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1 **Establishing a sub-sampling plan for waste-derived solid recovered fuels**  
2 **(SRF): Effects of shredding on representative sample preparation based on**  
3 **theory of sampling (ToS)**

4

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13 Declarations of interest: none

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## 25 **Abstract**

26 The uncertainty arising from laboratory sampling (sub-sampling) can compromise the  
27 accuracy of analytical results in highly inherent heterogeneous materials, such as solid waste.  
28 Here, we aim at advancing our fundamental understanding on the possibility for relatively  
29 unbiased, yet affordable and practicable sub-sampling, benefiting from state of the art  
30 equipment, theoretical calculations by the theory of sampling (ToS) and implementation of  
31 best sub-sampling practices. Solid recovered fuel (SRF) was selected as a case of a solid  
32 waste sample with intermediate heterogeneity and chlorine (Cl) as an analyte with  
33 intermediate variability amongst waste properties. ToS nomographs were constructed for  
34 different sample preparation scenarios presenting the trend of uncertainty during sub-  
35 sampling. Nomographs showed that primary shredding (final  $d_{90} \leq 0.4$  cm) can reduce the  
36 uncertainty 11 times compared to an unshredded final sub-sample ( $d \approx 3$  cm), whereas  
37 cryogenic shredding in the final sub-sample can decrease the uncertainty more than three  
38 times compared to primary shredding (final  $d_{90} \leq 0.015$  cm). Practices that can introduce bias  
39 during sub-sampling, such as mass loss, moisture loss and insufficient Cl recovery were  
40 negligible. Experimental results indicated a substantial possibility to obtain a representative  
41 final sub-sample (uncertainty  $\leq 15\%$ ) with the established sub-sampling plan (57 – 93% with  
42 95% confidence), although this possibility can be considerably improved by drawing two  
43 final sub-samples instead (91 – 98% with 95% confidence). The applicability of ToS formula  
44 in waste-derived materials has to be investigated as theoretical ToS calculations gave a  
45 poorer performance of the sub-sampling plan than experimental results.

## 46 **Keywords**

47 Resource recovery; Solid recovered fuel (SRF); Sub-sampling; Uncertainty; Theory of  
48 sampling (ToS); Shredding

49 **Nomenclature**

ANOVA	Analysis of variance
BC	Bomb calorimetry
c	Mineralogical factor
C	Sampling constant
CEN	European Committee of Standardization
Cl	Chlorine
d	Particle size
EC	European Commission
f	Shape factor
FE	Fundamental error
g	Granulometric factor
HDPE	High density polyethylene
IC	Ion chromatography
<i>l</i>	Liberation factor
MT	Mechanical treatment
MC	Moisture content
$M_s$	Mass of sample
$M_L$	Mass of lot
MSW	Municipal solid waste
NaCl	Sodium chloride
NIR	Near infrared
PET	Polyethylene terephthalate
PP	Polypropylene
PSD	Particle size distribution
PVC	Polyvinyl chloride
<i>R</i>	Recovery
SRF	Solid recovered fuel
Total [Cl]	Concentration of total chlorine
w/w <sub>d</sub>	Weight concentration on dry basis

## 51 1. Introduction

52 Quantifying and harnessing variability remains a major challenge for turning waste materials  
53 into secondary resources, and therefore a key barrier to a genuine circular economy  
54 (Esbensen and Velis, 2016). Inherent material heterogeneity can introduce significant  
55 uncertainty during sampling and laboratory sample preparation, i.e. sub-sampling, and  
56 therefore compromises the accuracy of analytical results (Edjabou et al., 2015; Nocerino et  
57 al., 2005). Laboratory sub-sampling is the process by which the initially obtained sample is  
58 split into sub-samples consecutive times until the generation of a final test sub-sample from  
59 which a small mass is drawn for analytical determination, known as test portion (Nocerino et  
60 al., 2005; Prichard and Barwick, 2007). Sub-sampling can be designed and executed with a  
61 high level of control, with a view to minimise introduction of bias within reason of available  
62 resources (time and effort) (Gerlach and Nocerino, 2003). Despite that, design and  
63 implementation of optimal sub-sampling plans have received minimal attention to date  
64 (Cuperus et al., 2005; Gerlach and Nocerino, 2003).

65 The relevant theoretical approaches and practical recommendations benefiting from the  
66 Theory of Sampling (ToS) (Pitard, 1993) to test sub-sampling variations have received  
67 almost no attention. If quantified evidence on the effectiveness of sub-sampling practices  
68 existed, optimal cost-effective sub-sampling approaches could be suggested and adopted  
69 (Dominy et al., 2018a; Dominy et al., 2018b). ToS addresses the factors that can induce  
70 sampling uncertainty and provides practices for its minimization. The fundamental principle  
71 of ToS states that “*all fragments in the lot (the entire body from which a sample is drawn)*  
72 *must end up in the final sample with identical and nonzero probability*” (Pitard, 1993). ToS  
73 developed a theoretical model for the prediction of the sampling uncertainty resulting from  
74 constitutional heterogeneity of material (Gy, 2012). Estimation of theoretical uncertainty due

75 to sub-sampling can be calculated and depicted as nomographs, enabling the design of  
76 optimal sub-sampling plans, associated with a targeted level of tolerable uncertainty (Gerlach  
77 and Nocerino, 2003).

78 The selection of sub-sampling techniques and shredding processes constitute the sub-  
79 sampling plan. The performance of a variety of sub-sampling techniques, such as riffle  
80 splitting, coning and quartering, fractional shovelling, etc. is described elsewhere (Gerlach et  
81 al., 2002; Gerlach and Nocerino, 2003). The beneficial role of shredding in sampling is  
82 double: material homogenization creating more uniform and equal probabilities of all  
83 particles to be included in the sample; and liberation of analyte which otherwise might be  
84 occluded in large particles making difficult to detect it during analysis (Gy, 2012).

85 However, incorrect practices induced during sub-sampling, such as human mistakes, loss of  
86 mass, contamination, chemical modification, physical and biological alteration of the sample  
87 (Edjabou et al., 2015; Pitard, 1993), may introduce bias increasing the uncertainty (Edjabou  
88 et al., 2015; Nocerino et al., 2005). Shredding can exceptionally induce such practices, albeit  
89 the beneficial role it plays in the sampling process. For example, the heat generated during  
90 shredding may induce evaporation of a highly volatile analyte, such as mercury (Gerlach and  
91 Nocerino, 2003). Insufficient shredding may lead to: i) a systematic error during analytical  
92 determination, e.g. incomplete recovery of chlorine (Cl) during bomb calorimetry (BC)  
93 (Cuperus et al., 2005); and ii) a wider range of particle size in the sample generating different  
94 probabilities of each particle to be included in the test sub-sample (Dominy et al., 2018a).

95 Loss of mass can occur during sub-sampling due to either inappropriate handling of  
96 equipment, (e.g. use of riffle splitters by an unskilled operator) or equipment operation (e.g.  
97 dropping grains during shredding) (Gerlach and Nocerino, 2003).

98 The establishment of a sampling and sub-sampling plan able to meet end-users requirements  
99 (fitness for purpose) is a critical quality assurance measure (Dominy et al., 2019; Dominy et  
100 al., 2018b). For example, waste-to-energy plants need accurately determined quality of the  
101 waste-derived material, such as solid recovered fuel (SRF), to ascertain efficient utilization  
102 (Flamme and Ceiping, 2014). SRF can contain considerable levels of chlorine (Cl) content, a  
103 technical limiting factor for SRF application, due to various chlorinated compounds present  
104 in waste items, such as plastic and textiles (Gerassimidou et al., 2020; Iacovidou et al., 2018).  
105 This condition in combination with SRF high inherent heterogeneity due to its origin (e.g.  
106 MSW (Cheng et al., 2017)), yet lower compared to MSW (Kallassy et al., 2008; Velis et al.,  
107 2010), features the importance of representative analytical results (Gerassimidou et al., 2020).  
108 Herein, we aim at advancing our fundamental understanding on the possibility for relatively  
109 un-biased, yet affordable and practicable sub-sampling, benefiting from state of the art  
110 equipment (e.g. riffle dividers and cryogenic shredding), theoretical calculations by ToS  
111 (nomograms) and careful implementation of best sub-sampling practices, with a view to  
112 minimize bias. To this, based on an empirically optimal sub-sampling configuration, we: (i)  
113 quantify the effects of alternative shredding options on the obtainment of representative test  
114 sub-samples based on ToS; (ii) examine the introduction of bias during sub-sampling; (iii)  
115 assess the performance of the selected sub-sampling plan according to experimentally derived  
116 results; and iv) establish a fitness for purpose sub-sampling plan for solid waste  
117 characterization. We demonstrate these for the case of SRF, chosen as a case of solid waste-  
118 derived material with intermediate heterogeneity; and for the analyte of total chlorine (Cl),  
119 chosen as the one with intermediate variability for solid waste mixtures. Results inform best  
120 practice and set the basis for incorporation in relevant sub-sampling standards.

121

## 122 **2. Materials and Methods**

### 123 **2.1 Materials**

124 We used a typical SRF sample (ca. 1kg) produced from residual MSW in a mechanical  
125 treatment (MT) plant in the UK, processing a mixture of residual household MSW and  
126 commercial waste (corporate name withheld for confidentiality reasons). The analytical  
127 technique for the determination of total Cl concentration (Total [Cl]) (see **2.2.6**) involved  
128 reagents, 0.2 M KOH as absorption solution, Palintest acidifying and silver nitrate tablets  
129 (Sigma-Aldrich, UK). Liquid nitrogen was used for the cryogenic shredding. Reference  
130 materials (Sigma-Aldrich, UK) were used to resemble SRF composition and calculate the  
131 recovery of Cl: powder microcrystalline cellulose, alkali lignin, xylan from beechwood, high  
132 density polyethylene (HDPE), isotactic polypropylene (PP), polyethylene terephthalate (PET)  
133 and polyvinyl chloride (PVC).

### 134 **2.2 Methodology**

135 We estimated the sub-sampling uncertainty for different sub-sampling scenarios using state  
136 of the art equipment and the ToS formula (see **2.2.2**) to examine the beneficial role of  
137 shredding and establish a sub-sampling protocol that fulfils the fitness for purpose  
138 requirements. The design of this protocol focused on the development of a straightforward  
139 and affordable sub-sampling process suitable for solid waste materials. During the established  
140 sub-sampling process relied on practices and equipment proposed by ToS, we monitored  
141 incorrect sub-sampling practices to examine the adverse effects of shredding on sub-sampling  
142 uncertainty. The selected critical component was Cl, which is the most important technical  
143 parameter for SRF applications (BS 15359, 2011). This choice was a compromise between  
144 SRF properties with low and high variability amongst waste components, such as moisture

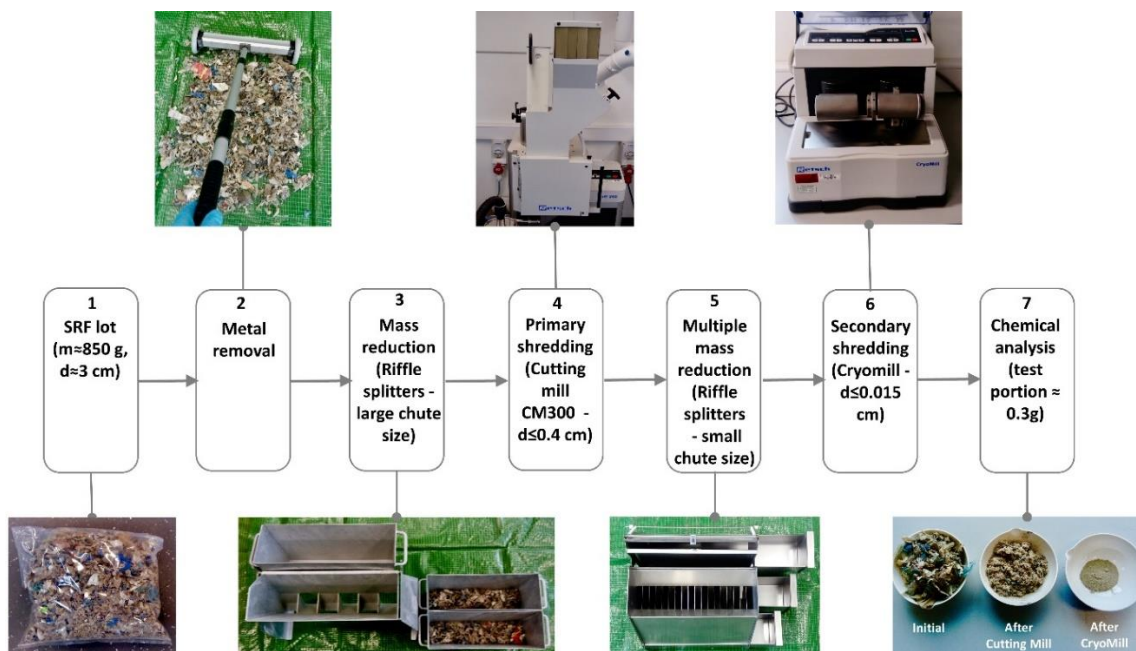
145 content and mercury, respectively (BS 15442, 2011). In addition, the selected mass of SRF  
146 sample (ca. 1kg) approximates the minimum typical sample mass received in the laboratory  
147 from the production plant, which can be ranged between 0.8 and 159 kg depending on the  
148 grain size and bulk density according to BS 15442 (2011).

### 149 **2.2.1 Sub-sampling protocol**

150 The sub-sampling process consisted of two stages of shredding and multiple stages of mass  
151 splitting according to BS 15413 (2011) (**Figure 1**). The sub-sampling operations and  
152 equipment were applied as follows: The SRF sample was pre-dried at 40 °C for 24 h to  
153 remove the moisture that could interfere with the shredding process (BS 15414-3, 2011) (**1**).  
154 After pre-drying the sample mass was reduced at 850 g. The pre-dried sample was spread on  
155 a canvas forming a thin layer ( $\leq 2$  cm) and a magnet passed over the layer to pick any ferrous  
156 metals that could damage the shredders (**2**). The pre-dried sample with a particle size ca. 3 cm  
157 was divided into two sub-samples with large riffle splitters (RT 75, Retsch, Germany) (**3**).  
158 The sub-samples were shredded with cutting mill (SM 300, Retsch, Germany) to a particle  
159 size  $d_{90} \leq 4$  mm (primary shredding) (**4**). The shredded sub-samples were divided with small  
160 riffle splitters (PFEUFFER GmbH, Germany) multiple times obtaining 16 sub-samples of ca.  
161 50 g each (**5**). A test sub-sample of 7 g was drawn from each of the 16 sub-samples with riffle  
162 splitting and cryogenically shredded (Cryomill, Retsch, Germany) to  $d_{90} \leq 150$   $\mu\text{m}$  (secondary  
163 shredding) (**6**). From these 16 test sub-samples of 7 g, we obtain three test portions for  
164 analytical determination of Cl (0.3 g) and moisture content (1 g) as specified by the related  
165 CEN standards (see **2.2.2**) (**7**).

166 Cutting mill is suitable for primary size reduction of highly heterogeneous materials, such as  
167 solid waste including soft, medium-hard, elastic and fibrous materials able to achieve a  
168 defined final fineness from the first shredding run (Retsch, 2020b). The process is conducted

169 by the sample comminution between the blades and the stationary double acting cutting bars  
 170 (Retsch, 2020b). Cryomill is suitable for secondary cryogenic shredding (material feed size  $\leq$   
 171 8mm) producing a fine particle size under inert atmosphere at very low temperature (-196 °C)  
 172 through an autofill liquid nitrogen system.(Retsch, 2020a). Cryomill provides programmable  
 173 shredding conditions depending on the configuration settings and the feed material, which  
 174 enables to adjust the cost of the process (Retsch, 2011). Cryogenic shredding prevents  
 175 component evaporation, oxidation and/or microbial degradation due to the integrated cooling  
 176 system earning interest on sample preparation of solid waste (Junghare et al., 2017). The  
 177 advantages of cryogenic shredding to sample preparation have been extensively discussed  
 178 (Junghare et al., 2017).



179

180 **Figure 1.** Sub-sampling protocol applied to SRF for quality characterization: operations and  
 181 equipment were informed by best practices according to the TOS. SRF was selected as a  
 182 representative solid waste-derived material with intermediate level of heterogeneity.

183 **2.2.2 ToS-based formula**

184 We used the theoretical model for the calculation of *fundamental error* (FE) provided by  
185 ToS. *Fundamental error* is the minimum sampling uncertainty that is attributed only to the  
186 physical and chemical constitutional heterogeneity of the sample, other factors related to  
187 sample preparation, sampling method and chemical analysis that may introduce additional  
188 uncertainty are not included (Pitard, 1993):

$$s_{FE}^2 = \left( \frac{1}{M_S} - \frac{1}{M_L} \right) Cd^3 \quad \text{Eq. 2.1}$$

189 where  $M_s$  is the sample mass [g],  $M_L$  is the mass of the lot [g];  $C$  is the sampling constant [g  
190  $\text{cm}^{-3}$ ]; and  $d$  is the nominal size of the particles [cm].

191 This formula could, also, be used in sub-sampling either for the calculation of minimum sub-  
192 sampling uncertainty (FE) for a given sample size or for the calculation of the required  
193 sample mass to obtain a specified FE (Dominy et al., 2019). At each stage of sub-sampling,  
194  $M_s$  is the mass of the sub-sample at this stage and  $M_L$  is the mass of sample or higher level of  
195 sub-sample (Gerlach and Nocerino, 2003).

196 The square root of  $s_{FE}^2$  gives the relative deviation of the FE expressed as (%). Every stage of  
197 mass splitting introduces FE, the summation of which gives the overall FE of the sub-  
198 sampling process. An overall  $FE \leq 15\%$  is a recommended acceptable reference limit  
199 (Dominy et al., 2019; Dominy et al., 2018b; Gerlach and Nocerino, 2003), although the limit  
200 value depends on the fitness for purpose requirements that are different for each application  
201 (Ramsey and Thompson, 2007).

202 Sampling constant,  $C$ , is the product of four factors related to the characteristics of the  
203 sample:

$$C = cflg \quad \text{Eq. 2.2}$$

204 where  $c$  is the mineralogical (or composition) factor [ $\text{g cm}^{-3}$ ];  $l$  is the dimensionless liberation  
205 factor;  $f$  is the dimensionless shape factor; and  $g$  is the dimensionless particle size range (or  
206 granulometric) factor. The physical characteristics of a sample change after shredding and  
207 therefore the values of these factors (BS 15442, 2011).

208 The mineralogical factor,  $c$ , is defined as follows:

$$c = \lambda_M \frac{(1 - a_L)^2}{a_L} + \lambda_g(1 - a_L) \quad \text{Eq. 2.3}$$

209 where  $a_L$  is the concentration of the critical component in the sample expressed as decimal  
210 proportion (Total [Cl] in the present study);  $\lambda_M$  is the density of particles containing the  
211 critical component (e.g. plastic, textile or food materials that contain Cl) [ $\text{g cm}^{-3}$ ]; and  $\lambda_g$  is  
212 the density of the sample (SRF in the present study) [ $\text{g cm}^{-3}$ ].

213 The factors required for the calculation of the sampling constant,  $C$  (Eq. 2.1) after each stage  
214 of shredding were determined as follows:

215 **Liberation factor ( $l$ ):** ranges between 0 and 1 depending on the degree of heterogeneity. The  
216 more homogeneous the sample, the lower the  $l$  value. For the heterogeneous SRF, we  
217 selected the value 1, as the maximum value is recommended for environmental applications  
218 (Gerlach and Nocerino, 2003). After primary shredding the value was set at 0.8 (considered  
219 as *very heterogeneous material*) and after secondary shredding at 0.4 (considered as  
220 *heterogeneous material*). The selection of these values was based on the optical observation  
221 of color uniformity in SRF sub-samples after each shredding process and the guidance on the  
222 liberation parameter estimates provided by ToS (Gerlach and Nocerino, 2003).

223 **Shape factor ( $f$ ):** ranges between 0 and 1 depending on closeness of particle's shape to a  
224 perfect cube (where  $f = 1.0$ ). SRF mainly manufactured from MSW is a fluff-type material  
225 and a value of 0.05 is recommended by BS 15442 (2011). We selected the 0.2 (*soft*

226 *homogeneous such as gold flakes*) and 0.5 (*all particles are spheres such as minerals*) for the  
227 stages of primary and secondary shredding, respectively. These values were selected based on  
228 the optical observation of the particle's shape of sub-samples and on characteristic values of  
229 shape parameters for several materials given by ToS (Gerlach and Nocerino, 2003).

230 **Granulometric factor ( $g$ ):** accounts for the particle size distribution (PSD) by adjusting the  
231 particle sizes to a nominal value. The more uniform the particles, the higher the  $g$  value.  
232 According to BS 15442 (2011), the  $g$  factor should be kept at 0.25 for PSD  $d_{95}/d_{05} > 4$ . Even  
233 after secondary shredding this ratio was higher than four (results presented in **Section 3.1.1**),  
234 so the factor remained constant.

235 **Mineralogical factor ( $c$ ):** Eq. 2.3 needs to define Total [Cl] of the sample and the density  
236 both of SRF and particles containing the Cl. The arithmetic mean of Total [Cl] in 16 sub-  
237 samples constituted the concentration of critical component ( $a_L$ ). We considered the most  
238 prevalent chlorinated compounds in MSW for the calculation of the density of particles  
239 containing Cl in SRF ( $\lambda_M$ ): PVC and NaCl with density 1.38 and 2.17 g cm<sup>-3</sup>, respectively  
240 (Guo et al., 2001; Ma et al., 2010; PubChem, 2019). Literature findings stated that 50-75%  
241 w/w of Total [Cl] in MSW mainly attributed to the presence of plastics and 25-50% w/w  
242 mainly attributed to the presence of food waste (Gerassimidou et al., 2020). We assumed that  
243 75% of Total [Cl] was due to PVC and 25% was due to NaCl, as the fraction of plastics in  
244 SRF can be higher than in MSW due to sorting processes applied in MT plant. The  
245 weighted average of PVC and NaCl set the  $\lambda_M$  value at 1.58 g cm<sup>-3</sup>. The SRF density was set  
246 at 0.15 g cm<sup>-3</sup> (CEN/TS 15401, 2010).

247 Note that the above selected values of sampling factors were used only as estimators based on  
248 ToS and SRF characteristics. The precise quantification of these factors is difficult as a  
249 significant amount of information, not available here, is required for the target material

250 (Ramsey and Thompson, 2007). The purpose of theoretical ToS calculations was the  
251 quantification of the effects of alternative shredding scenarios and not the precise calculation  
252 of FE.

### 253 **2.2.3 Fundamental error based on three shredding scenarios**

254 The FE was calculated based on three sample preparation scenarios: *sub-sampling without*  
255 *shredding (NS)*, where only riffle splitting took place; *sub-sampling with only primary*  
256 *shredding (PS)*, where riffle splitting and only primary shredding (with cutting mill) after the  
257 first stage of riffle splitting took place; and *current sub-sampling plan (CS)*, where riffle  
258 splitting and both primary and secondary shredding, took place based on the established sub-  
259 sampling process (see **2.2.1**). Specifically, we constructed nomographs that depict the trend  
260 of  $s_{FE}^2$  as a function of sample mass during sub-sampling for the three different shredding  
261 scenarios. The comparison amongst the different shredding scenarios enabled us to  
262 quantitatively determine the impact of shredding on the sub-sampling uncertainty based on  
263 ToS formula.

264 Special attention was paid to cryomill due to its effective shredding ability and confined  
265 laboratory application. We examined the effect of several configuration settings provided by  
266 the cryomill on the FE so that to select the most suitable shredding program. Specifically,  
267 four cryomill programs were selected: i) P2 with 2 grinding cycles, 2min grinding time, 1min  
268 intermediate cooling and 30 Hz grinding frequency; ii) P4 with 4 grinding cycles, 2min  
269 grinding time, 1min intermediate cooling and 30 Hz grinding frequency; iii) P5 with 5  
270 grinding cycles, 2min grinding time, 2min intermediate cooling and 30 Hz grinding  
271 frequency; and iv) P9 P5 with 9 grinding cycles, 2min grinding time, 2.5min intermediate  
272 cooling and 25Hz grinding frequency. Common metrics of PSD, such as  $d_{90}$ ,  $d_{50}$ ,  $d_{10}$  and  
273 span, were used to statistically compare the shredding programs. We calculated the FE

274 introduced during: the final stage of sub-sampling from test sub-sample (7 g) to test portion  
275 (0.3 g); and the entire sub-sampling from the initial sample (850 g) to test portion (overall  
276 FE). The particle size of the test sub-sample was replaced by the  $d_{90}$  of each program in **Eq.**  
277 **2.1.**

#### 278 **2.2.4 Incorrect sub-sampling practices related to shredding**

279 Despite the calculation of FE that provides the minimum uncertainty under a perfect sub-  
280 sampling process, we monitored practices that may introduce bias and increase the  
281 uncertainty arising from sub-sampling. Specifically, three main aspects of incorrect sub-  
282 sampling practices mostly related to shredding were checked:

283 (1) Loss of sample mass by weighing individually the sub-samples after each step of sub-  
284 sampling; (2) evaporation of moisture during primary and secondary shredding by obtaining  
285 3 test sub-samples of 7 g with riffle splitters from a pre-dried sub-sample of 50 g and taking 6  
286 replicates of residual moisture (see **2.2.6**) before and after each shredding process; and (3)  
287 analytical error respecting Cl recovery by using reference materials. Synthetic mixtures with  
288 known composition and consequently Total [Cl] resembling the composition of SRF were  
289 prepared and analysed. Specifically, two mixtures composed of powered biomass polymers,  
290 such as cellulose, xylan (common type of hemicellulose) and lignin, and plastic polymers,  
291 such as HDPE, PP, PET and PVC with Total [Cl] 0.62% w/w and 1.42% w/w, respectively,  
292 were prepared. The presence of Cl in the synthetic mixtures was attributed only to the  
293 presence of PVC with Total [Cl] 53.7 % w/w.

294 The recovery of Cl ( $R$ ) is given by the following equation (Prichard and Barwick, 2007):

$$R(\%) = \frac{\bar{x}}{x_0} * 100 \quad \text{Eq. 2.4}$$

295 where  $R$  (%) is the Cl recovery,  $\bar{x}$  is the mean value of Total [Cl] obtained from analysis and  
296  $x_0$  is the assigned Total [Cl].

297 The analytical results of Total [Cl] in SRF sub-samples were corrected as shown below:

$$C_{cor} = \frac{C_{obs}}{R(\%)} * 100 \quad \text{Eq. 2.5}$$

298 where  $C_{cor}$  is the corrected measurement result,  $C_{obs}$  is the observed measurement result and  
299  $R$ (%) is the recovery of Cl.

### 300 **2.2.5 Statistical analysis**

301 Analysis of variance (ANOVA) was conducted to statistically compare: the 4 different  
302 cryomill programs with respect to PSD metrics; and the moisture content of sub-samples  
303 before and after each shredding process (TIBCO Statistica™ 13.3.0 software). The key  
304 requirements to use ANOVA were checked (see **SI**).

305 Graphical illustrations were designed to assess the experimental results derived from the  
306 analysis of 16 test sub-samples, in which three test portions obtained for the determination of  
307 Total [Cl] and moisture content (MC) in SRF sample. Specifically, 95% confidence interval  
308 error bars of mean values for each test sub-sample were designed to assess the precision of  
309 analytical measurements. Additionally, boxplots were designed to provide the dispersion of  
310 Total [Cl] and MC arising from the average values of test sub-samples and classify the  
311 initially obtained SRF sample based on the classification scheme (BS 15359, 2011).

312 We estimated the possibility to obtain a representative test sub-sample following the  
313 established sub-sampling plan for determination of Total [Cl] by calculating the confidence  
314 interval for binomial proportions with three different methods (normal approximation, exact  
315 Clopper-Pearson and Wilson score method). Further details can be found in the supporting  
316 information (see **SI.6**). Assuming that a test sub-sample is representative if its average value

317 differs from the actual Total [Cl] in the initially obtained SRF sample less than 15%. We  
318 presumed that the average value of Total [Cl] from the 16 test sub-samples represents the  
319 actual Total [Cl] in the initially obtained sample.

## 320 **2.2.6 Analytical techniques**

321 Wet laser diffraction analysis was used to determine the PSD of the test sub-samples  
322 shredded by cryomill. Measurements performed by Mastersizer (2000E hydro SM, Malvern,  
323 UK) and five replicates taken for each cryomill program. The MC in SRF, expressed in %  
324 w/w, was determined according to the BS 15414-3 (2011). The residual MC is the remaining  
325 moisture after sample pre-drying at 40°C. The total MC was calculated as follows:

$$MC_{Total} = MC_b + MC_{residual} \left(1 - \frac{MC_b}{100}\right) \quad \text{Eq. 2.6}$$

326 The Total [Cl] in SRF measured with the standard method BC (BS 15400, 2011) and the  
327 photometric method of Palintest Chloridol test (BS 15400, 2011; Palintest-Test instructions,  
328 2019). This photometric method uses tablets of silver nitrate that react with the chlorides of  
329 the test portion (1:50 dilution ratio) producing silver chloride. The insoluble silver chloride is  
330 observed as turbidity in the test portion measured by Palintest Photometer, which is  
331 proportional to Total [Cl]. The analytical measurements were expressed in % w/w on a dry  
332 basis (w/w<sub>d</sub>).

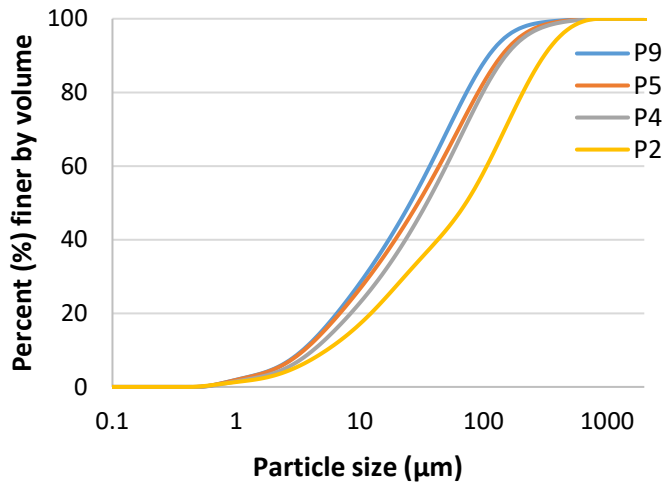
333

## 334 **3 Results and Discussion**

### 335 **3.1 Beneficial effects of shredding based on ToS**

#### 336 **3.1.1 Effect of cryomill settings on fundamental error**

337 **Figure 2** shows that shredding programs achieved similar PSD except for P2. Specifically,  
338  $d_{90}$  of P4, P5 and P9 ranges between 110-152  $\mu\text{m}$ , and it is more than twice larger for P2 (356  
339  $\mu\text{m}$ ) (see **SI.1**). ANOVA test showed statistical difference amongst the cryomill programs  
340 regarding all PSD metrics ( $d_{10}$ ,  $d_{50}$ ,  $d_{90}$  and span) (see **SI.1**).

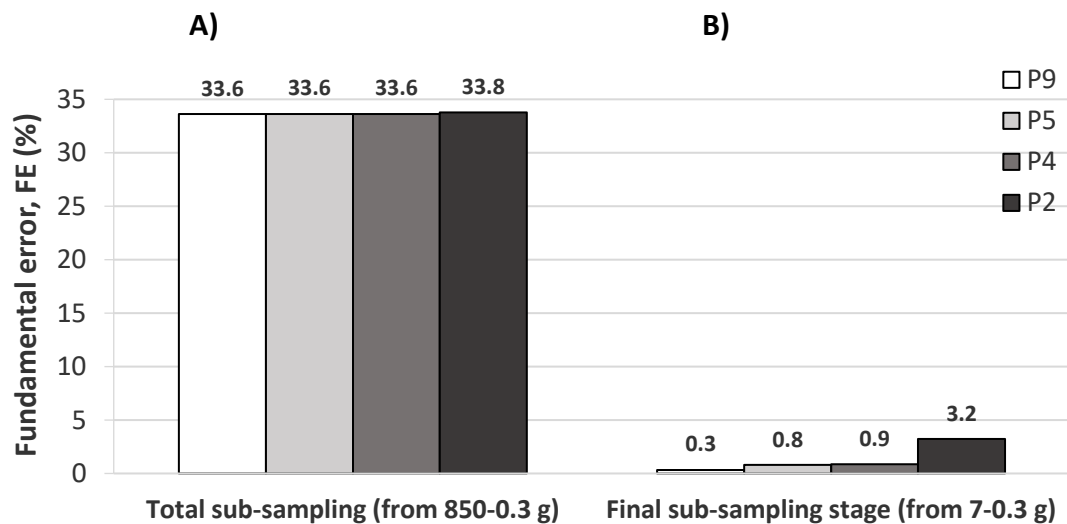


341  
342 **Figure 2.** Cumulative PSD for SRF particles shredded by cryomill under 4 different  
343 shredding programs.

344 However, the theoretical model of ToS (**Eq. 2.1**) showed that configuration settings of  
345 cryomill do not considerably affect the overall sub-sampling uncertainty (**Figure 3**). We  
346 found that the overall FE is identical for P9, P5 and P4 (33.6%), whereas for P2 a negligible  
347 rise is observed (33.8%). Considerable difference can be found only in the FE arising from  
348 the final stage of sub-sampling, from test sub-sample (7 g) to test portion (0.3 g). The highest  
349 difference is between P9 (0.3%) and P2 (3.2%), where the FE increases more than ten times  
350 at the final sub-sampling stage.

351 From the statistical point of view, the PSD is significantly different amongst the shredding  
352 programs. However, this difference ( $\mu\text{m}$ -scale) is negligible compared to the difference (cm-  
353 scale) between the particle size before (3 cm) and after (0.4 cm) primary shredding. The FE  
354 of the final sub-sampling stage is considerably lower than the FE of previous stages, where

355 the particle size is one order of magnitude greater. For example, in the most extended  
 356 shredding program (P9) the FE arising from the final stage (0.3%) constitutes less than 1% of  
 357 the overall FE (33.6%). Even in the least extended program (P2) the final stage constitutes  
 358 less than 10% of the overall FE. We selected P4, as it was the best combination of sample  
 359 homogeneity (low FE), cost and time savings.

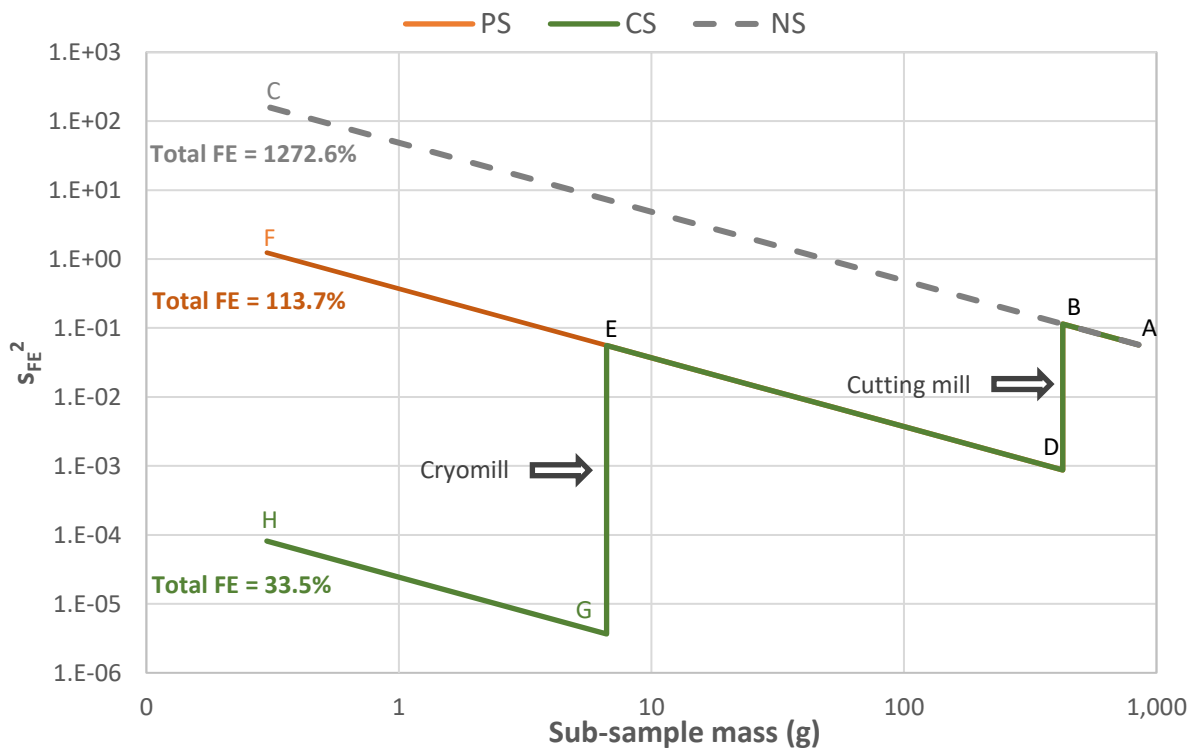


360 **Figure 3.** Fundamental error (FE) arising from the sub-sampling plan applied for the  
 361 determination of Total [Cl] in SRF after shredding of test sub-samples with cryomill  
 362 (secondary shredding) under four different configuration settings based on ToS: overall FE  
 363 during sub-sampling from the sample (850 g) to test portion (0.3 g) (A); and FE during the  
 364 final stage of sub-sampling from the test sub-sample (7 g) to test portion (B).

### 365 3.1.2 Trend of fundamental error under different shredding scenarios: Nomographs

366 Nomographs constructed for the three different shredding scenarios: sub-sampling without  
 367 shredding (NS), sub-sampling with primary shredding (PS), and current sub-sampling plan  
 368 (CS) (Figure 4). The points of nomographs (A to H) indicate the alteration of mass and  
 369 particle size of sub-samples during sub-sampling based on the three scenarios. The movement  
 370 from one point to another indicates the stages of shredding and riffle splitting. For example,  
 371 the sample was split into two sub-samples from point A to B (from 850 g to 425 g), the sub-  
 372 samples were shredded with the cutting mill (primary shredding) from point B to D,

373 consecutive stages of riffle splitting took place from point D to E, and so on.



374  
375

376 **Figure 4.** Trend of the variance of fundamental error ( $S_{FE}^2$ ) during sub-sampling (nomograph)  
 377 for the determination of Total [CI] in SRF under three shredding scenarios: NS -sub-sampling  
 378 without shredding (A-B-C); PS - sub-sampling with primary shredding (A-B-D-E-F); CS -  
 379 the current sub-sampling plan including both primary and secondary shredding (A-B- D-E-G-  
 380 H). The points above the trend lines demonstrate the mass and the particle size alteration of  
 381 sub-samples during sub-sampling. The movement from one point to another indicate the  
 382 stages of sub-sampling.

383 For the three scenarios the process from point A to B is identical as shredding took place after  
 384 the first stage of riffle splitting, while scenarios PS (points A-B-D-E-F) and CS (points A-B-  
 385 D-E-G-H) are identical from point A (from sample of 850 g) to D (test sub-sample of ca. 7 g)  
 386 as secondary shredding applied after the obtainment of the test sub-sample. For these two  
 387 scenarios (PS and CS), the 1<sup>st</sup> stage of riffle splitting (from A to B) applied before primary  
 388 shredding introduces the highest uncertainty (FE: 23.9%) compared to the next sub-sampling

389 stages due to the largest particle size ( $d \approx 3$  cm). This phenomenon indicates the urgent need  
390 for primary shredding, which drops the FE in the next stages of riffle splitting.

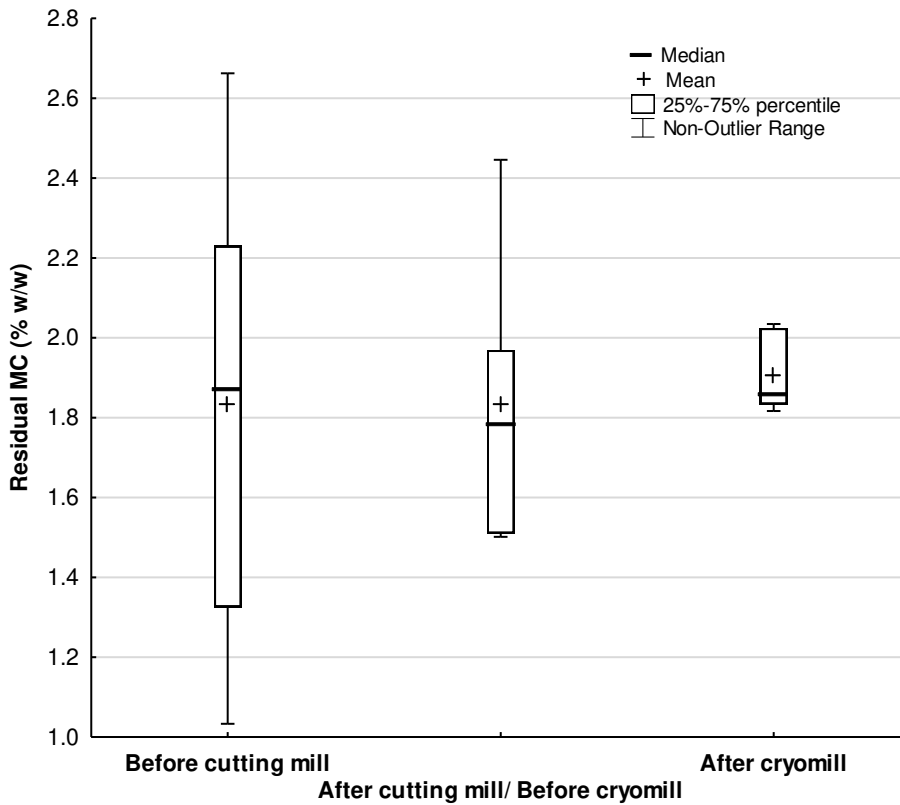
391 If no primary shredding applied, which is the NS scenario (A-B-C), the uncertainty would be  
392 increased logarithmically during sub-sampling (overall FE: 1272.6%). The considerably  
393 lower uncertainty observed in the PS scenario (overall FE: 113.7%) indicates that primary  
394 shredding applied after the 1<sup>st</sup> stage of riffle splitting can reduce the overall FE more than 11  
395 times. By comparing the PS with the CS scenario (overall FE: 33.5%), the overall FE  
396 decreases more than 3 times if the particle size of the test sub-sample drops from 0.4 cm to  
397 0.015 cm. The beneficial role of cryomill is also revealed by the contribution of the final  
398 stage of sub-sampling to the overall FE for the two scenarios: *PS* and *CS*. For the *PS*  
399 scenario, the FE arising from the final stage of sub-sampling (FE from E to F: 108.7%)  
400 contributes 96% to the overall FE, whereas the FE arising from the final stage for the *CS*  
401 scenario (FE from G to H: 0.9%) contributes less than 3% to the overall FE. Note that these  
402 differences do not include any bias that might be induced by a larger particle size (e.g.,  
403 insufficient CI recovery). The calculations conducted for the construction of nomograph  
404 (**Figure 4**) and the estimation of FE arising from each sub-sampling stage is presented in  
405 **SI.2**.

## 406 **3.2 Adverse effects of shredding: *incorrect* sampling practices**

### 407 **3.2.1 Moisture evaporation during shredding**

408 The moisture evaporation during shredding may lead to the miscalculation of residual MC  
409 and therefore of Total [CI] expressed on a dry basis. Based on the ANOVA test, we cannot  
410 reject the null hypothesis that shredding processes (primary and secondary) do not affect the

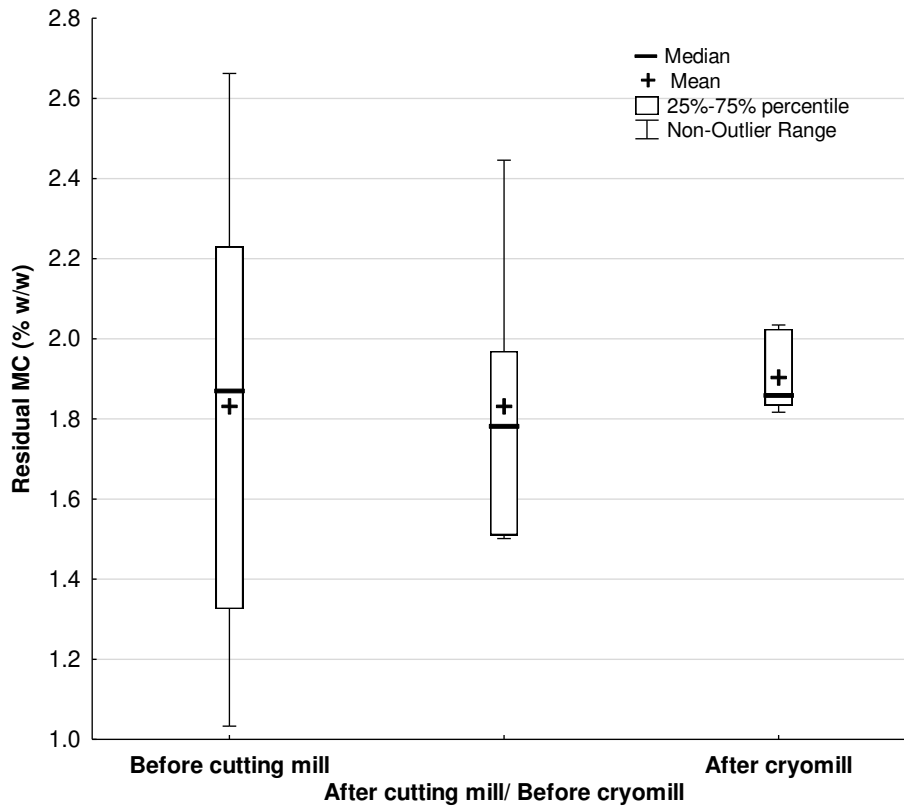
411 MC (see SI.3). Similarly,



412

413 **Figure 5** shows that residual MC is not affected by the shredding processes, although a  
414 negligible decrease after primary shredding with cutting mill is observed. There is a slight  
415 increase in residual MC after secondary shredding (cryomill). These insignificant differences  
416 of residual MC amongst the shredding stages can be attributed to SRF inherent heterogeneity.  
417 The test sub-samples for each shredding stage were drawn from the same sub-sample, but  
418 they were not identical.

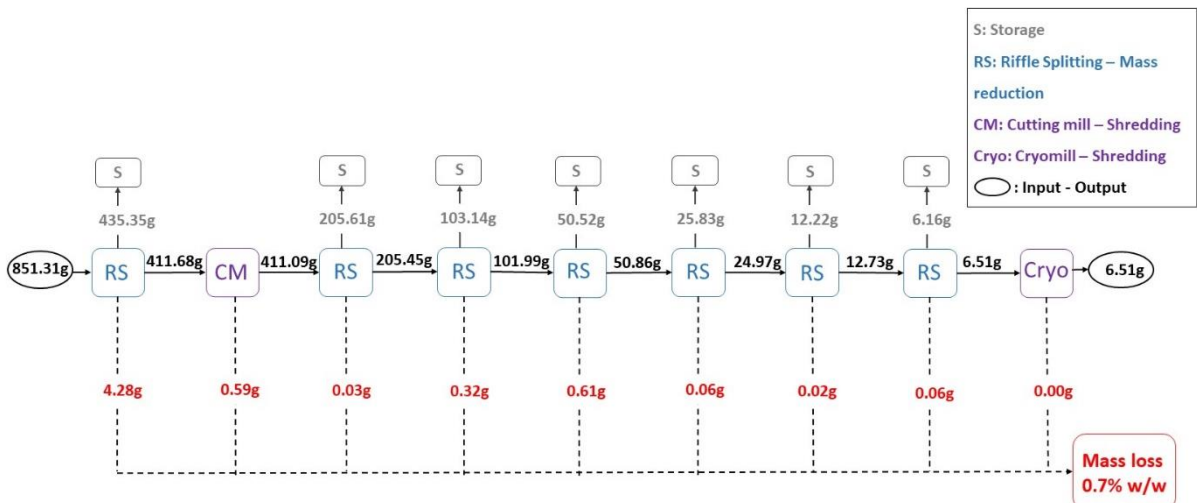
419



420

421 **Figure 5.** Residual MC in test sub-samples obtained by an SRF sub-sample of 50 g before  
 422 and after two shredding processes: primary with the use of cutting mill and secondary with  
 423 the use of cryomill.

424 **3.2.2 Loss of sample mass during sub-sampling**

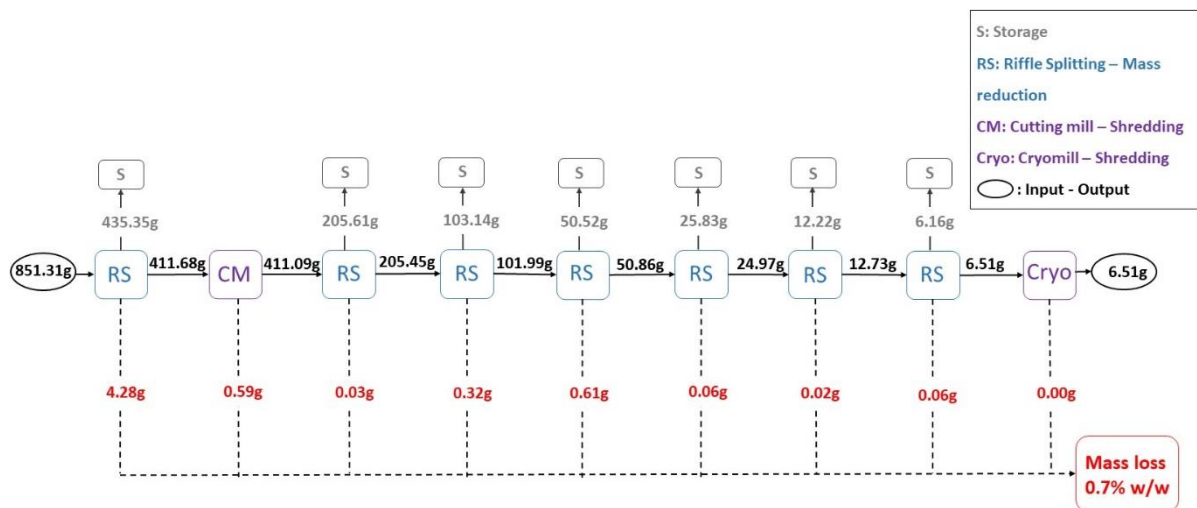


425

426 **Figure 6** shows the loss of sample mass induced at each stage of the sub-sampling process  
 427 (riffle splitting and shredding). We found that the mass loss cannot be zero, even under

428 careful sub-sampling practices conducted by a well-trained operator. It should be noted that  
 429 riffle splitters are composite sub-sampling devices with high performance depending on the  
 430 training skills of operator and the fraction of fines in the sample (Gerlach and Nocerino,  
 431 2003). The loss of sample mass is 0.7% w/w mainly due to the considerable fraction of fines  
 432 in SRF. The first stage of riffle splitting, that took place before primary shredding, induced  
 433 72% of the total mass loss (4.28 g out of 5.97 g) during the sub-sampling. At this stage of  
 434 mass splitting, the range of particle size and the sample mass are maximum making sample  
 435 handling more difficult. Primary shredding contributes nearly 10% to the total mass loss  
 436 which corresponds to 0.07% w/w of total sample mass, whereas no loss occurs during  
 437 secondary shredding. Although 5.97 g out of 851.31 g had zero probability to be included in  
 438 the test portion for analysis violating the fundamental principle of ToS, this amount can be  
 439 considered negligible (Edjabou et al., 2015).

440



441

442 **Figure 6.** Mass flow analysis of SRF sample (ca. 0.85 kg), expressed in grams, during the  
 443 sub-sampling process that consists of consecutive steps of mass reduction (riffle splitting) and  
 444 two shredding stages (by using cutting mill and cryomill) for the obtainment of a test sub-  
 445 sample (ca. 7 g).

446 **3.2.3 Recovery of Cl from cryogenically shredded sub-samples**

447 The recovery (*R*) of Total [Cl] from synthetic mixtures account for a range between 98.0 to  
 448 98.6% (**Table 1**). Even cryogenic shredding of synthetic mixtures did not reach 100% *R* of  
 449 Total [Cl]. Cuperus et al. (2005) estimated the *R* of the Total [Cl] in SRF by means of BC  
 450 combined with ion chromatography (IC), reporting that *R* can reach up to 100% when the  
 451 particle size of the test portion is < 5 mm. Here, the size is lower (0.15 mm), but *R* is not  
 452 100%. Hence, the reason might be the loss of Cl during the bomb ventilation. Ma et al.  
 453 (2010) reported that BC measures less Total [Cl] compared to other analytical methods due to  
 454 potential incomplete combustion in the bomb or Cl loss during bomb ventilation. The  
 455 analytical values of Total [Cl] in SRF sub-samples were corrected based on **Eq. 2.5** by taking  
 456 the average of the recoveries from both synthetic mixtures.

457 **Table 1.** Recovery of Total [Cl] from synthetic mixtures with assigned Total [Cl] resembling  
 458 SRF composition using BC – Palintest Chloridol analytical method.

SRF components	Synthetic SRF 1			Synthetic SRF 2		
	Composition (% w/w) <sup>1</sup>	Assigned Total [Cl] (% w/w)	Observed Total [Cl] (% w/w) <sup>2</sup>	Composition (% w/w) <sup>1</sup>	Assigned Total [Cl] (% w/w)	Observed Total [Cl] (% w/w) <sup>2</sup>
Cellulose	33.81	0		34.33	0	
Xylan	4.02	0		4.05	0	
Lignin	17.08	0		15.02	0	
HDPE	14.70	0		15.02	0	
PP	22.14	0		21.32	0	
PET	7.11	0		7.63	0	
PVC	1.15	53.71		2.64	53.71	
<b>Total</b>	<b>100</b>	<b>0.62</b>	<b>0.61</b>	<b>100</b>	<b>1.42</b>	<b>1.39</b>
<b>Recovery</b> (%) <sup>3</sup>			<b>98.58</b>			<b>98.03</b>

<sup>1</sup>The composition of the mixtures was based on literature evidences (Cuperus et al., 2005; Heikkinen et al., 2004); <sup>2</sup>The value derived from the arithmetic mean of three replicates; <sup>3</sup>Eq. 2.4.

### 459 3.3 Fitness for purpose of sub-sampling plan: Representativeness of test sub-samples

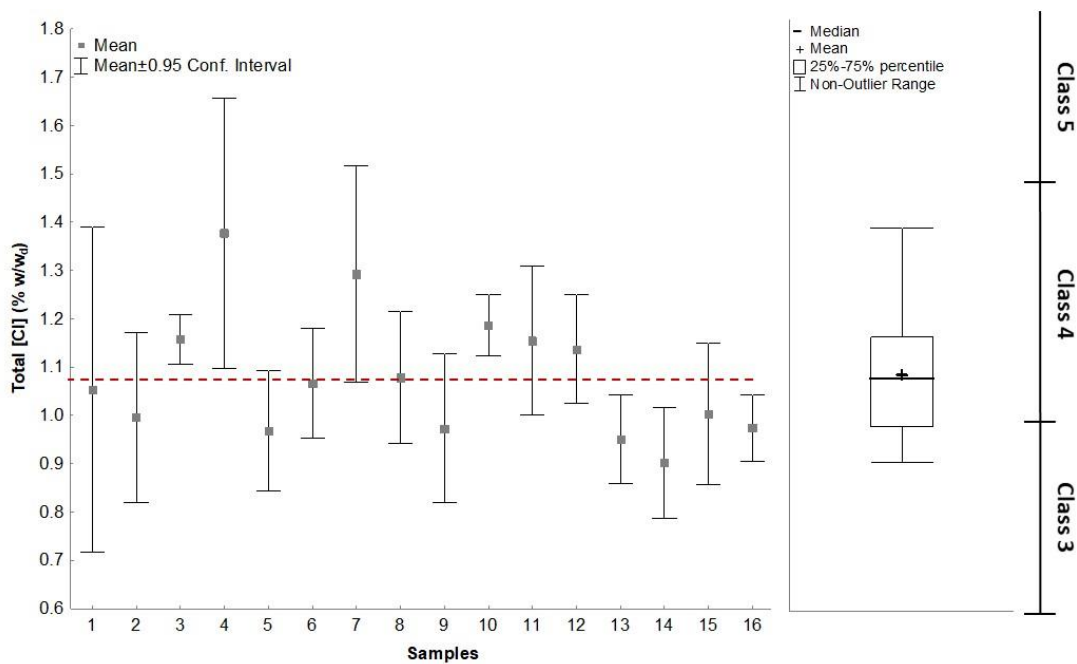
460 **Figure 7** shows the measurement precision (95% confidence interval error bars of mean  
461 values from each measurement) and the dispersion (boxplots) of the 16 test sub-samples  
462 obtained for the determination of Total [Cl] and MC. The dotted red lines indicate the  
463 arithmetic mean of Total [Cl] (1.08% w/w<sub>d</sub>) and MC (16.7% w/w) derived from the 16 test  
464 sub-samples. **Figure 7** provides an overview for the risk to obtain non-representative results  
465 for the determination of SRF properties with higher (e.g. Cl) or lower (e.g. moisture)  
466 variability.

467 Assuming that the average values of 16 measurements represent the actual Total [Cl] and MC  
468 in the initially obtained SRF sample, then the potential to over- or under-estimate the critical  
469 component in the sample is present by drawing one test sub-sample. For example, the  
470 selection of the 4<sup>th</sup> sub-sample with the highest Total [Cl] (1.38 % w/w<sub>d</sub>) would overestimate  
471 the Total [Cl] in the sample (1.08% w/w<sub>d</sub>) by 27.6%, whereas the 14<sup>th</sup> sub-sample with the  
472 lowest value (0.90% w/w<sub>d</sub>) would underestimate the Total [Cl] by 16.4%. However, the  
473 majority of the test sub-samples does not differ from the mean value more than 15% except  
474 from the 7<sup>th</sup> (19.9% overestimation), the 4<sup>th</sup> (27.6% overestimation) and 14<sup>th</sup> (16.4%  
475 underestimation) sub-samples (see **SI.4**).

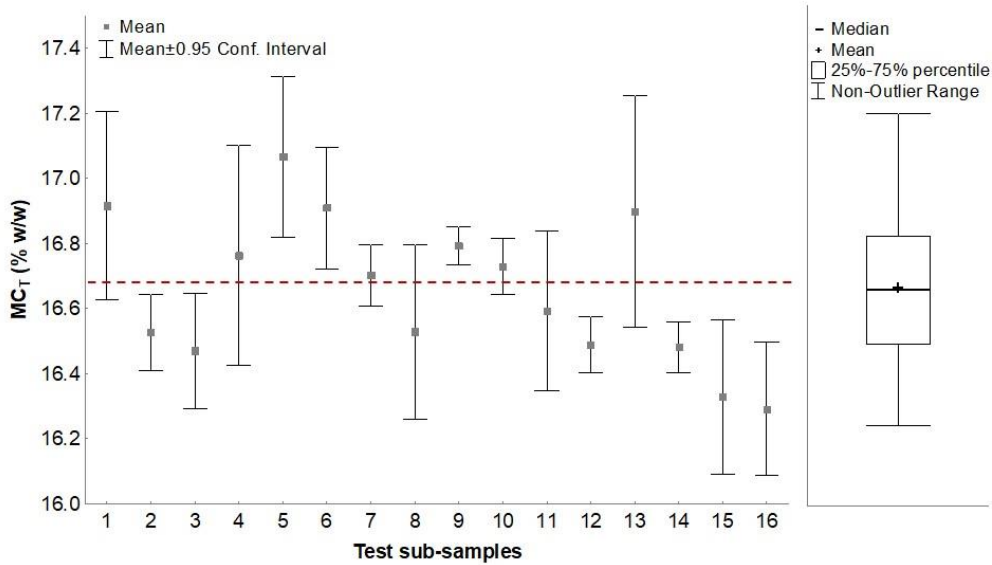
476 The difference between the minimum and maximum value leads to a range of 0.48% w/w<sub>d</sub>,  
477 which is equal with a relative range 44%. This range is comparable with the intervals  
478 between the class codes for the limit values of Cl content in SRF specified by the European  
479 Committee of Standardization (CEN) classification scheme (BS 15359, 2011). For example,  
480 the difference of Total [Cl] between class code 2 ( $\leq 0.6\%$  w/w<sub>d</sub>) and class code 3 ( $\leq 1\%$   
481 w/w<sub>d</sub>) is 0.4% w/w<sub>d</sub> which is lower than the range of Total [Cl] in the 16 test sub-samples,  
482 whereas the difference between class code 3 ( $\leq 1\%$  w/w<sub>d</sub>) and class code 4 ( $\leq 1.5\%$  w/w<sub>d</sub>) is  
483 slightly higher (0.5% w/w<sub>d</sub>).

484 The determination of Total [Cl] in the 16 sub-samples leads to different classification results  
485 amongst the SRF sub-samples: 7 out of 16 sub-samples are designated as class code 3 and 9  
486 out of 16 sub-samples are designated as class code 4 (Figure 7). The different classification  
487 amongst the 16 sub-samples is mainly due to the proximity of mean value (1.08% w/w<sub>d</sub>) in  
488 the border between the class code 3 and class code 4 (1.0% w/w<sub>d</sub>).

A)



B)



489 **Figure 7.** Variability of (A) Total [Cl] and (B) total MC (MC<sub>T</sub>) in SRF sample delivered to  
 490 the laboratory for analysis as calculated by the obtainment of 16 test sub-samples through the  
 491 established sub-sampling protocol.

492 In the case of MC, test sub-samples are more representative. For example, the 5<sup>th</sup> sub-sample  
 493 with the highest MC (17.1% w/w) would overestimate the MC in the sample by 2.5%,  
 494 whereas the 16<sup>th</sup> sub-sample with the lowest MC (16.3% w/w) would underestimate the MC  
 495 by 2.2%. The difference between these values leads to a range of 0.8% w/w, which is equal  
 496 with a relative range of 4.6%.

497 The interval estimations for binomial proportion showed that the total number of  
 498 representative SRF test sub-sample lies between 57 to 93% of total population with 95%  
 499 confidence following the current sub-sampling plan (see **SI.5**). Therefore, the possibility to  
 500 obtain a non-representative test sub-sample for the determination of Total [Cl] is not  
 501 negligible. However, this possibility can be considerably reduced if we obtain and analyse  
 502 two test sub-samples instead. By averaging the analytical results of two test sub-samples (see  
 503 **SI.4**), we found only 5 pairs out of 120 that were non-representative for the determination of

504 Total [Cl]. Specifically, the total number of representative pairs of test sub-samples lies  
505 between 91 to 98% of total population with 95% confidence (see **SI.5**).

506 The properties of SRF should be expressed as intervals and not as individual values due to  
507 high constitutional heterogeneity so that to address the quality assurance in analytical  
508 characterization of solid waste (Chen et al., 2016; Flamme and Ceiping, 2014; Velis et al.,  
509 2010). After the chemical analysis of 16 test sub-samples, Total [Cl] in the SRF sample lies  
510 within a range of 1.01-1.15% w/w<sub>d</sub> and the MC within a range of 16.5-16.8% w/w with 95%  
511 confidence.

512

#### 513 **4 Conclusions**

514 First, by comparing three different sample preparation scenarios through ToS nomographs,  
515 the beneficial role of shredding in the representativeness of test sub-samples for Total [Cl]  
516 determination in SRF was quantified. Primary shredding ( $d_{90} \leq 0.4$  cm) applied after the first  
517 stage of mass splitting resulted in the reduction of sub-sampling uncertainty, expressed as FE,  
518 more than 11 times compared to a non-shredded test sub-sample. The cryogenic, final  
519 shredding stage ( $d_{90} \leq 0.15$  mm) applied to the test sub-sample reduced the uncertainty more  
520 than 3 times compared to primary shredding scenario. The significant contribution of  
521 cryogenic shredding to the reduction of sub-sampling uncertainty is attributed to the  
522 logarithmic increase of uncertainty as the sample mass decreases based on ToS. Therefore,  
523 we here establish that it is a highly recommended sample preparation process step for  
524 chemical analysis of waste-derived materials featuring high inherent heterogeneity. The  
525 configuration settings of cryomill had a negligible effect on the decrease of the overall  
526 uncertainty; therefore, it is feasible to identify an affordable set of operation settings for the

527 cryogenic shredding, for example with low number of grinding cycles, reducing processing  
528 time and liquid nitrogen consumables cost.

529 Second, practices related to shredding that could introduce bias were assessed as negligible  
530 with careful execution of the suggested sub-sampling plan. Specifically, potentially incorrect  
531 sub-sampling practices were demonstrated here to be minimised: (1) shredding did not affect  
532 the MC, assuring the validity of analyte determination on a dry reporting basis; (2) the loss of  
533 sample mass was negligible (0.7% w/w) – but, the operator’s experience is crucial and mass  
534 loss could be higher if attention is not paid to best practice; and (3) the recovery of Total [Cl]  
535 from cryogenically shredded test portions of artificial SRF comprising a mixture of reference  
536 materials reached 98.3% - an acceptable level of analytical error.

537 Third, experimental results showed that the established sub-sampling plan lead to  
538 representative analytical results related to the determination of MC (relative range < 4.6%),  
539 an analyte with relatively low variability. However, in the case of Total [Cl], obtaining one  
540 test sub-sample entails the risk of incorrect classification of SRF. Less than 20% of total  
541 population of test sub-samples were not representative, assessed as exceeding the 15% upper  
542 limit suggested by the literature. However, the selection of this limit value is arbitrary as  
543 there is no relevant comparative evidence in the solid waste management sector. The  
544 possibility of obtaining a non-representative test sub-sample under the current sub-sampling  
545 plan lies between 7 - 43% (95% confidence), whereas drawing and averaging two test sub-  
546 samples instead, considerably reduces that risk (2 - 9% with 95% confidence). However, the  
547 cost and time of sub-sampling and analysis would be respectively increased.

548 Experimental results showed that the established sub-sampling plan can result in  
549 representative sub-samples (13 out of 16) with uncertainty less than 15%, whereas the  
550 maximum overestimation observed in the 4<sup>th</sup> test sub-sample (27.6%) did not exceed the

551 theoretical ToS calculations (FE: 33.5%). These findings support the need for exploring the  
552 suitability of the ToS-based formula applied for the determination of analytes with  
553 considerably variable concentrations amongst the particles/components of waste-derived  
554 materials.

555 The current sub-sampling scheme was conducted by using and adhering to optimal, yet  
556 practicable and affordable sampling practices and equipment, which is verified by the ability  
557 of such laboratory set up and operational regime to render satisfactory measurements.  
558 Therefore, the suggested sub-sampling plan can be used as a fitness for purpose approach to  
559 minimise potential bias, and could be incorporated in the relevant SRF sample preparation  
560 standards (BS 15413, 2011; BS 15443, 2011). To this, a round robin verification test would  
561 be needed.

562

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567

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572

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