

1 **Evolution of organic matter in a full-scale composting plant for the treatment of sewage**
2 **sludge and biowaste by respiration techniques and pyrolysis-GC/MS**

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Pre-print of: Font, X. et al. "Evolution of organic matter in a full-scale composting plant for the treatment of sewage sludge and biowaste by respiration techniques and pyrolysis-GC/MS" in *Bioresource technology* (Ed. Elsevier), vol. 102, issue 6 (March 2011), p. 4536-4543. The final version is available at DOI 10.1016/j.biortech.2010.12.108

18 **Abstract**

19

20 A full-scale composting plant treating, in two parallel lines, sewage sludge and the
21 source-selected organic fraction of municipal solid waste (OFMSW or biowaste) has been
22 completely monitored. Chemical routine analysis proved not to be suitable for an adequate
23 plant monitoring in terms of stabilization and characterization of the process and final
24 compost properties. However, dynamic respiration index demonstrated to be the most feasible
25 tool to determine the progression of the degradation and stabilization of organic matter for
26 both sewage sludge and OFMSW lines. Both lines exhibited an important degree of
27 stabilization of organic matter using rapid and cumulative respiration indices. Pyrolysis-
28 GC/MS was applied in the most important inputs, outputs and intermediate points of the plant.
29 It proved to be a powerful tool for the quantitative characterization of molecular composition
30 of organic matter present in solid samples. A full characterization of the samples considered is
31 also presented.

32

33

34 **Keywords:** Sewage sludge; Biowaste; Composting; Respirometry; Pyrolysis-GC/MS.

35 **1. Introduction**

36

37 According to the European legislation (Directive 99/31/EC) the total amount of
38 organic matter contained in source-separated collection of the organic fraction of municipal
39 solid waste (OFMSW) and the municipal solid waste (MSW) disposed in landfills must be
40 considerably reduced. Many studies have shown that MSW contains a high proportion of
41 organic materials, from 50 to 65% (Tchnobanoglous et al., 1993) and OFMSW from 80 to
42 95%. The need to reduce the biodegradable fraction allocated in landfills has favoured the
43 development of composting as useful biotechnology for transforming organic waste into
44 suitable agricultural products (Senesi and Brunetti, 1996).

45 In addition to the problem associated of MSW a large volume of municipal wastewater
46 are worldwide generated every year. Wastewater treatment requires both the management and
47 treatment of the produced sludge that represents more than 50% of the construction and
48 operating costs of wastewater treatment plants (Metcalf and Eddy, 2003). The application of
49 sewage sludge to soil is a current practice for returning valuable nutrients and organic matter
50 to reclaim degraded soils. However, sewage sludge should be stabilized and hygienized before
51 its application on agricultural soil and composting technologies can effectively decompose
52 organic matter into a stable end product (Gea et al., 2007).

53 In general, the stability of these products derived from sewage sludge and
54 OFMSW/MSW treatments plants should be considered prior to their soil applications.
55 Stability is defined as the extent to which readily biodegradable organic matter has
56 decomposed (Lasaridi and Stentiford, 1998). The analysis of a waste treatment plant requires
57 a reliable measure of the biological activity of the organic matter easily degradable (Lasaridi
58 and Stentiford, 1998). The application of respiration indices has proven to be very useful in
59 the monitoring of waste treatment plants and for the prediction of the stability of final

60 products such as compost (Adani et al., 2006; Barrena et al., 2009; Ponsá et al., 2010; Pognani
61 et al., 2010). Among the biological methodologies suggested, aerobic respiration indices have
62 been highlighted as the most suitable tool for the stability assessment (Barrena et al., 2009;
63 Wagland et al., 2009). Indeed, it has been used in recent works to analyze the performance of
64 different treatment processes (Ponsá et al., 2010), for instance Pognani et al. (2010) carried
65 out the complete respirometric monitoring of a combined anaerobic/aerobic municipal source-
66 separated waste treatment plant.

67 High levels of respiration are typical of non-stable materials, so their application may
68 immobilize inorganic nitrogen in soil, increase the production of phytotoxic compounds
69 (Senesi et al., 1996), reduce plant growth and produce unpleasant odours.

70 Composting is an aerobic thermophilic process, which requires oxygen to stabilize the
71 organic wastes and an optimal moisture content for the microorganisms development (Haug,
72 1993). The common control variables at compost facilities are temperature, oxygen, moisture
73 and porosity. The final product, the compost, is a stable, sanitized and humus-like material
74 (Haug, 1993). Composting stages are common for all composting systems. Initially high
75 microbial activity produces heat that causes an increase of temperature rapidly to the
76 thermophilic range (above 45°C). Usually temperature increase up to approximately 60°C and
77 remains there for several weeks depending on the size of the system and the composition of
78 raw materials. After the rapidly degradable components are consumed, heat generation
79 gradually declines during the maturation stage. At the end of this stage, the material is no
80 longer self-heating, and the finished compost is ready for use (Haug, 1993).

81 Often the application of composting to some organic wastes does not result as
82 expected because these materials do not achieve the biological requirements of C/N ratio to be
83 successfully composted (Charest and Beauchamp, 2002; Sánchez, 2007). It is known that an
84 optimal C/N ratio is required to perform the composting process because an insufficient

85 content of nitrogen causes a limitation of cellular growth (increased time of efficient
86 composting process). Furthermore a high concentration of nitrogen causes ammonia
87 emissions and consequently generation of offensive odours, atmospheric pollution (Pagans et
88 al., 2006) and a loss of fertilizer value of the final compost. Haug (1993) proposed an
89 optimum C/N ratio value between 15 to 30. Other authors reduced this range between 25 to 30
90 (Huang et al., 2004; Zhu, 2007). Normally the assessment of C/N ratio in solid samples has
91 been determined on organic matter through the determination of total organic carbon (TOC)
92 and total Kjeldahl nitrogen (NTK). In general, the C/N ratio, as an indicator of composting
93 process, has been determined assuming that both nutrient sources are biodegradables (Huang
94 et al., 2004; Zhu, 2007; Sánchez, 2007). However the biodegradable C/N ratio should be
95 based on total biodegradable organic carbon (BOC) content because the main part of nitrogen,
96 in organic samples, is present in protein-like molecules that are easily biodegradable (Haug,
97 1993), but a large part of non-biodegradable carbon source is present (Sánchez, 2007). BOC
98 can be also divided into two fractions i.e., readily and slowly biodegradable (Trémier et al.,
99 2005; Fernández et al., 2008). Organic samples with high fiber content such as lignin could
100 have a critical influence in the composting process due to its slow biodegradation as carbon
101 sources. The first references to the approach of a direct determination of the BOC in solid
102 wastes using the cumulative CO₂ production were proposed by Komilis and Ham (2006) and
103 Sánchez (2007).

104 During composting, organic matter is transformed through the successive activities of
105 different groups of microorganisms to more stable complex of organic compounds
106 (Hernández et al., 2006). Pyrolysis GC/MS is a technique already used for the characterization
107 of organic matter and its humic fraction (Genevini et al., 2002; 2003) and it could be more
108 revealing on chemical transformation than techniques that require sample manipulation
109 (Ceccanti et al., 2007). Its major advantage is that it can be applied directly to the organic

110 material to be analyzed with no prior extraction being necessary (Hernández et al., 2006). In
111 addition, the technique is fast and reproducible because it does not need any chemical
112 manipulation (Ceccant et al., 2007). Pyrolysis GC/MS has been applied to several materials
113 like digested sewage sludge, mulched soil and agricultural soil (Hernández et al., 2006;
114 Ceccanti et al., 2007). However, to our knowledge, it has never been applied to follow the
115 evolution of the organic matter in a complex full-scale waste treatment plant as the one
116 described in this work.

117 The aim of the study undertaken in this waste treatment plant was focused on
118 monitoring and comparing the OFMSW and sewage sludge lines in terms of respirometric
119 indices, biological organic carbon and changes of molecular composition of organic matter
120 using the pyrolysis GC/MS technique in a complete composting process.

121

122 **2. Material and methods**

123

124 *2.1 Analytical methods*

125 Analytical methods were carried out on a representative sample (approximately 40 kg)
126 obtained by mixing four sub-samples (10 kg each) taken from different points of the material.
127 Samples derived from the OFMSW line were ground to 15-20 mm particle size to reduce the
128 dimension of the original materials. The samples were frozen at -18°C within 12 hours after
129 sampling. Before every analysis samples were thawed during 24 hours at room temperature.
130 These representative samples were used to carry out the entire set of analytical tests. pH,
131 Electrical Conductivity (EC), Total Solid (TS), Volatile Solids (VS), Total Organic Carbon
132 (TOC), Total Kjeldahl Nitrogen (NTK) and N-NH₃ (determined directly in the plant on fresh
133 material) were determined according to the standard procedures recommended by the Test
134 Methods for the Examination of Composting and Compost (TMECC) (USDA, 2001). All tests

135 were run in triplicates and the results are presented as the average followed by the standard
136 deviation.

137

138 *2.2 Plant characteristics*

139 The composting plant studied in this work was located in the province of Girona
140 (Catalonia, Spain) and the sampling was carried out during the summer of 2009. This facility
141 treats around 6000 Mg y⁻¹ of OFMSW coming from a street bin collection system, 5500 Mg y⁻¹
142 of sewage sludge and 1200 Mg y⁻¹ of coffee roasted waste (CRW), which is used in
143 combination with sewage sludge. The plant used also 400 Mg y⁻¹ of wood chips as a bulking
144 agent and produced respectively 1500 Mg y⁻¹ of compost of each treatment line. The OFMSW
145 line generated 1000 Mg y⁻¹ of refuse that was landfilled. The plant consists of an area suitable
146 to discharge sewage sludge and OFMSW, seven composting tunnels completely closed and
147 monitored and a maturation area (only for the OFMSW line). Composts obtained from both
148 lines were stored in the plant before its commercialization. Compost obtained from OFMSW
149 line was suitable for agricultural use and compost obtained from sewage sludge line was used
150 only for civil works.

151 Samples were collected from the most significant points of the two lines of the facility.
152 The samples selected for this study were: raw material (both lines), input mixture of tunnels
153 (both lines); output materials of tunnels (both lines), output material at the end of maturation
154 phase (OFMSW line), rejected material of refining compost process (OFMSW line), final
155 compost (both lines) and CRW (sewage sludge line).

156

157 *2.3 OFMSW line*

158 Input material (OFMSW: TS of 400.8 ± 33.2 g kg⁻¹ wet weight (w.w.) and VS of 771.7
159 ± 62.4 g kg⁻¹ TS) as received at the plant was mixed with wood chips, used as bulking agent,

160 at volume ratio 1:2 (OFMSW : wood chips) using an industrial homogenizer. After mixing,
161 the material was introduced in the composting tunnels. Tunnels dimension were 15x5x5 m
162 (length, width, height) and each tunnel was filled to 80% of its maximum capacity (around
163 107 Mg). The decomposition phase took place in the tunnels under controlled conditions of
164 aeration and watering (leachate produced during the decomposition of organic matter matrix
165 was used to preserve the moisture content within the correct range: between 70 and 50%). The
166 process parameters such a temperature, moisture content and oxygen content were controlled
167 automatically. The residence time of the mixture in the tunnel was approximately two weeks.
168 After the decomposition phase, the tunnels were cleared out and the resulting material was
169 screened with a mesh trommel of 100 mm and it was sent to the maturation area. Maturation
170 phase was performed in aerated static piles. Prior to set up the maturation pile, an absorbent
171 layer mainly made of wood chips was placed over the perforated pavement to ensure the
172 correct distribution of air through the mass. Leachate produced during the maturation phase
173 was collected and treated at the nearby wastewater treatment plant (WWTP). These piles were
174 watered according to the evolution of moisture content during the process. During the first
175 three days of maturation air was provided continually. Following this period, the pile aeration
176 system was intermittent with 15 minutes of aeration followed by 15 minutes without aeration.
177 The total maturation stage lasts for approximately eight weeks. To obtain the final compost,
178 the matured material was screened to 10 mm by a trommel and refined using a ballistic
179 separator. The final compost (TS of $751.4 \pm 3.0 \text{ g kg}^{-1} \text{ w.w.}$ and VS of $637.6 \pm 3.6 \text{ g kg}^{-1} \text{ TS}$)
180 produced was stored in the plant before commercialization.

181 Wood chips not degraded during the process were separated and re-used. Refuse (TS
182 of $809.9 \pm 32.2 \text{ g kg}^{-1} \text{ w.w.}$ and VS of $460.2 \pm 13.2 \text{ g kg}^{-1} \text{ TS}$) generated during the screening
183 at 100 and 10 mm was landfilled. Extra production of leachate was collected and treated at the
184 nearby WWTP. Treated water used in the composting process comes from the same WWTP.

185

186 *2.4 Sewage sludge line*

187 Fresh sewage sludge (TS of $179.8 \pm 3.2 \text{ g kg}^{-1}$ w.w. and VS of $757.0 \pm 1.1 \text{ g kg}^{-1}$ TS)
188 came directly from the nearby WWTP, it was stored in a tank and successively mixed at
189 volume ratio 3:1 (v/v) with CRW (sewage sludge : CRW) (TS of $519.9 \pm 3.2 \text{ g kg}^{-1}$ w.w. and
190 VS of $987.6 \pm 0.9 \text{ g kg}^{-1}$ TS) used as a co-substrate. At the same time wood chips were added
191 as a bulking agent at volume ratio of 1:4 (v.v., sewage sludge + CRW : wood chips). A correct
192 homogenization was provided using an industrial homogenizer. Composting tunnels were
193 filled with this mixture and composting process took place under controlled conditions of
194 aeration and watering. The estimated residence time was approximately three weeks and the
195 process parameters like temperature, moisture content and oxygen content were controlled
196 automatically. After the tunnel phase the material resulting was screened with a mesh trommel
197 of 10 mm to obtain the final compost (TS of $696.7 \pm 3.7 \text{ g kg}^{-1}$ w.w. and VS of $769.0 \pm 39.7 \text{ g}$
198 kg^{-1} TS). Wood chips not degraded were separated and re-used. The compost was stored into
199 the plant until commercialization.

200

201 *2.5 Respirometric tests*

202 Respirometry can be used to determine the biological activity in a sample if the assay
203 is performed under optimal and controlled conditions (Adani et al., 2001). A respirometric
204 assay requires optimal moisture content, oxygen content and appropriate temperature. The
205 procedure established in this study for the determination and calculation of dynamic
206 respiration index (DRI), cumulative respiration activity after 4 days (AT_4) and cumulative
207 respiration index until ultimate time (AT_u) was based on previous works by Adani et al.
208 (2006), Sánchez (2007) and Pognani et al. (2010). DRI and AT_4 were recommended in the
209 Second Draft of the Working Document on the Biological Treatment of Biowaste as

210 parameters for the estimation of the stability of compost (European Union, 2001) and were
211 already used for the monitoring of other waste treatment plants (Ponsá et al., 2010; Pognani et
212 al., 2010). Microbial respiration was measured as O₂ consumption and CO₂ production in a
213 self-made dynamic respirometer (Ponsá et al., 2010; Pognani et al., 2010) based on the
214 methodology described by Adani et al. (2006).

215 In this paper respirometric indices were also expressed in mg of CO₂ produced per g of
216 TS in order to calculate the Biodegradable Organic Carbon (BOC) content. During the
217 respirometric tests the aerobic degradation of organic matter caused the production and
218 emission of CO₂ that was measured by a system of sensors. Knowing that one mol of CO₂
219 equal one mol of C, the BOC can be calculated from the final cumulative CO₂ emissions and
220 the molecular weight ratio between CO₂ and C. The time required for the ATu assay was in
221 function of the instantaneous measure of Oxygen Uptake Rate (OUR) that must be below of
222 the 5% of the maximum OUR achieved during the test. At the end of the assay it can be
223 considered that all the readily and almost all the slowly biodegradable organic matter were
224 consumed (Sánchez, 2007).

225

226 *2.6 Pyrolysis-GC/MS*

227 Pyrolysis was performed with the Pyroprobe 5100 (SRA Instrument, Cernusco sul
228 Naviglio, Italy) directly connected to a CG/MS system Agilent 5792 equipped with a fused
229 silica capillary column (5MS 30 m x 250 µm x 0.25 µm). The detector consisted of an Agilent
230 5975C mass selective detector (EI at 70 eV). The analyses were performed applying the
231 method reported by Dignac et al. (2005) partially modified. Approximately 0.2 mg of sample
232 was loaded in a quartz tube in the pyrolysis unit. The pyrolysis analysis was performed
233 starting from 625°C for 50 seconds. The final temperature was achieved at a rate of 20°C min⁻¹
234 and the end temperature of 650°C was maintained for 1 min. The pyrolysis product was then

235 transferred to the GC system through a split injector operated in splitless mode using He as
236 carrier. The temperature program of the GC oven was set at the start temperature of 30°C with
237 an increase of temperature at 2°C min⁻¹ from 30°C to 320°C, while the column was
238 maintained at this temperature for 15 min. Compounds were identified based on their mass
239 spectra, GC retention time and comparison with library mass spectra (NIST).

240

241 **3. Results and Discussion**

242

243 *3.1 Chemical and respiration properties*

244 The chemical composition of the samples studied is presented in Table 1. Regarding
245 the OFMSW line the input samples are characterized by an acid pH (5.12) as a consequence
246 of the anaerobic processes occurring in the plastic bags in which the material is stored before
247 its collection (Adani et al., 2006). The addition of the bulking agent (normally recirculated) to
248 improve the porosity does not change the value of TS and VS, only the DRI_{24h} decrease 8.3%.
249 At the end of the tunnel phase, the DRI_{24h} and TOC of the organic material decrease
250 respectively 48.5% and 17.5% indicating that the decomposition phase took place correctly.
251 TS increase 22.3% and VS remained approximately the same, due to the effect of
252 concentration of the bulking agent not degraded. Before the maturation process (aerated static
253 pile) bulking agent and inert materials (such as plastic, glass and metals) are removed by
254 sieving the organic matrix using a 100 mm mesh trommel. At the end of the maturation
255 process DRI_{24h} dropped until 0.8 g O₂ kg TS⁻¹ h⁻¹ (52.9% decrease), VS decrease 17.1% and
256 TS increase 25.5%. To obtain the final compost the organic material coming from the
257 maturation area was sieved in a mesh trommel of 10 mm. The concentration of organic
258 fraction in the final compost caused an increase of DRI_{24h} of 11.1% (0.8 to 0.9 g O₂ TS⁻¹ h⁻¹).
259 However bulk and refined compost presented a low DRI_{24h}, indicating that it was a stable

260 material. This phenomenon has been observed in other experiences when refining compost
261 from the OFMSW (Pognani et al., 2010). Compost refuse (Table 1) had a value of DRI_{24h} of
262 30.8% higher than the final compost. This increase of DRI_{24h} can be explained due to the
263 introduction of semi-composted organic matter refuse (derived from the first sieving at 100
264 mm at the end of tunnel phase) in the compost reject from the refining phase.

265 In relation to the sewage sludge line, the raw sludge was characterized by a high
266 moisture content (82%), high NTK content ($64 \text{ g N kg TS}^{-1}$) and a high respirometric activity
267 ($7.1 \text{ g O}_2 \text{ TS}^{-1} \text{ h}^{-1}$) (Table 1). Before filling the tunnels, raw sludge was mixed with CRW
268 (3:1) as a co-substrate used to reach a more suitable C/N ratio (from 6.3 to 16.9) and wood
269 chips (1:4) to improve porosity. This also caused a drop of: moisture content (62.9% less than
270 fresh sewage sludge), total nitrogen (57.8%) and respirometric activity (74.7% of DRI_{24h}).
271 Composting process caused a further drop of 30% of moisture content and a high reduction in
272 the respirometric activity (88.9%). At the end of the composting process (tunnel phase) the
273 bulking agent not degraded was separated from the organic matrix and reused. The compost
274 obtained (Table 1) had a higher DRI_{24h} (50%) than before due to the effect of concentration of
275 organic matter, a lower content of VS about 10% and an accumulation of total nitrogen of
276 36.7%. Final DRI_{24h} ($0.4 \text{ g O}_2 \text{ TS}^{-1} \text{ h}^{-1}$) indicated that the sewage sludge compost was very
277 stable.

278 Final composts obtained from both treatment lines were particularly rich in N-NH_3
279 ($2.8 \pm 0.3 \text{ g kg TS}^{-1}$ and $6.9 \pm 0.2 \text{ g kg TS}^{-1}$ from OFMSW treatment line and sewage sludge
280 treatment line, respectively). For this reason a detailed study of biodegradable organic carbon
281 (BOC) and nitrogen content was undertaken. To establish the real quantity of BOC of the
282 samples, ATu were performed using the method as described before. In Table 2 the values of
283 ATu in terms of O_2 consumed and CO_2 emitted for the samples of the main steps of both lines
284 are presented. Respirometric indices decrease during the main phase of treatment confirming

285 the efficiency of both treatment lines (Pognani et al., 2010). Using the quantity of CO₂
286 emitted, the real value of BOC for each sample could be calculated (Table 2). Results showed
287 that the value of BOC are always lower than TOC, since C/N and BOC/N ratios were
288 calculated using the N_{tot} content (NTK plus N-NH₃) (Haug 1993). Given that composting is a
289 biological process the C/N ratios calculated using the chemical methodology are not suitable
290 for this type of biological tests, being the ratio BOC/N the one that should be used for the
291 characterization of an organic waste.

292 The differences found between C/N and BOC/N ratio were very high (especially for
293 sewage sludge treatment line); BOC/N was lower on average of three times of C/N values.
294 The results, shown in Table 2, indicated that the samples of the OFMSW line had a BOC/N
295 ratio between 2 to 13. The BOC/N value of sewage sludge line was within 1 to 3. The BOC/N
296 ratio found for fresh OFMSW was 12.9 similar to that reported by Kayhanian and
297 Tchobanoglous (1992). All the values of BOC/N were lower than 13, which could cause an
298 important loss of nitrogen during the composting process in the form of ammonia (Pagans et
299 al., 2006) and provoke environmental contamination and odour problems. Sewage sludge had
300 a very low BOC/N ratio (Table 2) due to the usual high nitrogen content (fresh sewage sludge:
301 71 g kg TS⁻¹). Moreover, in this facility, CRW was added to the sewage sludge as a co-
302 substrate before starting the composting process to include an extra input of carbon source
303 (VS: 988 g kg TS⁻¹) with a low content of nitrogen content (N_{tot}: 18 g kg TS⁻¹). Unfortunately,
304 none sample of this mixture is available for technical reasons. Also a great quantity of bulking
305 agent (1:4 v.v.) was added to the mixture before starting the composting process. As expected
306 C/N and TOC values increased until 16.9 and 507 g kg TS⁻¹ respectively (Table 2).

307 In accordance with the results presented in Table 2, total BOC can be directly related
308 with the biological stability of the material. In fact, a low respirometric activity (in terms of
309 consumption of O₂ or CO₂ emitted) corresponds to a low BOC value.

310 A new process index (TOC/BOC), useful to indicate the state of biodegradation of the
311 organic matter of the samples coming from a waste treatment plant, can be proposed (Table
312 2). Not biodegraded samples (fresh sewage sludge and fresh OFMSW) presented a low ratio
313 TOC/BOC (around 2), due to that the quantity of BOC is still high. When the biological
314 treatment took place the quantity of BOC decreases much more than TOC and the value of the
315 ratio TOC/BOC increases. The TOC/BOC ratio increase rate will change according to the
316 biodegradability of the material composted and the effectiveness of the process. Thus, in the
317 sewage sludge line the ratio increased from 2.4 to 10.5 after tunnel decomposition whereas in
318 the OFMSW line, the increase was from 1.8 to 3.8. Biodegraded material (like compost) had a
319 low value of BOC and a respective high value of ratio TOC/BOC indicating that the
320 remaining organic matter is composed mainly of long term biodegradable organic matter or by
321 recalcitrant organic molecules.

322 To reduce the time of analysis and find a rapid method to calculate the values of BOC,
323 a potential function between TOC/BOC index versus DRI_{24h} and AT_4 values was found
324 (Figure 1). Curve equations showed a good R square for each respirometric test (0.88 and 0.87
325 using AT_4 and DRI_{24h} respectively). In Figure 1 only six points were used to calculate the
326 curve equations so, in order to obtain a more representative curve, other different samples
327 would need to be processed in the future. Also, from the BOC analysis of a broad number of
328 different wastes, it should be interesting to evaluate the BOC value at different test times to
329 determine if it is possible to report a valid BOC value in a shorter period.

330 Further research should be performed on this ratio (TOC/BOC), as it could be used as
331 an indicator of the waste biodegradability, similarly to the Chemical Oxygen Demand/
332 Biochemical Oxygen Demand (COD/BOD) ratio used in water characterization. Furthermore,
333 the increasing rate TOC/BOC during the process should be used as an indicator to compare
334 different technologies.

335

336 *3.2 Pyrolysis GC/MS*337 *3.2.1 OFMSW line*

338 From the pyrograms of the samples studied a large number of molecules can be
339 identified (278-199 molecules) (Table S1-supporting information). In order to interpret the
340 results obtained, molecules were grouped on the basis of their chemical characteristics. A total
341 of 16 classes were identified: fatty acids, cycle-alkanes, alkanes, cycle-alkenes, alkenes,
342 alcohols, ketones, cycle-ketones, aldehydes, furans, isoprenoids, alogenurs, nitrogen
343 compounds, pyran compounds, silanes and aromatic molecules.

344 The raw material (OFMSW+wood chips) showed a high content of aliphatic
345 hydrocarbon molecules (Table S1-supporting information, Table 3). Alkenes (that account for
346 the 28% of the pyrogram) were represented mainly by 1-alkene and 2-alkene compounds (C7-
347 C17) that represented the pyrolysis products of bacteria lipids (Dignac et al., 2006; González-
348 Vila et al., 2009). On the other hand, alkane compounds (8.9% of the pyrogram), that showed
349 the same range of C number of the alkenes (C7-C17), represented the pyrolysis product of
350 lipids coming from the organic matter of waste (Dignac et al., 2006). Both cyclo-alkanes (C4-
351 C16) and cyclo-alkenes (C5-C6) that only account for a small percentage of the pyrograms
352 (respectively 3% and 1.6%) come from cyclization phenomena during the pyrolysis of
353 triglycerides (Alencar et al., 1983). The small molecules of fatty acids, such as acetic acid
354 found in the pyrogram, probably comes from bacteria (Dignac et al., 2005).

355 The N compounds class (11.3 % of pyrogram) (Table 3) was mainly constituted by
356 pyridine and pyrrole molecules, suggesting their origin from both microbial proteins and
357 vegetables and animal proteins contained in the organic fraction of waste (i.e. food) (Dignac
358 et al., 2005; González-Vila et al., 2009).

359 Furan molecules were less represented in the pyrogram with respect to other organic
360 compound classes (1.5 % of the pyrogram). These molecules came from the polysaccharides
361 fraction of microorganisms. On the other hand, cyclo-ketones (mainly of the cyclopent-1-one
362 derivates) and pyrans molecules indicated the presence of polysaccharides fraction from
363 vegetal material (cellulose) degraded and not degraded, respectively (Dignac et al., 2005).

364 Aromatic molecules that represented the most abundant compounds in the pyrogram
365 can be divided into sub-classes on the basis of the different chemical properties and origin i.e.,
366 methoxy-phenols and methyl ketones (aromatic molecules from lignin) (González-Vila et al.,
367 2009), benzene ethenyl (aromatic molecules from plastic) (Dignac et al., 2005), and benzenes
368 and phenols (aromatic molecules from unknown origin) (Table S1- supporting information)
369 (Dignac et al., 2006; González-Vila et al., 2009). The lignin presence indicated the presence
370 of ligno-cellulose fraction in the starting mixture (wood chips and vegetal material).
371 Nevertheless, the low content of lignin-derived molecules (0.6 % of the pyrogram) identified
372 in the program was due to both the composition of the OFMSW and also, to the low
373 resolution capability of the columns adopted (apolar phase) for these molecules, that enhanced
374 the resolution of apolar compounds (lipids) (Dignac et al., 2006).

375 The isoprenoids molecules class was attributed to the terpenes fraction derived from
376 vegetable material contained in the organic fraction of waste (Dignac et al., 2005; González-
377 Vila et al., 2009).

378 Poliaromatic molecules, i.e. naphthalene, alkylnaphthalene and indene were probably
379 originated from poly-aromatic molecules such as humic-like substances (Schulten and
380 Gleixner, 1999).

381 Classes of alcohols and aldehydes are not well defined although literature reported that
382 they could come from lignin and/or lipids.

383 Finally, plastic derived molecules (benzene ethynil), silane and alogenure compounds,
384 that were found in a very small amount, were due to the presence of chemical and others
385 impurities (like plastics) in the OFMSW.

386 Composting process did not modified significantly the chemical composition of the
387 pyrograms (Table 3), except for the alkene class, which showed in the composted materials
388 the presence of dienes (pentadiene and hexadiene) that represented the pyrolysis products of
389 partially degraded triglycerides (Alencar et al., 1983). From a quantitative point of view the
390 modification of the organic compounds by composing the organic material could be followed
391 by studying the specific pyrograms (Table 3). During the composting process there was a
392 progressively reduction of the lipid and polysaccharides fractions. In particular, the
393 polysaccharides from plants (cycle-ketones) showed the highest reduction, while the same
394 fraction coming from microorganism increased. At the same time, the protein content
395 increased because of a concentration effect as a consequence of the high rate degradation of
396 the other fractions. The proteins class increase could be attributed to the higher presence of
397 bacteria, such it is suggested by the increase of the polysaccharide fraction. Lignin-like
398 fraction did not showed a significant increase indicating that degradation was compensated by
399 the concentration effect due to degradation of other molecules. Moreover, the fact that poly-
400 aromatic fractions increase during composting could indicate that lignin-like molecules did
401 not degrade but were humified (Adani et al., 1997).

402 The compost sieved after maturation did not permit discussing the evolution of the
403 organic matter with respect to the raw material as the composition was artificially altered.
404 However, the comparison between the raw material and the final compost showed a lower
405 presence of lipid and polysaccharides and a higher content of recalcitrant fractions as
406 previously reported (Adani et al., 1997).

407

408 3.2.3 Sewage sludge line

409 The pyrograms of the sewage sludge mixture were very similar to those of OFMSW
410 mixture composting process, from both quantitative (number of pyrogram compounds, i.e.
411 252-161) and qualitative (compounds classes) point of view. Anyway the pyrolysates of
412 sewage sludge mixture indicated a higher presence of proteins, probably due to presence of
413 proteins in sewage sludge (Dignac et al., 2009), lignin and polysaccharides, due to the higher
414 presence of lignocelluloses with respect to the OFMSW (Table 3) and due to the added of
415 CRW in the mixture. In general, sewage sludge contains a high amount of lipids (Rèveillè et
416 al., 2003), which probably were diluted in the mixture because of the presence of bulking
417 agent and CRW.

418 During the composting process (before the final sieving phase) a reduction of both
419 proteins and lipid contents occurred because of degradation process (Table 3). Polysaccharide
420 fraction also showed a decrease during composting, as a result of the degradation of the
421 vegetable fraction, being the fraction of polysaccharides of microbial origin more abundant.
422 However, the increase of lignin compounds suggested a concentration effect of the more
423 recalcitrant fraction of the organic matter because of the degradation of labile fractions.

424

425 4. Conclusions

426

427 ATu was a suitable assay to calculate the BOC/N and correct the C/N ratio in organic
428 mixtures avoiding the deficiency or excess of nitrogen. Correct definition of BOC/N ratio
429 instead of C/N ratio should be the key to obtain optimal mixtures to carry out successfully a
430 biological treatment such as a composting process. TOC/BOC ratio could be a new process
431 index to estimate the real state of biodegradation of the organic samples during the different
432 treatment phases in a complex waste treatment plant. Pyrolysis GC/MS can be a good

433 opportunity to investigate the change of the molecules of organic matter after every process
434 step.

435

436 **Acknowledgements**

437 Financial support was provided by the Spanish Ministerio de Educación y Ciencia
438 (Project CTM2009-14073-C02-01). Michele Pognani has a pre-doctoral scholarship from the
439 Spanish Ministerio de Ciencia e Innovación (Ref. BES-2007-17634). Raquel Barrena was
440 supported by Juan de la Cierva post doctoral contract from the Spanish Ministerio de Ciencia
441 e Innovación (Ref. JCI-2008-1989).

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Tables

Table 1: Chemical characterization of samples from the OFMSW and sewage sludge treatment line.

| Sample | pH | EC (mS cm ⁻¹) | TS (g kg ww ⁻¹) | VS (g kg TS ⁻¹) | NTK (g kg TS ⁻¹) | N-NH ₃ (g kg TS ⁻¹) | N _{tot} (g kg TS ⁻¹) | TOC (g kg TS ⁻¹) | C/N | AT ₄ (g O ₂ kg TS ⁻¹) | DRI _{24h} (g O ₂ kg TS ⁻¹ h ⁻¹) |
|-----------------------------|------|------------------------------|--------------------------------|--------------------------------|---------------------------------|---|--|---------------------------------|------|--|---|
| OFMSW (as received) | 5.12 | 5.69 | 401 ± 33 | 771 ± 62 | 19 ± 1 | 1.4 ± 0.3 | 20 ± 1 | 459 ± 19 | 23.0 | 256 ± 28 | 3.6 ± 0.1 |
| Input composting tunnels | 4.84 | 4.04 | 395 ± 27 | 748 ± 66 | 24 ± 1 | 1.8 ± 0.1 | 26 ± 2 | 445 ± 14 | 17.1 | 226 ± 5 | 3.3 ± 0.1 |
| Output composting tunnels | 7.04 | 6.20 | 508 ± 4 | 758 ± 31 | 21 ± 1 | 5.1 ± 0.2 | 26 ± 1 | 367 ± 9 | 14.1 | 133 ± 5 | 1.7 ± 0.1 |
| Output maturation | 8.10 | 6.27 | 682 ± 75 | 629 ± 78 | 24 ± 1 | 0.8 ± 0.1 | 25 ± 1 | 345 ± 10 | 13.8 | 60 ± 4 | 0.8 ± 0.1 |
| Final compost | 7.07 | 8.48 | 751 ± 3 | 637 ± 3 | 27 ± 1 | 2.8 ± 0.3 | 30 ± 2 | 403 ± 43 | 13.4 | 77 ± 3 | 0.9 ± 0.1 |
| Compost reject | 7.33 | 6.12 | 810 ± 32 | 460 ± 13 | 20 ± 1 | 1.2 ± 0.1 | 21 ± 5 | 267 ± 11 | 12.7 | 94 ± 19 | 1.3 ± 0.3 |
| Sewage sludge (as received) | 6.85 | 2.99 | 180 ± 3 | 757 ± 1 | 64 ± 2 | 6.7 ± 0.8 | 71 ± 34 | 448 ± 17 | 6.3 | 312 ± 10 | 7.1 ± 0.3 |
| Input composting tunnels | 7.53 | 2.14 | 484 ± 29 | 918 ± 11 | 25 ± 2 | 5.0 ± 0.1 | 30 ± 3 | 507 ± 10 | 16.9 | 111 ± 19 | 1.8 ± 0.2 |
| Output composting Tunnels | 8.08 | 2.87 | 692 ± 11 | 862 ± 14 | 26 ± 2 | 5.2 ± 0.0 | 31 ± 2 | 390 ± 10 | 12.6 | 15 ± 6 | 0.2 ± 0.1 |
| Final compost | 8.18 | 3.08 | 697 ± 4 | 769 ± 39 | 42 ± 2 | 6.9 ± 0.2 | 49 ± 3 | 457 ± 18 | 9.3 | 32 ± 2 | 0.4 ± 0.1 |
| Roasted coffee waste | 5.65 | 0.10 | 520 ± 3 | 987 ± 1 | 18 ± 1 | n.d. | 18 ± 1 | 573 ± 1 | 31.8 | 43 ± 7 | 0.5 ± 0.1 |

Abbreviations: OFMSW: Organic Fraction of Municipal Solid Waste; EC: Electrical Conductivity; TS: Total Solids; VS: Volatile Solids; NTK: Total Kjeldahl Nitrogen; N-NH₃: ammonia; TOC: Total Organic Carbon; N_{tot}: Total Nitrogen; AT₄: cumulative respiration index (4 days); DRI_{24h}: dynamic respiration index (average of 24 hours of maximum activity); n.d.: not detected.

Table 2: Ultimate cumulative respirometric activity and biological organic carbon of the samples extracted from the main process of both treatment lines.

| Sample | ATu (gO₂/kgTS) | ATu (gCO₂/kgTS) | N_{tot} (g kg TS⁻¹) | TOC (g kg TS⁻¹) | BOC (g kg TS⁻¹) | TOC/BOC | BOC/N | C/N | BOC/N/C/N (%) |
|--|--------------------------------------|---------------------------------------|---|---------------------------------------|---------------------------------------|----------------|--------------|------------|--------------------------|
| OFMSW (as received) | 783 ± 20 | 944 ± 27 | 20 ± 1 | 459 ± 19 | 257 ± 7 | 1.8 | 12.9 | 23.0 | 178 |
| Output composting tunnels | 466 ± 5 | 351 ± 8 | 26 ± 1 | 367 ± 9 | 96 ± 2 | 3.8 | 3.7 | 14.1 | 381 |
| Final compost | 204 ± 6 | 222 ± 32 | 30 ± 2 | 403 ± 43 | 61 ± 9 | 6.6 | 2.0 | 13.4 | 670 |
| Sewage Sludge (as received) | 606 ± 40 | 694 ± 50 | 71 ± 34 | 448 ± 17 | 189 ± 14 | 2.4 | 2.7 | 6.3 | 233 |
| Output composting tunnels | 69 ± 43 | 133 ± 57 | 31 ± 2 | 390 ± 10 | 37 ± 16 | 10.5 | 1.2 | 12.6 | 1050 |
| Final compost | 137 ± 1 | 131 ± 1 | 49 ± 3 | 457 ± 18 | 36 ± 1 | 12.7 | 0.7 | 9.3 | 1329 |

Abbreviations: OFMSW: Organic Fraction of Municipal Solid Waste; ATu: cumulative respiration index until ultimate time; N_{tot}: Total Nitrogen; TOC: Total Organic Carbon; BOC: Biodegradable Organic Carbon.

Table 3: Chemical characterization of samples based on the pyrolysis results.

| Chemical class (% pyrogram) | Example of molecules found in each class | Parental molecules | OFMSW line | | | | Sewage sludge line | | |
|-----------------------------------|--|--------------------------|-------------------|---------------------------|-------------------------------|-------------------------------------|---------------------------------|-------------------------------|-------------------------------------|
| | | | OFMSW + wood chip | Sample after active phase | Sample after maturation phase | Final compost (after sieving 10 mm) | Sewage sludge + wood chip + CRW | Sample after maturation phase | Final compost (after sieving 10 mm) |
| Fatty acid | Acetic acid; Formic acid phenyl ester | Polysaccharide, lipid | 2.2 | 1.2 | 0.9 | 1.9 | 4.2 | 6.1 | 9.1 |
| Alkane | Pentadecane, Heptane, Decane, Hexadecane | Lipid | | | | | | | |
| Cyclo-alkane | Cyclododecane, Cyclohexadecane | Lipid | | | | | | | |
| | | | 53.9 | 51.8 | 45.2 | 47.3 | 18.1 | 17.5 | 22.7 |
| Alkene | 2-Butene, 1-Nonene, 1-Tetradecene, 3-Hexyne, 1-Hexadecene | Lipid | | | | | | | |
| Cyclo-alkene | Cyclohexene, Cyclopentene,3-methylene, | Lipid | | | | | | | |
| Aromatic lignin derived | Phenol, 2-methoxy-4-methyl, mequinol, 2-Methoxy-4-vinylphenol | Lignin | 0.6 | 0.6 | 0.7 | 1.8 | 6.9 | 8.4 | 3.1 |

| | | | | | | | | | | |
|---------------------------|---|-------------------------|------|------|------|------|------|------|------|--|
| Ketone | 2-Butanone, 3-methyl, 2-Butanone, 3-methyl, 2,3-Pentanedione | Lignin | | | | | | | | |
| Cyclo-ketone | 2-Cyclopenten-1-one, 2-Cyclopenten-1-one, 3-methyl, 2-Cyclopenten-1-one, 2,3,4-trimethyl | Polysaccharide | | | | | | | | |
| Furan derivatives | Furan, 2,5-dimethyl, Furfural, Benzofuran, 2-methyl | Polysaccharide | 5.9 | 4.7 | 3.7 | 4.1 | 11.3 | 10.5 | 8.4 | |
| Pyran derivatives | 2H-Pyran-2-one, 4-hydroxy-6-methyl | Polysaccharide | | | | | | | | |
| Nitrogen compounds | Pyrrole, Pyridine, 2-methyl, Butanenitrile, 2-methylene, 1H-Indole, 2-methyl, 1H-Pyrazole, 1-methyl-3-vinyl | Protein | 11.3 | 16.6 | 17.7 | 16.4 | 19.8 | 17.9 | 19.2 | |
| Aromatic undefined | Styrene, Ethylbenzene, o-Xylene, Benzene, Phenol, 3-methyl- | Lignin, protein, tannin | 11.5 | 15.7 | 16.6 | 14.8 | 15.6 | 21.4 | 21 | |
| Polyaromatic | Naphthalene, 1,2-dihydro-6-methyl, Indene, 1H-Indene, 1-methyl | Humic substances, coal | 0.4 | 2.4 | 3.3 | 2.4 | 0.5 | 1.2 | 0.7 | |
| Isoprenoid | Bicyclo[5.2.0]non-1-ene, Bicyclo[6.4.0]dodeca-9,11-diene, Bicyclo[5.2.0]non-1-ene | Isoprenoid, terpenes | 2.2 | 3.6 | 2.1 | 3.1 | 1.2 | 0.6 | 1.4 | |
| Alcohol | 1-Pentanol, 2-methyl, 4-Methyl-dodec-3-en-1-ol | Lipid, lignin | 4.8 | 0.9 | 8 | 0.5 | 1.3 | 4.8 | 2.9 | |

| | | | | | | | | | |
|------------------------------|---|---------------------|-----|-----|-----|-----|-----|-----|-----|
| Aldehyde | Butanal, 2,2-dimethyl, Propanal, 2-methyl- | Lipid, lignin | 8.8 | 0.4 | 2.8 | 1.4 | 3.5 | 2.4 | 3.6 |
| Aromatic from plastic | Benzene, 2-propenyl, Benzene, 1-ethenyl-3-methyl | Plastic | 2.2 | 1.5 | 1.8 | 2.2 | 0 | 0 | 0 |
| Silane | Cyclotrisiloxane, hexamethyl | Biomass contaminant | 0 | 0 | 0 | 0 | 1.7 | 2.7 | 3.2 |
| Alogenure | Methane, chloro, Pentane, 2-bromo, Pentadecyl pentafluoropropionate | Biomass contaminant | 0 | 5 | 2.7 | 3 | 0.2 | 0.2 | 2.5 |

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Table S1. Elaboration of the pyrolysis results. Classification of the pyrolysis peaks in chemical class (OFMSW+ chip wood sample)

| Classe | % area | molecule |
|---------------------|-----------------------------|--|
| Fatty acid | 0.751 | Acetic acid |
| | 0.569 | Formic acid phenyl ester |
| | 0.399 | Acetic acid, 2-ethylbutyl ester |
| | 0.292 | Hex-5-noic acid, methyl ester |
| | 0.180 | 2-Cyclopentene-1-undecanoic acid, (+)- |
| Total | 2.190 | |
| Alkane | 1.037 | Pentadecane |
| | 0.978 | Heptane, 4-methyl- |
| | 0.948 | Octane |
| | 0.805 | Heptane |
| | 0.610 | Octane |
| | 0.606 | Decane |
| | 0.593 | Nonane |
| | 0.567 | Undecane |
| | 0.541 | Tridecane |
| | 0.478 | Tetradecane |
| | 0.437 | Dodecane |
| | 0.297 | Hexane, 3-ethyl- |
| | 0.181 | Octane, 2-methyl- |
| | 0.181 | Heptadecane |
| | 0.133 | Hexadecane |
| Total | 8.391 | |
| Cyclo-alkane | 0.646 | Cyclododecane |
| | 1.588 | cis-1-Butyl-2-methylcyclopropane |
| | 0.097 | Cyclododecane, ethyl- |
| | 0.073 | Cyclohexadecane |
| | 0.347 | Cyclopropane, trimethylmethylene- |
| 0.268 | Cyclopropanecarboxylic acid | |
| Total | 3.019 | |
| Alkene | 7.454 | 2-Butene |
| | 2.701 | 1-Undecene |
| | 1.698 | 1-Nonene |
| | 1.581 | 1-Decene |
| | 1.082 | 1-Heptene |
| | 1.016 | 1-Tridecene |
| | 0.996 | 4-Penten-1-yl acetate |
| | 0.883 | 1-Tetradecene |
| | 0.669 | 1-Pentadecene |
| | 0.590 | 5-Undecene |
| | 0.414 | 3-Octen-1-yne, (E)- |
| | 0.257 | 2-Hexen-4-yne |
| | 0.210 | 3-Hexyne |
| | 0.131 | 2-Hexyne, 4-methyl- |
| | 0.111 | 1,9-Decadiyne |
| | 0.119 | 1-Penten-3-yne, 2-methyl- |
| | 0.289 | 1-Hexadecene |
| | 0.263 | 2-Octene, (Z)- |

| | | |
|--------------------------------|--------|------------------------------------|
| | 0.172 | 5-Dodecene, (E)- |
| | 0.138 | 2-Tetradecene, (E)- |
| | 0.096 | 8-Heptadecene |
| | 0.517 | 1-Butene, 3-methyl- |
| | 0.523 | 1,3,5-Hexatriene, (Z)- |
| | 0.969 | 1,3,5-Cycloheptatriene |
| | 0.554 | 1,3-Hexadiene,c&t |
| | 0.480 | 1,3-Butadiene-1-carboxylic acid |
| | 0.287 | 4-Methyl-1,3-heptadiene (c,t) |
| | 0.236 | E-1,8-Dodecadiene |
| | 0.914 | 1,3-Cyclopentadiene |
| | 0.668 | 1,4-Pentadiene |
| | 0.664 | 1,3-Pentadiene, (Z)- |
| | 0.564 | 1-Methoxy-1,4-hexadiene |
| | 0.427 | 2,4-Hexadiene |
| | 0.505 | 2,3-Heptadien-5-yne, 2,4-dimethyl- |
| Total | 28.179 | |
| | 0.376 | Cyclohexene |
| | 0.268 | Cyclopentene, 1,2,3-trimethyl- |
| Cyclo-alkene | 0.353 | Cyclopentene,3-methylene- |
| | 0.334 | 1-Methylcycloheptene |
| | 0.274 | Cyclopentene, 3-ethenyl- |
| Total | 1.606 | |
| | 2.841 | 1-Pentanol, 2-methyl- |
| | 0.276 | cis-3-Hexen-1-ol, methyl ether |
| Alcohol | 0.234 | 4-Methyl-dodec-3-en-1-ol |
| | 0.954 | Cyclohexanepropanol, 2-acetoxy- |
| | 0.177 | Benzenemethanol, .alpha.-ethynyl- |
| | 0.317 | (3-Methyl-oxiran-2-yl)-methanol |
| Total | 4.799 | |
| | 5.867 | Butanal, 2,2-dimethyl- |
| Aldehyde | 0.870 | 2-Pentenal, 2-methyl- |
| | 1.626 | Propanal, 2-methyl- |
| | 0.386 | Butanal, 3-methyl- |
| Total | 8.749 | |
| Aromatic lignin derived | 0.648 | Phenol, 2-methoxy-4 |
| Total | 0.648 | |
| | 0.476 | Benzene, 1-butynyl- |
| | 0.451 | Benzene, 2-propenyl- |
| Aromatic from plastic | 0.357 | Benzene, 1-ethenyl-3-methyl- |
| | 0.294 | Benzene, 1-propenyl- |
| | 0.588 | (1-Methylenebut-2-enyl)benzene |
| | 2.166 | |
| | 4.670 | Toluene |
| | 1.498 | Styrene |
| | 1.275 | Ethylbenzene |
| Aromatic undefined | 1.217 | o-Xylene |
| | 0.831 | Benzene |
| | 0.417 | Benzene, 1-ethyl-4-methyl- |
| | 0.352 | Phenol, 3-methyl- |
| | 0.290 | Benzene, pentyl- |

| | | |
|---------------------------|---------------|---|
| | 0.269 | Benzene, butyl- |
| | 0.258 | Benzene, 1-ethyl-3-methyl- |
| | 0.182 | Benzene, propyl- |
| | 0.128 | Benzene, 1-ethyl-2-methyl- |
| | 0.097 | Phenol, 3-methyl- |
| | 0.036 | Benzocycloheptatriene |
| Total | 11.482 | |
| | 0.136 | 4-Methylphenyl acetone |
| | 1.129 | Methyl Isobutyl Ketone |
| | 1.123 | 2-Butanone, 3-methyl- |
| | 0.698 | 2-Pentanone |
| Ketone | 0.695 | 2-Decanone |
| | 0.550 | 2-Propanone, 1-hydroxy- |
| | 0.455 | Spiro[2.4]heptan-4-one |
| | 0.362 | 2-Butanone, 3-methyl- |
| | 0.284 | 2,3-Pentanedione |
| | 0.196 | 1-Oxetan-2-one, 4-methyl-3-methylene- |
| Total | 5.628 | |
| | 1.609 | 2-Cyclopenten-1-one |
| | 1.251 | 2-Cyclopenten-1-one, 2-methyl- |
| Cyclo-ketone | 1.046 | 2-Cyclopenten-1-one, 3-methyl- |
| | 0.268 | 4-Cyclononen-1-one |
| | 0.220 | 2-Cyclopenten-1-one, 2,3,4-trimethyl- |
| Total | 4.394 | |
| Alogenure | 0.228 | Ethene, 1-chloro-1-fluoro- |
| Total | 0.228 | |
| | 0.635 | Furan, 2-methyl- |
| | 0.373 | 2-Furanmethanol |
| Furan derivates | 0.323 | Furan, 2,5-dimethyl- |
| | 0.094 | trans-2-(2-Pentenyl)furan |
| | 0.079 | Furan, 2-ethyl- |
| Total | 1.504 | |
| | 0.592 | 2-Oxabicyclo[3.2.0]hepta-3,6-diene |
| | 0.499 | 7-Formylbicyclo[4.1.0]heptane |
| | 0.355 | Bicyclo[5.2.0]non-1-ene |
| Isoprenoid | 0.072 | cis-Bicyclo[3.3.0]oct-2-ene |
| | 0.278 | Bicyclo[6.4.0]dodeca-9,11-diene |
| | 0.227 | Bicyclo[2.2.1]heptan-7-ol |
| | 0.170 | Bicyclo[3.2.0]hepta-2,6-diene, 5-methoxy- |
| Total | 2.193 | |
| | 1.837 | Pyrrole |
| | 1.710 | 1H-Pyrrole, 1-methyl- |
| | 0.931 | N-Cyano-2-methylpyrrolidine |
| | 0.796 | 1H-Pyrrole, 2-methyl- |
| | 0.560 | 1H-Pyrrole, 2-ethyl- |
| Nitrogen compounds | 0.552 | Pyridine, 4-methyl- |
| | 0.492 | Pyridine, 2-methyl- |
| | 0.467 | Indolizine |
| | 0.449 | Pyridine |
| | 0.413 | 1H-Pyrrole, 2,5-dimethyl- |
| | 0.364 | Butanenitrile, 2-methylene- |

| | | |
|---|---------------|---------------------------------------|
| | 0.352 | 2-Methyl-5-(butyn-1-yl)pyridine |
| | 0.276 | 1H-Indole, 2-methyl- |
| | 0.253 | 1H-Pyrrole, 1-methyl- |
| | 0.244 | 1H-Indole, 1-ethyl- |
| | 0.232 | 1H-Pyrrole, 3-methyl- |
| | 0.231 | 1H-Indole, 2-methyl- |
| | 0.187 | 1H-Pyrrole, 1-pentyl- |
| | 0.170 | Benzonitrile, 3-methyl- |
| | 0.117 | 1H-Pyrazole, 1-methyl-3-vinyl- |
| | 0.113 | 1H-Inden-1-one, 2,3-dihydro-3-methyl- |
| | 0.275 | Benzeneacetamide |
| | 0.249 | dl-2-Amino-1-phenylethanol |
| Total | 11.269 | |
| | 0.387 | Naphthalene, 1,2-dihydro-6-methyl- |
| Polyaromatic | 0.358 | Indene |
| | 0.338 | 1H-Indene, 1-methyl- |
| Total | 0.387 | |
| | 0.633 | Cyclotrisiloxane, hexamethyl- |
| Silane | 0.333 | Cyclotetrasiloxane, octamethyl- |
| Total | 0.967 | |
| <hr/> | | |
| Total of the program interpreted | 97.799 | |

Pre-print

Legends to Figures

Figure 1: Evolution of the ratio TOC/BOC values and a) dynamic respiration index (DRI_{24h}) or b) cumulative respiration index at four day (AT_4).

Pre-print

Fig.1a

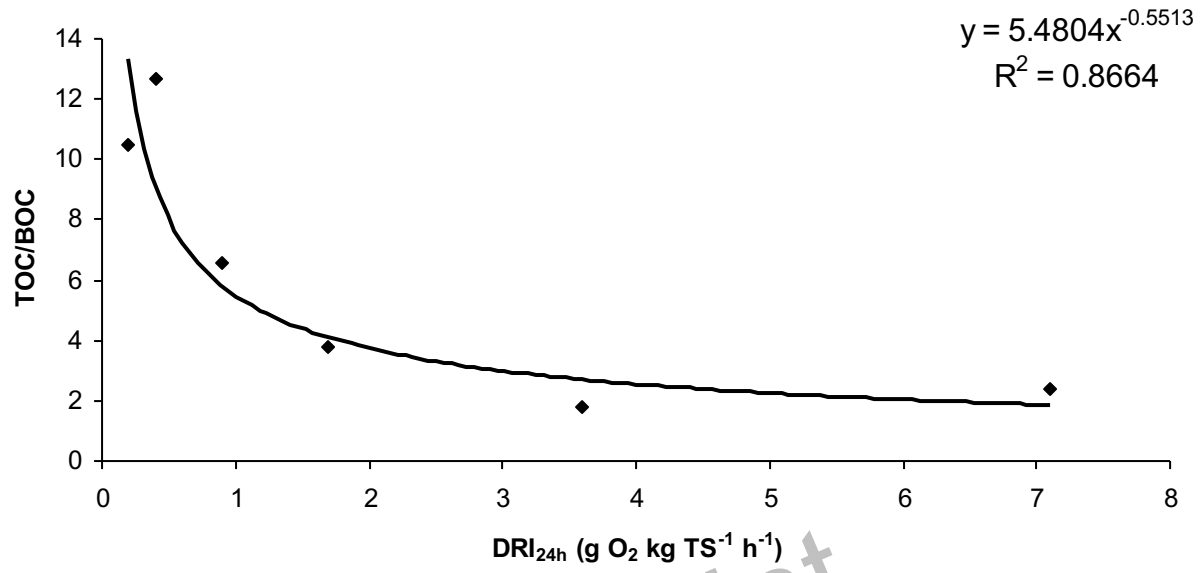


Fig.1b

