 28 d). Because the readily biodegradable material had already decomposed during in the biodrying stage, the moisture lowered below moisture stress biodegradation inhibition level, and the sufficiently low storage temperature, no change in the biogenic content of the samples is anticipated to have occurred during this storage stage. The initial sample size (300–15,000 g) was defined by reference to the estimated heterogeneity of each process stream. Any differences in the sample mass between INCs for each SP, were corrected for by producing sub-samples using a riffle divider Retsch RT 75 (Leeds, UK).

<insert Fig. 2. Waste treatment plant process and sampling points>

2.2 Manual sorting

For the manual sorting method, samples were sieved for the separation of fines and then sorted into categories to obtain an ‘as-received’ (denoted $_{ar}$) mass (g) at four decimal place precision. Fines passed through a perforated surface of a sorting table (\varnothing 10 mm). The remaining material was manually separated into 24 identifiable categories (Table 2). This represented a detailed categorisation of each process stream, expanding beyond the 14 categories stipulated by CEN for χ_B by the MSM (European Committee for Standardisation, 2006a). It also supported a concurrent analysis of MBT process performance and materials flow through the plant.

<insert Table 2. Categories into which process streams were sorted manually using the MSM>

Samples from different process streams (SPs) produced varying recoveries of material by category (reflecting their stage of processing) and posed different sorting challenges. Large items upstream of the secondary shredder (SP1, 16) contained fixed sub-components of different categories: e.g., plastic and metal and hazardous items, such as printed circuit board. These items were separated from one another manually or with scissors, as far as was possible. Conversely, waste fragments in process streams downstream of the secondary shredder are finely shredded to <40 mm (SP11-13, 15) and pose their own identification difficulties; e.g., for fragments stemming from shoes, sanitary products, and composite packaging. Identifiable screws and nails in the fines were reassigned to the metal categories.

For each sample, the 16 shreddable waste component categories were remixed into a reassembled fraction (Table 2) whilst 8 non-shreddable categories (Table 2) were discarded, where the shredders could not tolerate substantial quantities of aggregates and metals. Where fines were constituted mainly of aggregates (SP3, 7, 15; Fig. 2), they were excluded from the

reassembled fraction as non-shreddable materials. Discarded fractions were accounted for in the calculations of both MSM and SDM.

To investigate the influence of the level of detail in manual sorting and the approach to the estimation of the biogenic content of the fines <10 mm (χ_{B_fines}), the χ_B was calculated for three different methodological variations (groupings, G) of the waste component categories and/or χ_{B_fines} using the INC1 and INC2 samples: (G1) the 24 detailed categories (Table 2), with χ_{B_fines} being inferred from the extra increment INCad by measurement, applying the selective dissolution method (see section 2.5); (G2) the manual sorting results re-grouped in the 14 DD CEN/TS 15442:2006 categories (European Committee for Standardisation, 2006a), following specific re-grouping choices denoted in Table 3, and with deemed χ_B of each category as proposed to be amended by QUOVADIS (QUOVADIS, 2007) apart from the χ_{B_fines} , being inferred from the extra increment by SDM as in G1; and (G3) the same 14 re-grouped categories as in G2, with χ_{B_fines} being prescribed and fixed at 50% ^{w/w_d} (QUOVADIS value).

<insert Table 3. Grouped categories with commentary on potential impact on final results>

Biogenic content χ_B on a dry mass basis was calculated using:

$$\chi_B = \frac{\sum_i (dry\ mass_i \times \chi_{Bi})}{\sum_i dry\ mass_i} \quad \text{Eq.1}$$

The MSM was performed once on each of INC1 and INC2 in this study, allowing no estimation of repeatability. Manual sorting is extraordinarily lengthy and replication not practicable given the volumes and types of material considered.

Moisture (M_T) was measured in a two stages: bulk drying (24h, 40°C) (M_b in % ^{w/w_{ar}}); residual drying (M_r in % ^{w/w_b}) (24h, 105°C), (European Committee for Standardisation,

2006d). Total moisture was computed according the relevant CEN standard for SRF (European Committee for Standardisation, 2006c). The moisture of the individual waste component categories was approximated. Ash content was measured in accordance with the DD CEN/TS 15403:2006 for SRF samples. These are further detailed in Supplementary Material.

2.3 Final general analysis sample preparation for the SDM

For the measurement of χ_B using the selective dissolution method, the reassembled fractions were sub-sampled in accord with the theory of sampling (Gerlach and Nocerino, 2004; Nocerino et al., 2005). Samples from the process streams SP1, 16 were shredded to <40 mm passing them twice through a slow rotation rotary shear Rodan Engineering CS 3000 (Stoke-on-Trent, UK). All samples were then bulk dried (40°C, 24 h) in advance of dry processing through a slow rotation cutting mill (RETSCH SM 2000, Leeds, UK) to <4 mm. Where necessary, sample mass was homogenised and further reduced by sub-sampling through an A/S Rationel Kornservice riffle divider (5 L, hinged container type 2, 18 splits; Esbjerg, Denmark), before shredding to <1 mm in a RETSCH ultra-centrifugal mill ZM200 (12,000 rpm). These final general analysis samples (GAS) were then sub-sampled to 50-100 g, and stored in air-tight bags at ambient temperature, in darkness. Grinding to a size of <1 mm was thought as sufficient for the SDM. The QUOVADIS study indicates no significant difference for χ_B between samples prepared at <1 and <0.5 mm (QUOVADIS, 2007).

2.4 Selective dissolution (SDM)

The SDM was performed in triplicate following the DD CEN/TS 15442:2006 (European Committee for Standardisation, 2006a). Attempted improvements, which constitute departures from the standard, and specific choices are explained.

For each replicate, an aliquot of 5 g from the GAS was weighed to 4 decimal places into Erlenmeyer flasks. In a fume cupboard, 150 mL of 84% v/v H_2SO_4 (prepared from >95% v/v , analytical grade; Fisher Scientific, Loughborough, UK) was added using a bottle dispenser. The slightly higher concentration than advised by the standard (78 % w/w H_2SO_4) has the advantage of being easily prepared from commercially available concentrations. However, a properly designed statistical experiment is necessary to establish that this departure from the standard method as proposed by CEN leads to fully equivalent results. As a gross check, visual observation of the solid residue revealed no differences between these two versions.

Flasks were gently stirred to impregnate the powder, and the mixture left to react for 16 h under slight continuous agitation achieved using an IKA KS60 mechanical orbital shaker (50 rpm; Staufen, Germany). Hydrogen peroxide (35% v/v analytical grade, Acros Organics, Geel, Belgium) was added in three 10 mL aliquots, separated by ca 10 min, whilst submerging flasks in a 3 cm deep cooling bath to control the reaction and avoid the deposition of material on the flasks walls. Mixtures were digested for 5 h, before 300 mL deionised water was added. The final mixture was filtered through a pre-weighed dried Whatman GF/B \varnothing 90 mm glass microfibre filter (Maidstone, UK) into a Büchner funnel and rinsed with 400 mL of deionised water to a final pH of ≥ 3.0 . Filters were dried at 105°C for 24 h, weighed, and kept in air-tight plastic containers at ambient temperature.

2.5 The reporting basis for χ_B and ash content

Biogenic content χ_B determined by the selective dissolution method can be expressed in a variety of ways, contingent on the specific uses and data demands. Draft standard CEN/TS 15442:2006 introduces the concept of ‘pure biomass.’ The proposed by CEN computation formula includes a series of corrections pertaining to the ash content. This is necessary because during the selective dissolution a non-negligible part of the ash of the

sample dissolves. This ‘pure biomass’ is referred to as being biomass on a dry basis (European Committee for Standardisation, 2006a). The relevant CEN/TS formula is shown in Eq. 2, adapted for analysis performed only on the shreddable part of each sample.

$$\chi_{B,pure,d} = \left[1 - \left\{ \frac{m_{d,residue \& filter} - m_{ash residue \& filter}}{m_{d,test sample}} + \frac{A_{db,test sample}}{100} \right\} \right] \times \frac{m_{d,reassembled fraction}}{m_{d,full sample}} \quad \text{Eq. 2}$$

We have shown elsewhere that around half of the ash content present in SRF of this plant is dissolving during the selective dissolution (Velis, 2009), making necessary to account for this for an unbiased determination of the biogenic content. This dissolved ash may originate from any of the inert, biogenic and non-biogenic parts of the sample, not enabling a straightforward correction. The formula proposed by CEN, attempts to overcome these complexities, resulting in removing all the ash content present as part of biogenic materials from the ‘pure biomass.’ Hence, the CEN termed pure biomass on a dry basis is effectively biomass without any of its ash. Thus, it constitutes an underestimation of the biogenic content on a dry mass basis.

On one hand, expressing the biogenic content on a dry mass basis without any ash content ($\chi_{B,pure,d}$) can be potentially useful, if the energy content present in a biogenic material is to be computed in a dry-ash-free basis because the ash portion of χ_B is not combustible. Similarly, some of the ash content present in materials generally considered as biogenic may be of inert origin: characteristic case is chalk used as the filler material in paper-making (which completely dissolved during the selective dissolution procedure) (Cuperus and van Dijk, 2002). On the other hand, it may well constitute a natural part of a biogenic material and where suitable it has to be reported as such. The practical limitations of the selective dissolution computation are not able to justify its reporting only in pure form and solutions have to be investigated

Here, a comparison between the selective dissolution and the manual sorting methods are made for the uncorrected for ash content values ($\chi_{B,with\ ash,d}$), as explained below. Despite that, pure biomass ($\chi_{B,pure,d}$) results as measured with the proposed CEN formula are also reported to enable future comparisons of our data with those from other researchers.

When reporting on a dry mass basis alone, it is suitable to report a mass percent value, uncorrected for ash, on dry basis: $\chi_{B,with\ ash,d} (w/w_d)$. Note that the Eq. 1 for the determination of biogenic content by the manual sorting method returns the uncorrected for ash biomass ($\chi_{B,ash-free,d}$) rather than the pure biomass ($\chi_{B,pure,d}$). Because the ash content of each category sorted using the manual sorting method is unknown and not determined (this would involve substantive and prolonged additional effort, and destruction of the samples needed for the SDM), the DD CEN/TS 15442:2006 suggests a correction termed ‘sorting precision’. We instead introduce the term ‘ $\chi_{B,with\ ash,d}$ by SDM’ which allows direct comparison with the uncorrected for ‘sorting precision’ χ_B MSM data.

The $\chi_{B,with\ ash,d}$ by SDM can be either an underestimation or overestimation of the actual biogenic content percentage in a sample, depending on the relative ratios of the ash in both the initial sample and the dried residues. Note that both dissolved and undissolved ash fractions (i.e., of biogenic, or non-biogenic, or inert sources) cancel in the $\chi_{B,d}$ formula, limiting any bias introduced. The Eq. 3 corrects for the mass fraction of the discarded, non-shreddable components:

$$\chi_{B,withash,d} = \left\{ \frac{m_{d,test\ sample} - m_{d,residue}}{m_{d,test\ sample}} \right\} \times \frac{m_{d,reassembled\ fraction}}{m_{d,full\ sample}} \quad \text{Eq. 3}$$

2.6 Statistical analysis

Data were analysed using Statistica v8.0[®] (StatSoft, 2008). Being bulk characteristics and reasonably homogeneous within each sample, moisture, ash and χ_B were assumed to follow a normal distribution for each sample. For selective dissolution data, the uncertainty

is expressed as a combined extended uncertainty (U_c) for each data point (Ellison et al., 2000), using a coverage factor of 1.96. Despite the limited degrees of freedom available, this coverage factor is thought as conservative enough to provide 95% confidence intervals around the mean values. Uncertainty from the duplicate determinations of moisture and ash content and the triplicate experimental χ_B values for initial sample mass and dry residue was propagated into the U_c .

To assess the correlation between the MSM and SDM estimates of the uncorrected for ash biogenic content ($\chi_{B,with\ ash,d}$), a geometric mean regression (GMR) was selected, reflecting the fact that both variables have random measurement errors (Leng et al., 2007). Standard errors for the GMR parameters were approximated using standard errors of the least square linear regression parameters (Sokal and Rolf, 1995), and tested using the t -statistic at 95% confidence. Ideally, a correlation of the two methods would involve at least triplicate results for both, with measurements being performed on exactly the same number of samples. Due to practical limitations, sorting was performed once for each sample. Obtained values should be accepted as such, although no replicates are available to spot spurious errors or quantify the MSM repeatability. Furthermore, sorting needs to be performed on large samples (300-15,000 g), while dissolution is carried out on aliquots from the GAS (5 g).

Extrapolating the value of the biogenic content ($\chi_{B,ash-free,d}$) of the fines from the additional increment (INCad χ_{B_fines}) back to the samples on which the correlation is estimated upon (INC1 and INC2 samples), as done in the G1 and G2 methodological versions, assumes limited between-increment variation. Although the bias introduced by this is not quantifiable, we speculate the INCad χ_{B_fines} values could be closer to the true INC1 and 2 values, than the fixed value of 50% $^w/w_d$. When we perform the comparison of the SDM $\chi_{B,ash-free,d}$ with the MSM $\chi_{B,ash-free,d}$ and use the INCad χ_{B_fines} values as part of the MSM determination (cases G1 and G2 above), we equalise the influence of the fines category;

hence any difference should be allocated to the grouping of the rest of the materials into categories. This is valid to the extent to which an approximation of the INC1 and 2 χ_{B_fines} by the INCad χ_{B_fines} is accurate.

Two contributions to the random variation can be identified here: sub-sampling between MSM and SDM samples, which affects representativeness of SDM test-samples; and picking of three test-samples from the small, though slightly heterogeneous GAS, which affects the measured SDM repeatability by introducing between-replicate differences. To keep these random sources of variability as low as possible, precautions were taken: (i) sub-sampling followed the theory of sampling (see Section 2.2 on manual sorting) to ensure the GAS is representative of the initially sorted sample; and (ii) the GAS, where comprising two discrete sub-fractions which could be described as a fluffy, cotton-like material and a granular, heavy material, was manually homogenised before picking the three aliquots for the SDM. A nested experiment for the analysis of the components of variability (data not shown here) of the SDM showed that the entire sub-sampling procedure introduced only very small variability.

3 Results and discussion

Results are presented and discussed in three parts. Firstly, the results of the three manual sorting method variations are presented, along with certain intermediate results necessary, such as those for the biogenic content of the fines <10 mm. Then, the results of the selective dissolution method are discussed. Finally, the correlation between these datasets is covered.

3.1 Manual sorting method

Higher values for the biogenic content of the fines <10 mm part of a sample ($\chi_{B_fines,d}$) might have been anticipated than for the entire sample. Indirect verification comes from the $\chi_{B_fines,d}$ values in Table 4 and the $\chi_{B,pure,d}$ in Fig. 3 (discussed in detail in Section 3.2). Whilst

a direct comparison between them is not feasible because of the different reporting base, it is noted that for all process streams with a significant proportion of fines category (i.e., excluding SP1, 16), the $\chi_{B_fines,d}$ values are considerably higher than the biogenic content of the overall sample, despite that the former ($\chi_{B_fines,d}$) is ‘with ash’ and the latter ‘pure’ ($\chi_{B,pure,d}$).

<Insert Table 4. Biogenic content of fines>

<Insert Fig. 3. Selective dissolution experimental results (value \pm Uc (= 1.96* SE))>

The manual sorting method data obtained through the 3 different methodological variations (G1,2,3) suggest that categorisation and use of deemed vs. measured values for the biogenic content of the fines (χ_{B_fines}) has a noticeable impact on estimating the biogenic content of the entire sample (χ_B), though not consistently across all the sampled process streams (SPs) (Fig. 4). One might expect that detailed categorisation using 24 categories (G1) would give the most accurate results, whilst the grouped categorisation (G3) with fixed χ_{B_fines} would infer the most bias. Because all these methods constitute empirical approximations, this cannot be directly tested and verified. However, this assertion is indirectly supported by the results of the correlation study (Section 3.3).

<insert Fig. 4. Effect of categorisation on estimations of biogenic content using the MSM>

Re-grouping categories as in the 14 CEN ones (G2 and G3), results in a similar or higher χ_B than that estimated from the analysis of 24 categories (G1), for most of the process streams, except for SRF-type ones (Fig. 4). This reflects the between-process stream variability. Using a fixed value for χ_{B_fines} , as in G3, influences χ_B by virtue of (i) the fines

mass proportion in a process stream, which is considerable (namely $>20\% \text{ }^w/w_{ar}$ and $>40\% \text{ }^w/w_{ar}$ for 61% and 36% respectively of the studied population); and (ii) the difference between the proposed by QVOVADIS deemed value of $50\% \text{ }^w/w_d$ and the true value of χ_{B_fines} . The determination of the biogenic content of the fines $<10 \text{ mm}$ component category of samples (χ_{B_fines}) by the selective dissolution method shows highly variable values (Table 4). This justifies use of SDM to estimate it at each SP, especially for this study. This between-process stream variability can be partly accounted for by the progressive separation of increasingly homogeneous fractions within the MBT plant, achieved by concentrating different types of materials. However, a high variability is also evident for the χ_{B_fines} of the process streams with composition similar to SRF (SP13): SP 10, 11, 12.

Furthermore, a high variability can be anticipated for the composition of the fines of SRF, produced from different source materials (such as residual MSW input to MBT plants) and through varying processing concepts to differentiated end-use specifications. Additionally, the weight fraction of the fines would be significant for most commercially specified types of SRF having undergone size reduction at $<30\text{-}40 \text{ mm}$ (Velis et al., in press): a typical mass fraction of fines in the SRF can be $40\% \text{ }^w/w_{ar}$ (Velis, 2009). These results imply that deeming of the biogenic content of the SRF fines might lead to considerable bias. As a result, investigating whether the determination of $\chi_{B_fines,d}$ by the selective dissolution method can prove useful in enhancing the determination of the $\chi_{B,d}$ by the MSM, is fully justified.

Generally, the G1 and G2 waste component grouping versions, not using a fixed value for the χ_{B_fines} , are in better agreement compared to the agreement of each of G1 and G2 with the G3. This suggests that the impact of deeming or not the χ_{B_fines} is higher than the impact of collapsing the 24 categories into the 14 suggested by CEN. For MBT process streams very close in composition to the SRF (SP11, 12), the use of a fixed $\chi_{B_fines} = 50\% \text{ }^w/w_d$ results in an

underestimation of the biogenic content in all 4 cases examined, compared with the values measured by the selective dissolution method (ca 70% ^w/_{w_d}, Table 4). However, this cannot be generalised to every SRF production line.

The most heterogeneous MBT stream amongst those sampled and those with the lowest percentage of fines are SP1, 8 and 16; their low homogeneity is mainly due to their large particle size and low gravimetric recovery. Here, the high between-increment variability indicates that any benefits from the extra effort to perform a more detailed sorting (G1) or to identify the χ_{B_fines} separately by the selective dissolution method (G1 or G2) may not be justified unless an SRF production line is sufficiently stable in time.

For the cases where additional resources can be justified, an improved classification is proposed (Table 5), retaining those categories required to optimise sorting consistency, accuracy and repeatability. Here: (i) composites, fines < 10 mm and fluff are generic heterogeneous categories, in which material composition, χ_B and proportion of fines <10 mm may vary according to the SRF production input and flowsheet; (ii) their χ_B value could be estimated using the selective dissolution method (e.g., on triplicates), where effort is justified or suitably deemed per SRF case (clear guidance and rules should apply); (iii) fragments of shoes and sanitary products (nappies) are difficult to indentify in finely shredded SRF: hence, they would be identified possibly as composites; (iv) batteries typically do not reach the SRF stream, hence there is no need for them to appear in the standard classification; and (v) the household hazardous waste category comprises almost 100% non-biogenic materials and can be allocated to plastics or metals.

Some categories have been merged without influencing the results of the method, because they are attributed the same coefficient (e.g., wood and biological waste). If the method is applied to process streams other than SRF (especially input to the processing

section and large rejects), the soft plastic category should be separated and its χ_B recalculated, because of the potential for substantial food contamination. However, it is expected that these simplifications would only slightly reduce the sorting time, because fragment recognition takes more time than sorting into categories.

<Insert Table 5. Proposed classification for standard optimisation>

3.2 Selective dissolution method

Fig. 3 presents the (arithmetic) mean ($n=3$ for each sample) pure biogenic content values ($\chi_{B,pure,d}$) determined by the SDM for various process streams (SPs) within the mechanical processing section of the MBT plant, for the first 2 increments (INC1,2). Notably these results are not necessary for the evaluation of the correlation between the manual sorting method variations and the selective dissolution method but are presented here for the future benefit of researchers who will produce results in full agreement with the DD CEN/TS 15442:2006.

These results are consistent with those anticipated for the plant flowsheet configuration resulting in an enrichment of the biogenic content of the SRF in comparison to the biodried input (SP1). However, this is by-and-large due to the removal of the mineralised waste components ('inert' fraction) the- relevant issues are detailed elsewhere (Velis, 2009).

The between-process stream-variability is high, reflecting the differences in the composition at each process stream which can be visualised in the texture of the final general analysis samples, and the aspect of filtrates and residues. The within-process stream and between-increment (INC1 and INC2) variability is considerable, but lower than the between-process stream. The combined extended uncertainty (U_c) for each data point varies between 0.02% $^w/w_d$ and 1.6% $^w/w_d$, with an average of 0.5% $^w/w_d$.

Regarding the repeatability of the selective dissolution method, the relative standard deviation (RSD) varied between 0.1% and 2.4%, with a mean of 0.9%. Ninety-three percent of the samples studied show an RSD <1.5%, which is comparable to validated standard methods. Empirical observations show that parameters influencing method repeatability are: reaction time; reaction intensity, resulting in the degree of foaming which may lead to undigested sample depositions on the walls of the flasks; stability of drying; the ashing conditions (in all cases full ashing was evident), and the consistency of test-sample picking, especially for heterogeneous GAS, such as the partly fluffy – partly granular ones.

Because the method is destructive, measurements cannot be repeated on the same test-samples, and therefore the within-final general analysis sample variability, caused by sample heterogeneity, cannot be unravelled from analytical variability. For SRF samples, the combined extended uncertainty (U_c) varied from 0.36% $^{w/w_d}$ to 0.89% $^{w/w_d}$ while standard deviation on triplicates varied from 0.06% $^{w/w_d}$ to 0.79% $^{w/w_d}$. The method appears to have a remarkably good repeatability when used for SRF, confirming the QUOVADIS findings (standard deviation of triplicates around 1.2% $^{w/w_d}$) (QUOVADIS, 2007).

3.3 Correlation between the MSM and the SDM

Correlations are calculated for the biogenic content, on a dry mass basis and uncorrected for ash content, between each of the three sets of manual sorting methodological variations ($\chi_{B, \text{with ash,d}}$ MSM results, by G1,2,3) and the single set of data obtained from the selective dissolution method ($\chi_{B, \text{with ash,d}}$ SMS results) (Table 6, Fig. 5).

<Insert Table 6. Geometric mean regressions parameter>
<Insert Fig. 5. MSM and SDM correlations>

Correlations are commonly used for method validation, using a reference method, or reference samples. Currently, no reference method exists for SRF biogenic content. ^{14}C

method can potentially measure more accurately the biogenic content, but it is not yet fully mature despite significant research (European Committee for Standardisation, 2007; Fellner and Rechberger, 2009; Staber et al., 2008). Here, the empirical surrogate of selective dissolution method is used to estimate the MSM precision because it is recognised by the DD CEN/TS 15442:2006 (European Committee for Standardisation, 2006a) as the “*main [...] method*” (European Committee for Standardisation, 2006a). In this study, manual sorting method results are assessed for their similarity with selective dissolution method results. But no statement can be made regarding accuracy, as the true value of the measured biogenic content is unknown for all samples, especially in the absence of readily available and matrix-matched certified reference materials.

$$\chi_{B,withash,d,MSM} = a \times \chi_{B,withash,d,SDM} + b \quad \text{Eq. 4}$$

Eq. 4 provides the model fitted using geometric mean regression. For all regressions, $a \neq 1$ and $b \neq 0$ (at level of significance $\alpha = 0.05$). Our data show that the variations of the manual sorting method and the selective dissolution method provide statistically significantly different results (Table 6). However, depending on accuracy required for practical applications, they can be regarded as providing similar results, for a range of biogenic content values ($\chi_{B,withash,d}$). Based on detailed sorting (G1) regression model, the relative difference between MSM and SDM results is $<5\%$ for $\chi_{B,withash,d}$ ranging from $21\% \text{ }^w/w_d$ to $72\% \text{ }^w/w_d$. Considering the 95% confidence intervals, the regression parameters are not considerably different from one another for the three models based upon for the 3 manual storing method variations (G1,2,3) (Table 6).

Results from the two manual sorting approaches using variable χ_{B_fines} as estimated by the selective dissolution method (G1, 2) are closer to the ones of exclusively selective dissolution method. No practical difference can be established between the detailed (G1) and grouped (G2) approaches. Both are high quality regressions, experimental values being

tightly distributed around the linear models (coefficient of determination: $r^2 > 0.96$, small confidence intervals for both a and b).

Although no statistical difference can be asserted on the 95% confidence basis, applying a fixed, deemed value to the biogenic content of fines (χ_{B_fines}) reduces the quality of the regression ($r^2(G3) < r^2(G1/2)$) and increases the gap between the regression and the ideal equation $\chi_{B,with\ ash,d,MSM} = \chi_{B,with\ ash,d,SDM}$ ($a = 1$, $b = 0$). This means the improved method suggested in this study (based on G1 manual sorting methodological variation) provides results marginally closer to those of the selective dissolution method than those achieved by the manual sorting method as defined by the DD CEN/TS 15442:2006 (European Committee for Standardisation, 2006a) and incorporating the QUOVADIS suggestions (G3 case).

No particular trend was found showing a link between sample composition, texture and aspect, and relative results of the two methods. Hence, it seems feasible to use suitable manual sorting data to estimate biogenic content on a dry mass basis uncorrected for ash content for a sample, for a wide range of MBT-related material flows. However, if only the SRF and similar types of samples were considered (generally $\chi_{B,d,SDM}$ between 50-70% $^w/w_d$), the correlation between the methods would not have been as evident, as it can be inferred from visual inspection of Fig. 5. Hence, further investigation is necessary to establish that the manual sorting method can sufficiently differentiate and accurately match the biogenic content of SRF-like materials (i.e., in the range of 50-70% $^w/w_d$).

The manual sorting method variations show a tendency to return lower results than the selective dissolution method for SRF-types of samples (Fig. 5). This is different to both the QUOVADIS conclusions (QUOVADIS, 2007), but all studies were limited in their number of samples and classification categories. It is not fully clear how the QUOVADIS and the German inter-laboratory studies have compared the two methods, especially regarding the reporting basis of the results. In addition, this discrepancy may be indicative of, and

attributed to, the variability in sorting practices: whilst sorting for biogenic content determination is relatively straightforward (albeit lengthy), there is always the possibility for differentiated interpretations and applications by research groups and individual sorters.

4 Conclusions and recommendations

- (1) The manual sorting method is long and tedious, while the selective dissolution method necessitates laboratory staff and equipment. In practice, the method selection should be based on the objective of the measurement and how often it needs to be carried out.
- (2) Further research is necessary to enable the measurement of the biogenic content of waste-derived product such as SRF, accurately accounting for the part of its ash that is genuinely of biogenic origin, overcoming the limitations of the ‘pure’ biomass or ‘uncorrected for ash content’ methodological approaches.
- (3) The manual sorting method, as defined by the draft standard amended by the QUOVADIS suggestions, introduces uncertainty due to the grouping of some heterogeneous categories and the use of a fixed deemed coefficient for the biogenic content of the fines <10 mm (χ_{B_fines} : 50% ^w/_{w_d}), despite their unpredictable content. An optimised categorisation has been proposed here, keeping the number of categories as low as possible and strategically chosen to allow an attribution of biogenic content coefficients as subtly and precisely as possible. This is expected to slightly reduce sorting time and necessary skills, while enhancing result quality and accuracy.
- (4) The estimation of the biomass content of the fines <10 mm fraction by the selective dissolution method for use within the computations of the manual sorting method can further improve the ability of the method to simulate of the biogenic

content (on a dry mass basis uncorrected for ash) as measured by the selective dissolution method DM; the necessary additional effort and cost could be practically meaningful if the long-term variability of the examined material stream is low enough.

- (5) The SDM is considered as the most accurate method, repeatability and result uncertainty seem satisfactory especially for SRF. This high repeatability can be partly assigned to a careful implementation of the standard, by mitigating potential sources of variability as far as practicable, especially regarding sample preparation. No conclusion could be drawn regarding methods accuracy; results from round-robin tests carried on certified reference SRF available both as large fragments and final general analysis samples can assist to appraise repeatability, reproducibility and accuracy of both methods. Despite the inherent methodological difficulties and a series on inevitable assumption and approximations, the selective dissolution method and manual sorting method correlate remarkably well ($0.89 < r^2 < 0.96$) for the range of materials studied, but provide statistically different results for biogenic content, on a dry mass basis, uncorrected for ash ($\chi_{B,with\ ash,d}$) (at the level of significance $\alpha = 0.05$). However, for SRF-type of samples a correlation able to sufficiently differentiate within the encountered range of values is not implied, suggesting that closer examination for SRF-only materials is necessary.
- (6) The manual sorting method returns lower results than the selective dissolution method for SRF-types of samples, which contradicts previous evidence and seeks further investigation. Although intended for use on SRF, the two methods seem to perform adequately for very different waste streams. It would be of interest for MBT process monitoring purpose to include in the standard a section covering the

application of the methods to various MBT streams, including practical adjustments and expected accuracy. This result also enables to estimate the biogenic content of the SRF and rest outputs, from the plant processing input, assuming a known composition of section input and sufficient knowledge of relevant transfer coefficients for processing of waste components.

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Nomenclature

Symbol	Explanation	Units
U_c	combined extended uncertainty	
a	slope of regression curve	
b	intercept of regression curve	
m	mass	
r^2	coefficient of determination	
α	significance level	
χ_B	biogenic content by mass	% $^w/W_d$
A	ash content	% $^w/W_d$
M	moisture content	% $^w/W_{ar}$
INC	Increment	
SP	Sampling point	
G	Grouping of waste component categories – manual sorting methodology variation	
Subscripts		
INC _x	x: 1,2,ad	
SP _x	x: 1-16	
G _x	x: 1,2,3	
d	dry basis	

i	index for sorting categories
j	index for SPs
ar	as received (i.e. wet) basis
finer	of the fine fraction (<10 mm)
T	total
r	residual
b	bulk
test sample	of the aliquot of the GAS analysed
dry residue	of the dry undissolved residue by SDM
full sample	of the entire sample sorted for the MSM
reassembled	of the shreddable fraction of the full
fraction	sample, further processed to the GAS
residue and filter	of both the residue deposited on the
	filter by the SDM and the filter
ash	of an ashing residue

Abbreviations

CEN	European Committee for Standardisation
DD	Draft for development
GAS	General analysis sample
GMR	Geometric mean regression
INC	Increment (sample collected in a single occasion)
MBT	Mechanical-biological treatment
MSM	Manual sorting method
MSW	Municipal solid waste
RSD	Relative standard deviation
SDM	Selective dissolution method
SP	Sampling point
SRF	Solid recovered fuel
ToS	Theory of sampling

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Table 1: A qualitative comparison of SDM and MSM methods

	SDM	MSM	
Analytical considerations	Accuracy ^{a*}	+	–
	Representativeness of test sample	–	+ +
	Analytical variability ^{a*}	Low	High, difficult to quantify
	Biogenic content expressed as	Pure biomass matter (% ^w / _{w_d}), percent by calorific value (% _{CV}), percent by total carbon (% _{TC})	Dry matter, uncorrected for ash (% ^w / _{w_d})
	Accuracy limitations	Rubber, viscose, biodegradable plastics, fatty and oily materials, leather and wool don't behave the way they should. However, the error introduced by such materials is limited, due to the small amount they represent in SRF.	- Confusion (biodegradable plastics, fake leather, synthetic rubber) - Contamination (biological residues sticking to containers, composites) - Attribution of semi-empirical values, especially for fines (mixture of random materials in undefined proportions) - “ <i>lack of visual recognisability</i> ” (Fellner et al., 2007) and limited human reliability
Cost	Capex	– – if outsourced + + + otherwise	+
	Opex	–	+
Other considerations	Restrictions of use	+ (not applicable to SRF with high quantities of problematic materials)	–
	Sample preparation	+ + (sub-sampling, shredding, drying)	–
	Effort and duration	–	+
	Destructive method	+	–
	Delay in result	At least 3 days	Few hours
	Analysis of replicates	+	– (tedious and lengthy)
	Health and safety risk	+ + + (equipments: shredder, oven; chemicals: sulphuric acid, hydrogen peroxide, microbiological: waste particles <1mm)	+ (bio-dried material not fully sanitised, hence microbiological risk)
	Skilled staff	+	–
	Analysis of several samples in parallel	+	–
	Place of analysis	Laboratory	In the field
Application	Routine analysis	Punctual control	

^{a*} Source: Cuperus and van Dijk (2002) and QOOVADIS (2007)

Table 2: Waste component categories into which process streams were sorted manually using the manual sorting method (MSM). All these 24 categories were used in the computation of χ_B in the ‘G1 grouping’.

Categories	Details/main constituents	$\chi_{B,i}$ (% w/w _d)	Fraction
Biological	Non-treated wood, feathers, food	100	
Carpet/mats		0 ^{^,a}	
Cartons	Milk/juice packaging. Several layers of card, film, aluminium	80 [*]	
Composites	Residual plastic, cleaning wipes, cigarette filter, polystyrene foam	0 ^{^,a}	
Fines	≤10 mm	variable	
Fluff	Dust, fibres, fluffy material	30 [^]	
Hard plastic	Toys, durable plastic items	0	
Intermediate plastic	HDPE bottles	0	Reassembled fraction
Nappies		95 [^]	
Paper/card		100	
Rubber/leather		80 [*]	
Shoes		30 [^]	
Soft plastic	Plastic bags	0	
Textiles	Piece of clothes, wool fibres	35 [*]	
Tissues		100	
Treated wood		100	
<hr/>			
Batteries		0	
Coal		0	
Electric wires		0	
Ferrous metal		0	
Glass		0	Discarded fraction
Hazardous	Chemical containers, WEEE	0	
Non-ferrous metal		0	
Stone/ceramic		0	

* As proposed by QUOVADIS (2007)

[^] Assumed in this study: values assigned according to visual inspection of the material components of each category and in line with the results of a wider material characterisation research

^a In the presence of high percentage in materials of non-fossil fuel origin (cigarette filters and other biopolymers, wool-based carpets), these values should be increased accordingly

HDPE: High density polyethylene

WEEE: Waste electrical and electronic equipment

Table 3: Grouped categories with commentary on potential impact on final results. These were used in the G2 and G3 waste component groupings for the determination of the χ_B by the manual sorting method.

Grouped category	Grouped		Detailed	
	$\chi_{B,i}$ (% w/w _d)	Corresponds to	$\chi_{B,i}$ (% w/w _d)	Potential impact
Biological waste	100	<ul style="list-style-type: none"> ▪ biological ▪ ¼ fluff 	100 30	Overestimation
Fabric	35	<ul style="list-style-type: none"> ▪ fabric ▪ ⅓ shoes ▪ ¼ fluff 	35 30 30	Overestimation, especially for SP1, SP8, SP16, where shoes are found
Non ferrous metal	0	<ul style="list-style-type: none"> ▪ non-ferrous metal ▪ electric wires ▪ ½ hazardous ▪ batteries 	0 0 0 0	Null
Paper/card	100	<ul style="list-style-type: none"> ▪ paper/card ▪ ¼ fluff 	100 30	Overestimation
Rigid plastic	0	<ul style="list-style-type: none"> ▪ hard plastic ▪ ⅓ shoes ▪ ½ composite ▪ ½ hazardous 	0 30 0 0	Underestimation for SP1, SP8, SP16, where shoes are found. Null for other SP.
Rubber/leather	80	<ul style="list-style-type: none"> ▪ rubber/leather ▪ ⅓ shoes 	80 30	Overestimation for SP1, SP8, SP16, where shoes are found. Null for other SP.
Soft plastic	0	<ul style="list-style-type: none"> ▪ plastic films ▪ intermediate plastic 	0 0	Null
Stone	0	<ul style="list-style-type: none"> ▪ stones/ceramic ▪ coal 	0 0	Null
Tissue	100	<ul style="list-style-type: none"> ▪ tissue ▪ nappies ▪ ½ composite ▪ ¼ fluff 	100 95 0 30	Overestimation

Table 4: Biogenic content of fines <10 mm ($\chi_{B_fines,d}$) for the MBT plant process streams. As measured by the selective dissolution method on triplicates of samples of an extra increment (INCad). Reported on a dry basis, and uncorrected for ash content. These results are used in the computation of the biogenic content of the entire samples by the manual sorting method in the methodological approaches G1 and G2 (Fig. 4).

Sampling point	$\chi_{B_fines,d}$		
	Arithmetic mean	95% confidence interval*	Standard deviation
SP1	39.8	± 0.3	0.2
SP2	32.5	± 0.7	0.4
SP3	29.0**	-	-
SP4	40.4	± 1.0	0.5
SP5	42.4	± 1.4	0.7
SP6	56.2	± 3.5	1.8
SP7	29.0	± 0.2	0.1
SP10	59.6**	-	-
SP11	72.0	± 1.2	0.6
SP12	68.1	± 1.6	0.8
SP13	50.0**	-	-
SP14	53.3	± 3.2	1.7
SP15	29.0**	-	-
SP16	44.9	± 2.9	1.5

* Combined extended uncertainty ($U_c = 1.96 \times$ standard error)

** Missing data, values interpolated from SPs with similar material composition

Table 5: Proposed classification for standard optimisation

Categories	Details/main constituents	$\chi_{B,i}$ (% w/w _d)
Aggregates	Stones, ceramic, coal, glass	0
Biological and wood	Non-treated and treated wood, feathers, food	100
Carpet/mats		0*
Cartons	Milk/juice packaging	80
Composites	Residual plastics, disposable cleaning wipes, cigarette filter, polystyrene foam	
Fines	≤10 mm	Variable**
Fluff	Light materials (dust, fibres, small pieces of paper, etc.) intimately tangled and virtually impossible to separate	
Metal	Ferrous metal, non-ferrous metal, electric wires, WEEE, batteries	0
Paper/card		100
Plastic	All kinds of plastic	0
Rubber/leather		80
Textiles	Pieces of clothes, wool fibres	35
Tissues	Tissues	100

* Might need to adjust if significant percentage of wool-based carpets are evident

** To be measured by selective dissolution, where effort is justifiable

Table 6: Geometric mean regression parameters and coefficient of determination (r^2)

Manual sorting method variation	a (GMR slope)	b (GMR intercept)	r^2_{GMR}
G1: Detailed 24 categories, variable $\chi_{\text{B fines}}$ by selective dissolution	0.9098 ± 0.0389	0.0293 ± 0.0174	0.9607
G2: Grouped 14 CEN categories, variable $\chi_{\text{B fines}}$ by selective dissolution	0.9308 ± 0.0363	0.0311 ± 0.0162	0.9673
G3: Grouped 14 CEN categories, deemed fixed $\chi_{\text{B fines}} = 50\% \text{ }^w/w_d$ (QUOVADIS)	0.8529 ± 0.0608	0.0716 ± 0.0272	0.8884

All reported 95% confidence intervals are combined extended uncertainty ($U_c = 1.96 \times$ standard error)

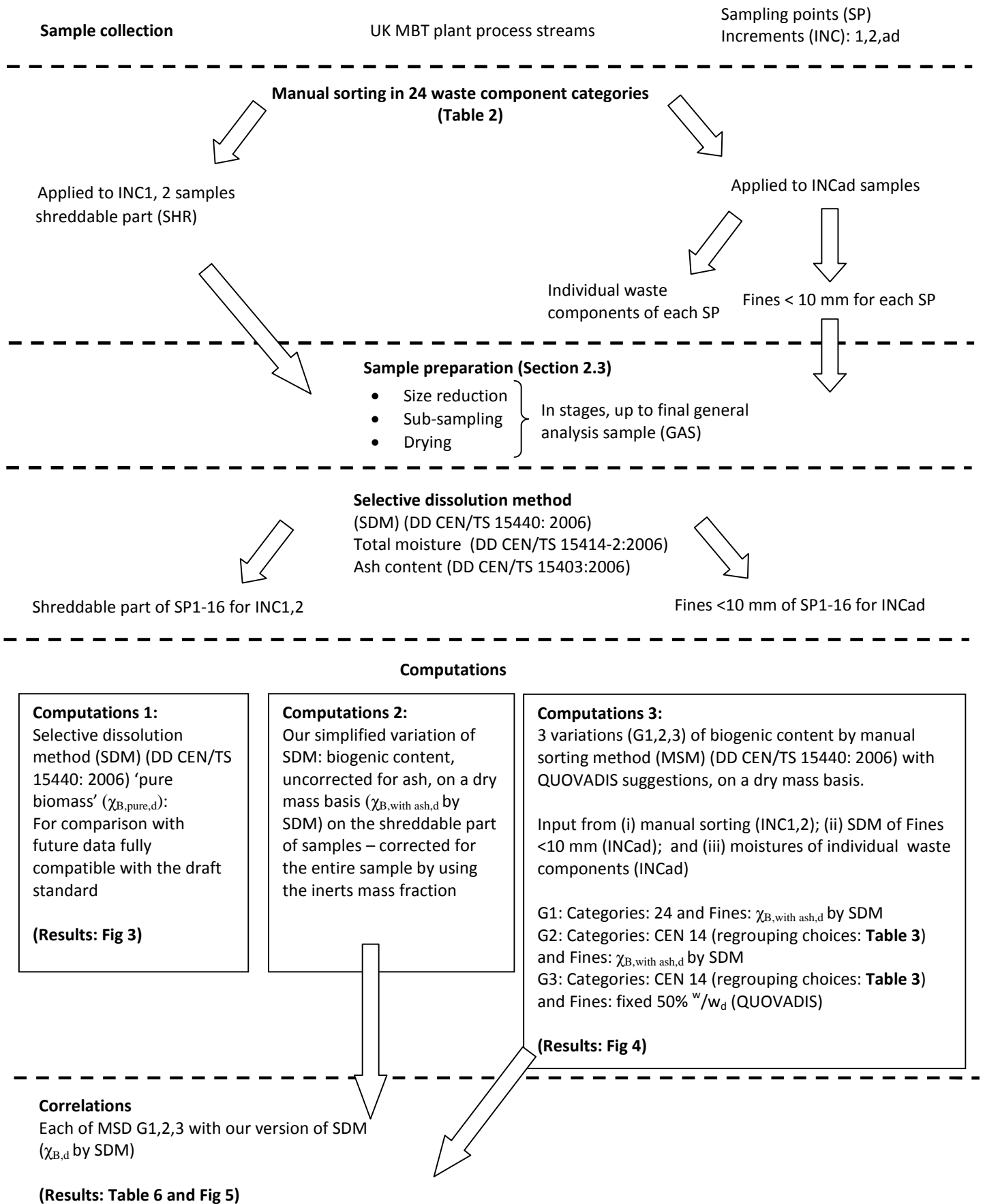


Fig. 1. Overview of the methodology

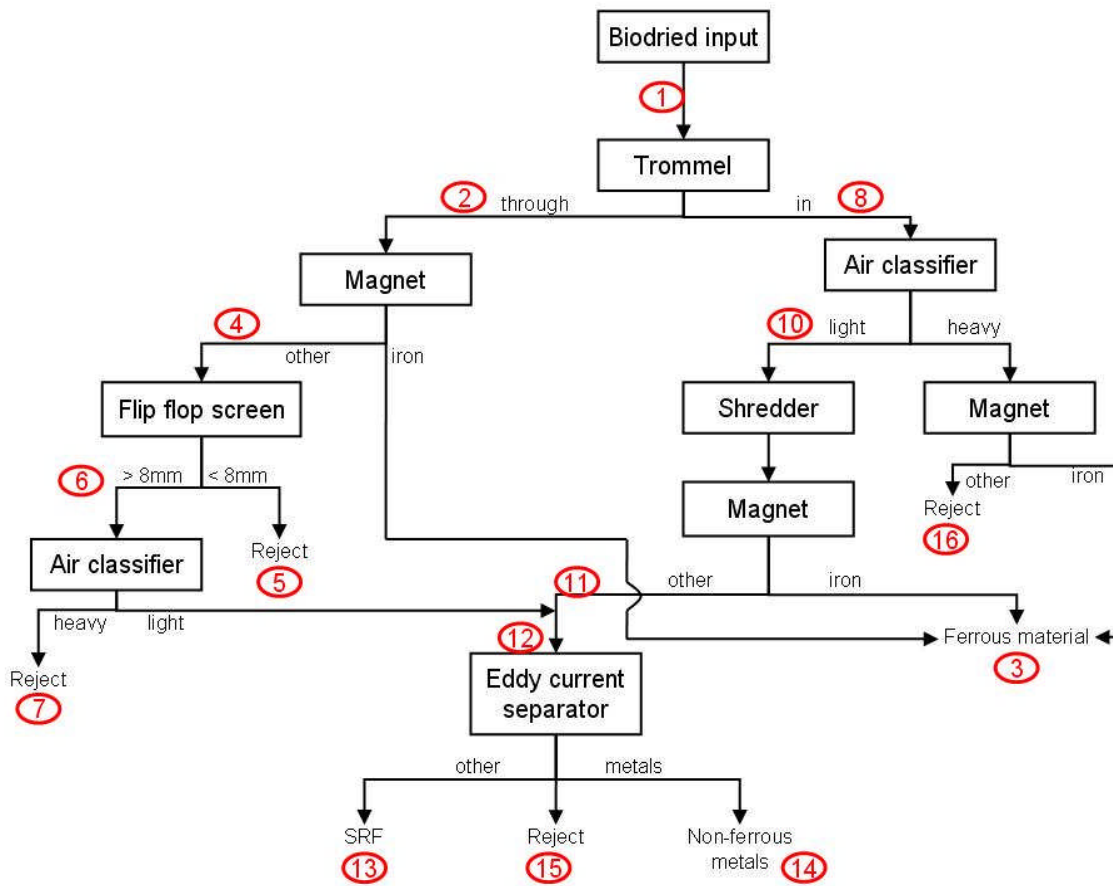


Fig. 2. Mechanical-biological treatment plant flowsheet, with indication of the sampled process streams (SP: sampling point)

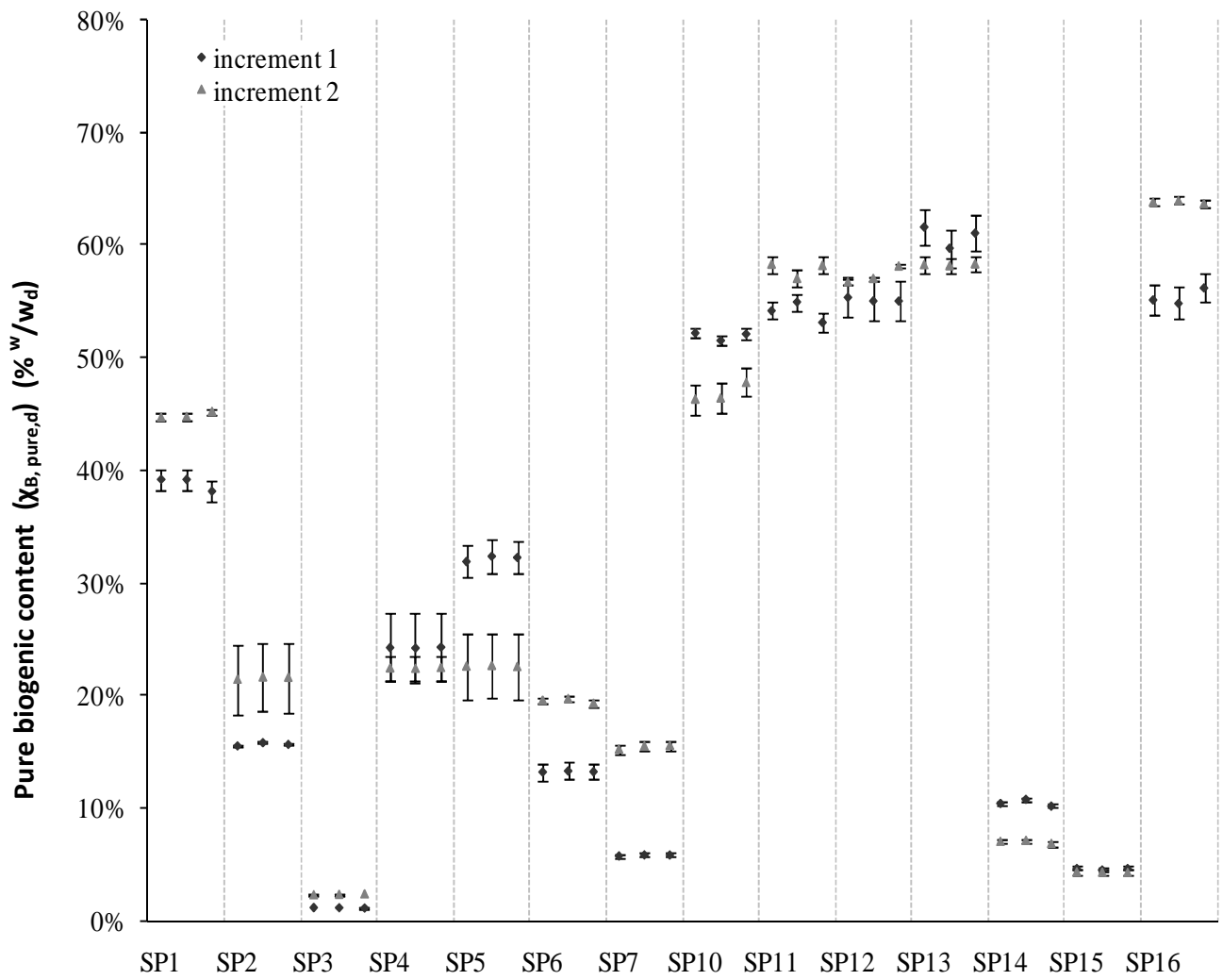


Fig. 3. Selective dissolution experimental results (arithmetic mean \pm U_c ($= 1.96 * SE$))

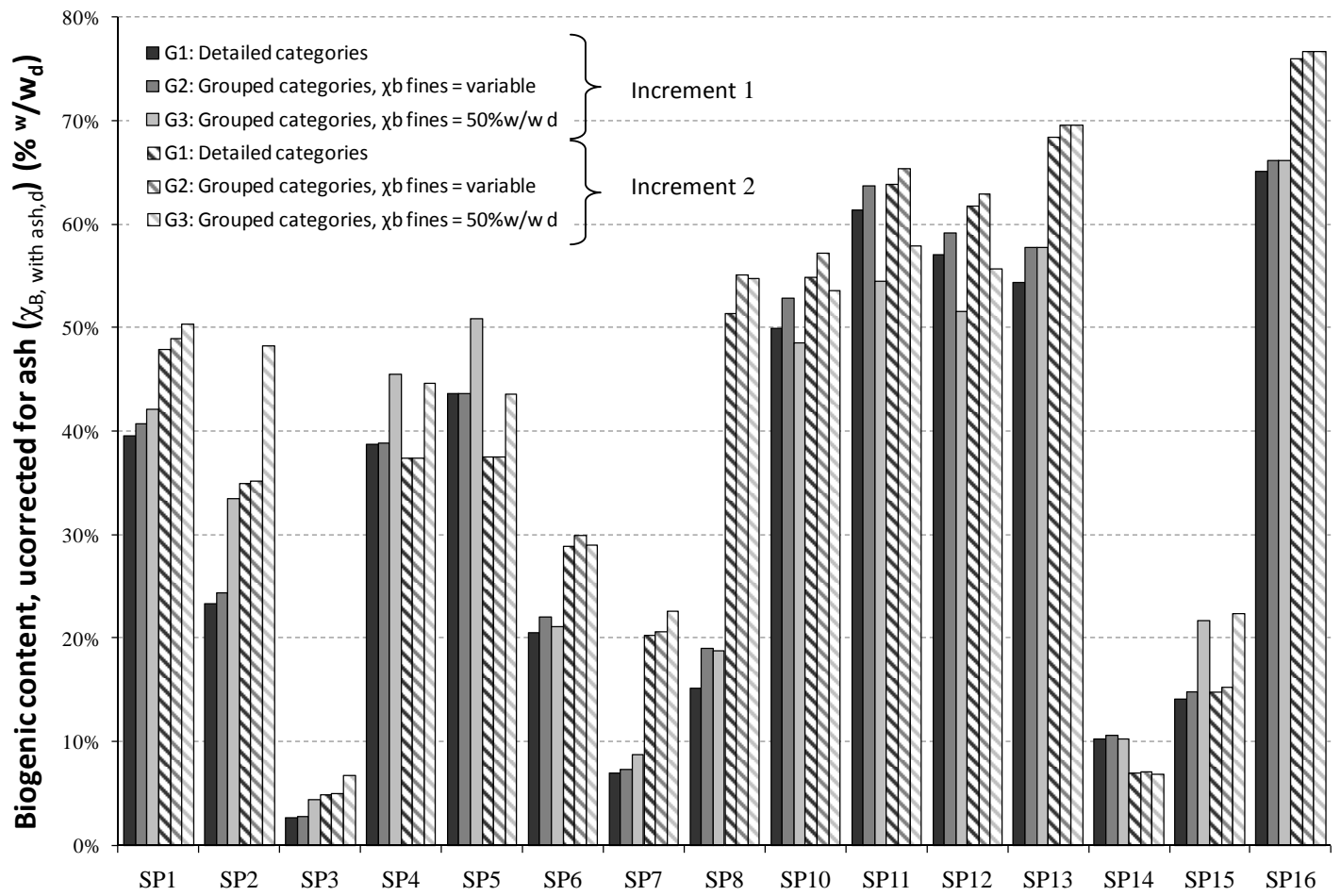


Fig. 4. Effect of categorisation on estimations of biogenic content using the MSM

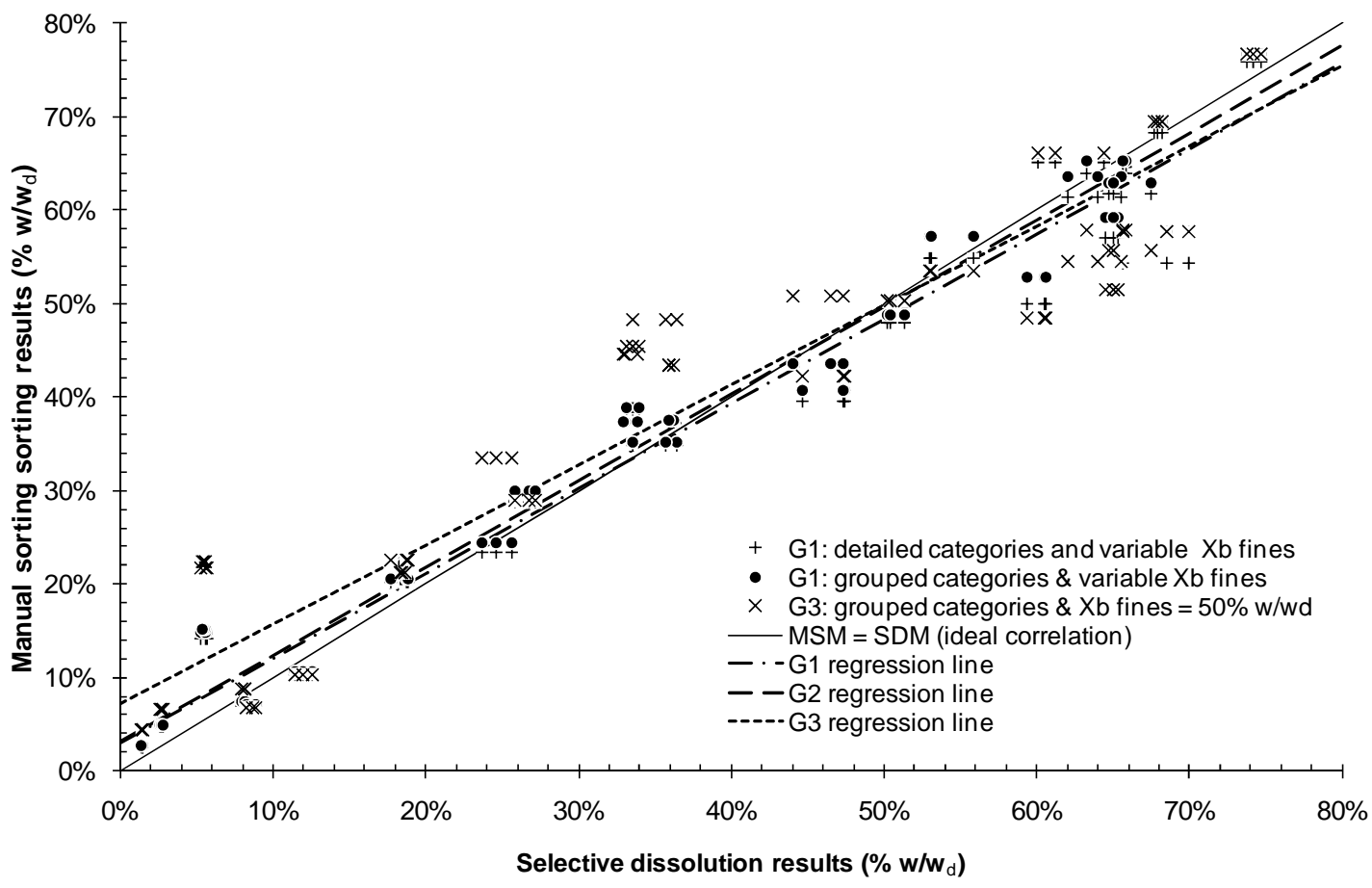


Fig. 5. Biogenic content uncorrected for ash content of MBT process streams: MSM and SDM correlations