

1           DECOMPOSITION OF TWO TYPES OF ELECTRIC WIRES  
2                    CONSIDERING THE EFFECT OF THE METAL IN THE  
3                    PRODUCTION OF POLLUTANTS

4           *Juan A. Conesa\*, Silvia Egea, Julia Moltó, Nuria Ortuño and Rafael Font*

5           Department of Chemical Engineering. University of Alicante. P.O. Box 99, 03080

6           Alicante (Spain). Phone: + (34) 96 590 38 67 Fax: + (34) 96 590 38 26

7           \*Corresponding author. Email: [ja.conesa@ua.es](mailto:ja.conesa@ua.es)

8

9

10 DECOMPOSITION OF TWO TYPES OF ELECTRIC WIRES CONSIDERING THE  
11 EFFECT OF THE METAL IN THE PRODUCTION OF POLLUTANTS

12 ABSTRACT

13 Combustion runs at 700 °C in a horizontal laboratory furnace were carried out on two  
14 different electric wires (PVC and halogen-free wire). Tests were performed in the  
15 presence and in the absence of the metal conductor of the wires. The analyses of the  
16 polycyclic aromatic hydrocarbons (PAHs), chlorobenzenes (CBzs), chlorophenols  
17 (CPhs), mono- to octa-chlorodibenzo-p-dioxin and dibenzofurans (PCDD/Fs), and  
18 dioxin-like PCBs are shown. Regarding semivolatile compounds, PAHs production  
19 decreases in the presence of metal, while a higher amount of chlorinated compounds are  
20 emitted. Respect to the PCDD/Fs, the PVC wire in the presence of metal presents the  
21 highest emission, with a much more emission of furans than dioxins. The maximum  
22 emission is with 2 or 3 chlorine atom PCDD/Fs. PCBs emission correlates with  
23 PCDD/F production and represents 3-4% of total toxicity, determined by using  
24 WHO2005 factors.

25 KEYWORDS: WEEE, cables, dioxins, PAHs, PCBs, combustion.

27           1. INTRODUCTION

28   The wire and cable industry manufactures a wide range of products that support a  
29   multitude of applications. Some of the major markets are communication cables, power  
30   and cable wire, automotive wiring, control and signal cables, and building wiring.  
31   Generally wires differ in conducting and isolation materials. The classic conductor  
32   material has been copper but aluminium is also used frequently today.

33   Many wire insulation and covering compositions contain materials, such as lead,  
34   halogenated compounds, and other compounds, that impart electrical insulation and fire  
35   performance properties. Specifically, fire retardants are used to avoid the propagation of  
36   fire. One of the most frequently used types of fire retardant, Halogenated Flame  
37   Retardants (HFRs), have been proven to be a hazard to human life and environment,  
38   which has led to regulations on their use with the ultimate goal of removing from the  
39   market.

40   Recently, The European Parliament has considered to review the Restriction of  
41   Hazardous Substances (RoHS) Directive to include compounds not previously covered  
42   by the legislation such as PVC and some HFRs in electronic equipment . The former  
43   directive is closely related to the directive on Waste Electrical and Electronic  
44   Equipment also known as WEEE directive (2003). WEEE directive promotes the reuse,  
45   recycling, and recovery of these wastes as well as the collection of electrical and  
46   electronic wastes as a separate waste stream, which enhances the prospects for  
47   economic recycling. In this sense, End-Of-Life (EOL) communications and low-voltage  
48   cables are valuable because these consist of approximately 50 percent copper by weight.  
49   The high price of copper ensures that an estimated 95 percent of EOL cable and wire is  
50   recycled .

51 In traditional metal recycling, physical techniques are used to separate metals and  
52 plastics. The result of this operation is a waste formed by a single mixed fraction of  
53 different polymers (PVC, PE, LLDPE, HDPE, PP, etc). Until now plastic fractions of  
54 EOL cables have been landfilled because it was considered as a waste product with low  
55 value; however, today it is known that this waste has a great value and it is suitable for  
56 recycling, by material, chemical or energy recovery. In all cases previous polymer  
57 separation is advisable. Material recovery is an attractive option for PVC; whereas  
58 either material or energy recovery are equally attractive for polyolefin waste (Hagstrom  
59 et al., 2006).

60 Thermal treatment of PVC wastes it is a problematic way of recovery. Besides  
61 hydrogen chloride, chlorinated aromatic compounds are evolved during pyrolysis or  
62 combustion of PVC, such as chlorobenzenes (CBzs), chlorophenols (CPhs),  
63 chlorobiphenyls (PCBs) and, polychlorodibenzo-p-dioxins and polychlorodibenzofurans  
64 (PCDD/Fs) (Aracil et al., 2005). This could be especially alarming when the process is  
65 uncontrolled. Illegal recycling, open burning at landfills or accidental fires involves a  
66 serious damage to health and to environment. Moreover, when copper is present during  
67 combustion process, a catalytic formation of chlorinated compounds and dioxins, both  
68 in gas and solid phases, from phenols have been observed (Stanmore, 2004; Ryu et al.,  
69 2005; Ryu, 2008; Altarawneh et al., 2009).

70 Behaviour of cables and wires considering their heat release has been previously studied  
71 (Hirschler, 1994), showing that cables with excellent fire performance can be made by  
72 using a variety of materials, so that it would seem to follow that it is important to  
73 specify fire performance and leave material choice to manufacturers.

74 There is not extensive information of the emissions from thermal degradation processes  
75 of electric wires in oxidative atmosphere, and less in the presence of conductive metal  
76 (Chaala et al., 1997; Thibert and Gautier, 1999; Gullett et al., 2007; Kantarelis et al.,  
77 2009). The present work aims to extend the information in this issue providing the basis  
78 for the analysis of environment impact and development of new products, taking special  
79 interest on the effect of the metal on the decomposition and the previsible differences  
80 between PVC and halogen-free wires.

## 81 2. MATERIAL AND METHODS

### 82 2.1 Electrical Wires

83 Supplied by General Cable, Co., two kinds of commercial cables have been employed  
84 in this work. The first one is a common wire (designed as P), with PVC cover and  
85 reticulated polyethylene as insulation. The second one is a special fire-resistant and  
86 halogen-free wire (designed as H). Figure 1 shows the scheme of electrical wire, the  
87 composition of the two materials used and the weight percentage of each part. As we  
88 can see in Figure 1, the material used in the cover (or jacket) of the halogen free wire is  
89 a mixture of polyethylene, a thermoplastic elastomer, and aluminium trihydroxide (PE-  
90 TPE-ATH). Elemental analysis of the wires and some more details can be found in a  
91 previous work (Conesa et al., 2010). To ensure the homogeneity, the samples were  
92 crushed (1-3 mm) using a laboratory blender by DINKO, 8010 model (DINKO,  
93 Barcelona, Spain).

94 In order to study the effect of the presence of copper during the decomposition, for each  
95 kind of wire two different samples were prepared: one consisting of the plastic parts,  
96 named P1+P2 and H1+H2, and the other one representing the entire wire named  
97 P1+P2+P3 and H1+H2+H3, where P3 and H3 refers to the metal (see Figure 1).

### 98 2.2 Experimental system

99 Experiments were performed in a moving tubular reactor which consists in a quartz tube  
100 (10 mm wide), where the material is introduced uniformly along. This tube is introduced  
101 in a horizontal furnace, maintained at the desired temperature, at constant velocity using  
102 a horizontal actuator. Figure SM-1 (Supplementary Information) shows a scheme of the  
103 experimental system. More details of the equipment can be found elsewhere (Barneto et  
104 al., 2009; Conesa, 2011). In all runs the temperature of the oven was 700 °C. Synthetic  
105 air was introduced parallel to the sample, with gas flowing at 300 mL/min (measured at  
106 1 atm and 20 °C). All runs were performed under fuel-rich atmosphere, with a oxygen  
107 ratio of 0.5 (ratio between actual and stoichiometric oxygen (Conesa et al., 2007;  
108 Conesa et al., 2009)).

109 The outlet gas stream was sampled to analyze semivolatile compounds such as PAHs,  
110 CPhs and CBzs, PCDD/Fs, and dioxin-like PCBs. Emitted gases were collected using a  
111 poliaromatic Amberlite® XAD-2 resin as sorbent (Supelco, Bellefonte, USA) placed at  
112 the outlet of the furnace during the whole experiment. Before the decomposition runs, a  
113 control containing no sample was carried out using the same experimental conditions  
114 (blank).

115 Amberlite® XAD-2 resin was extracted in toluene by Accelerated Solvent Extraction  
116 (ASE-100, Dionex-Thermo Fisher Scientific Inc., California, USA) and the extracted  
117 solution was divided as follows: approximately 30 wt. % was employed to analyze  
118 PAHs (US-EPA 8270D method), CPhs and CBzs; the rest (over 70 wt. %) was used for  
119 the analysis of PCDD/Fs and “dioxin-like” PCBs (EPA 1613 and 1668A methods).

120 PAHs, CPhs and CBzs were analyzed by GC–MS in SIM mode (Agilent GC  
121 6890N/Agilent MS 5973N, Agilent Technologies, USA) using the isotope dilution  
122 method. CPhs and CBzs were also specifically analyzed in SIM mode with mixture

123 standards containing all isomers, following an analogous procedure to that of the 16  
124 PAHs. Additionally, the identification of each isomer was confirmed by checking the  
125 ratio between the areas of the primary and the secondary ions, since they are known due  
126 to presence of  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$ .

127 For the analysis of PCDD/Fs and “dioxin-like” PCBs, cleanup was performed using the  
128 Power Prep system (FMS, Inc., Boston, MA) with three different columns: silica,  
129 alumina, and activated carbon (FMS, Inc., Boston, MA). The analysis was completed by  
130 HRGC/HRMS. For HRGC, an Agilent HP5890 gas chromatograph equipped with  
131 programmable temperature vaporization (PTV) inlet with a septumless head was used.  
132 For HRMS, a Micromass Autospec UlitmaNT mass spectrometer (Micromass, Waters,  
133 UK) with a positive electron impact (EI+) source was employed. All congeners of  
134 dioxins and furans were determined, from mono- to octachlorinated species.

135 The standards used for the analysis of 16 PAH were supplied by Dr. Ehrenstorfer-  
136 Schäfers (Augsburg, Germany) and the standards of CPhs, CBzs, PCDD/Fs and  
137 “dioxin-like” PCBs were obtained from Wellington Laboratories (Ontario, Canada). All  
138 the solvents for organic trace analysis were purchased form Merck (Germany).

### 139 3. RESULTS AND DISCUSSION

140 Table 1 shows the results on the emission of PAHs for the four runs done in the  
141 laboratory reactor. Note that these results are expressed in mg/(kg of consumed  
142 material), i.e., considering only the plastic fractions in the basis; if the whole weight is  
143 considered in the weight base, emission of runs P1+P2+P3 and H1+H2+H3 will be  
144 approximately halved (composition is shown in Figure 1). In the first column (Table 1)  
145 we can see the results for the combustion of the halogen free wire with no metal, the

146 second column is in the presence of metal, and third and fourth columns are the ones  
147 obtained with the PVC wire.

148 The main PAHs emitted in all cases are naphthalene and acenaphthylene. It seems in both  
149 cases that the presence of metal reduces the production of this kind of pollutants,  
150 probably due to the catalysis of cracking reactions that produces low molecular weight  
151 compounds. Also it is possible that the presence of metal catalyses chlorination  
152 reactions as will be presented later. The emission of each of the species shown in Table  
153 1 is decreased almost in the same proportion for each one of the wires, being  
154 approximately a 80 % of the emission in the absence of the metal in the case of halogen-  
155 free wire, and a 6 % in the case of PVC wire.

156 Previous works (Andersson et al., 2004) analyzed the pollutants derived from  
157 combustion of electric wires under well-ventilated and vitiated conditions, at small and  
158 large scale, but unfortunately the experimental conditions of the runs performed were  
159 not well controlled and a clear conclusion was not found. The authors find emissions of  
160 total PAHs equivalent to approximately 50-250 mg/kg for PVC and halogen-free wires,  
161 finding an increase in PAHs production for vitiated atmosphere (poor oxygen  
162 availability) using the PVC wire but not in the case of halogens-free wire.

163 The total emission of CBzs and CPhs is presented in Table 2. The emission of each  
164 isomer analysed is presented in Tables SM-1 and SM-2 (Supplementary Information),  
165 for CBzs and CPhs respectively. For both kind of compounds the formation is much  
166 more important for the PVC wire, and is enhanced in the presence of metal. This would  
167 explain, at least partly, the decrease in PAHs shown before. Transformation of PAHs to  
168 chlorinated species has been already reported at temperatures between 300 and 1000 °C  
169 (Zhang et al., 2011). Both wires present a much more emission of CPhs than CBzs.



170 Furthermore, the highest chlorobenzene emission is in the mono-chlorobenzene species,  
171 and 3,4-dichlorophenol in the case of chlorophenols. Chlorinated phenols are known to  
172 be the most direct precursors of the formation of PCDD/Fs congeners (Ballschmiter et  
173 al., 1988; Born et al., 1989; Sidhu et al., 1995), and these are among the most abundant  
174 aromatic compounds found in municipal solid waste incineration emissions  
175 (Tuppurainen et al., 2000). On the other hand, many authors have confirmed the  
176 formation of chlorinated compounds and dioxins, both in gas and solid phases, from  
177 phenols when there is an oxidative atmosphere and in the presence of copper chloride  
178 (Stanmore, 2004; Ryu et al., 2005; Ryu, 2008; Altarawneh et al., 2009).

179 Figure 2 presents the distribution of the congeners contributing to the toxicity of the  
180 PCDD/Fs emission in the four experiments, with H and P wires in the presence or  
181 absence of metal. Data in Figure 2 has been calculated by using I-TEQ factors ( $f_i$ ) and  
182 normalizing the contribution of each congener to the total toxicity:

$$183 \quad \% \text{ PCDD/Fs toxicity congener } i = \frac{f_i C_i}{\sum_{\text{all 17 congeners}} f_i C_i} \times 100$$

184 where  $C_i$  represents emission of toxic congener  $i$ .

185 Some points should be noted. On the one hand, the distribution of congeners depends on  
186 the material but rarely on the presence of metal. In this sense, the major contribution to  
187 the total toxicity is from 2,3,7,8-tetrachlorodibenzofuran in the case of H wire and  
188 2,3,4,7,8-pentachlorodibenzofuran in the combustion of PVC. On the other hand, it is  
189 important to note that in the runs performed, furans contribute much more to the toxicity  
190 than dioxins. Specifically, congener 2,3,4,7,8-pentachlorodibenzofuran has been found  
191 to be the most represented in industrial incinerators emissions (Fiedler et al., 2000).  
192 Another work (Li et al., 2008) determined the concentrations and profiles of PCDD/Fs,

193 PCBs and polybrominated diphenyl ethers (PBDEs) in the ambient air of an e-waste  
194 dismantling area, in the southeast of China; and they found that congener 2,3,4,7,8-  
195 pentachlorodibenzofuran contributed dominantly to the total I-TEQs in all the samples  
196 analyzed.

197 Concerning the total toxicity, not the congener distribution, the values obtained for  
198 halogen free wire were 65 pg WHO/g in the case of no metal (sample H1+H2) and 61  
199 pg WHO/g in the presence of the metal (sample H1+H2+H3); for PVC wire the  
200 emission was 5690 pg WHO/g in the run performed with no metal (P1+P2), and 33840  
201 pg WHO/g in the presence of the metal (P1+P2+P3). In this way, it is clear that  
202 halogen-free wire does not produce a high amount of these pollutants, independent of  
203 the presence or absence of metal. On the other hand, PVC wire emission is almost 100  
204 times the one observed in H wire, and there is a great increase in the presence of the  
205 copper metal. Note that the level of PCDD/Fs emission is expressed in pg/g that is one  
206 million times lower than the results presented for PAHs and CBzs and CPhs.

207 In their study, (Andersson et al., 2004) find a emission of dioxins equivalent to  
208 approximately 70-1400 pg WHO/g, with a clear increase in the case of PVC wires.  
209 Conesa et al. (2009) compared the emissions of PCDD/Fs (pg I-TEQ/g) during the  
210 combustion at 850 °C in fuel-rich conditions with a similar horizontal reactor to that  
211 used in the present work for different wastes. Combustion of waste oil and electronic  
212 circuits (Moltó et al., 2011) generates similar PCDD/F amount than combustion of  
213 halogen-free wire. In the case of PVC wire, the level of PCDD/Fs found is closer to that  
214 obtained for PVC wastes or some types of sewage sludges. It must be emphasized that  
215 PVC wire in the presence of the metal presents a worrying huge emission of these  
216 dangerous pollutants.

217 The data of the production of PCDD/Fs in the laboratory horizontal reactor cannot,  
218 obviously, be directly extrapolated to a real scale fire, bearing in mind that the results  
219 would differ depending on the temperature and oxygen availability. In this sense, it is  
220 difficult to estimate the actual pollutant production in an open fire; the paper by  
221 (Andersson et al., 2004) presents a very interesting research with real fires that, as  
222 mentioned, is in accordance with results presented here. Also the work of (Hull et al.,  
223 2008; Blomqvist et al., 2012) presents a number of large-scale fire experiments  
224 comparing the emission found with that of open burning fires.

225 As has been already commented, not only toxic congeners were determined, but all  
226 congeners from mono to octachlorinated PCDD/Fs. Figure 3 shows the total emission of  
227 dioxins and furans in all four runs. In this Figure, 1F makes reference to  
228 monochlorofurans, 1D to monochlorodioxins, 2F represents dichlorofurans... and so on.  
229 It is clear that the emission with PVC in the presence of metal is much more important  
230 than the other three runs. It is also important to note that there are much more furans  
231 than dioxins. This is due to the major thermal stability of the furans (Xhrouet et al.,  
232 2001; Conesa et al., 2002), considering that the runs were performed at 700 °C. Note  
233 than, although it is not shown in the tables, in all the runs, the sum of toxic dioxins and  
234 furans represents less than 0.8 % of the total emission of dioxins and furans.

235 Also note that the maximum is at 2 or 3 chlorine atoms PCDD/Fs in the case of PVC  
236 wire decomposition in the presence of metal. This can be explained by the presence of  
237 copper and calcium in the composition of the sample (Conesa et al., 2010). Some  
238 studies showed that high calcium and copper levels, together with elevated  
239 temperatures, promote degradation of high chlorinated PCDD/Fs (Weber et al., 2002;  
240 Lundin et al., 2011).

241 In the PVC combustion with no metallic part, we can again find much more furans than  
242 dioxins, but the maximum is displaced to more chlorinated species. This is expected  
243 because, at high temperature and in presence of abundant chlorine, the most chlorinated  
244 isomers are usually the most stable compounds (Christmann et al., 1989; Kim et al.,  
245 2004; Conesa et al., 2005).

246 Figure 3 also shows that during the halogen-free wire decomposition it is almost not  
247 produced congeners of more than 3 chlorine atoms, and also that there are much more  
248 emission of furans than dioxins.

249 From the data presented, we can calculate the average number of chlorines in the  
250 emission both for dioxins and furans. Calculation results indicate that both dioxins and  
251 furans behave in a similar way, with average chlorination degree of dioxins slightly  
252 higher than that of furans.

253 Finally Figure SM-2 (Supplementary Information) shows the emission of PCBs. This  
254 time the y-axis in figure is done in logarithmic scale because again there is much higher  
255 emission in the case of PVC wire. The number of chlorines of these molecules goes  
256 from 4 to 6 so a conclusion on the chlorination degree is difficult. It is interesting to  
257 point out that the formation of PCBs is completely correlated with the formation of  
258 dioxins and furans, in such a way that PVC wire emission is almost 100 times the one  
259 observed in H wire, and there is a magnification in the presence of the copper metal.  
260 The contribution of PCBs to total toxicity is in all cases between 3 and 4 %, considering  
261 the toxicity calculated according to WHO-TEF-2005 values (Van den Berg et al., 2006),  
262 this is because the I-TEQ does not consider the dioxin-like PCBs.

263 In previous studies (Moltó et al., 2011) there were performed combustion runs of  
264 electronic circuits. In this study the emission of PCDD/Fs was much higher at 850 °C

265 than at 500 °C. This behavior was studied in detail (Conesa et al., 2005) with a different  
266 material, meat and bone meal, where it was found that the maximum PCDD/Fs  
267 production is at intermediate temperatures of approx. 700 °C.

268 The results obtained in this work show the importance of avoiding the open burning of  
269 this kind of wastes, usually carried out in developing countries to recover the valuable  
270 parts of the electric wires.

#### 271 4. CONCLUSIONS

272 Combustion runs of two different wires, one of them halogen-free and another PVC  
273 based, have been performed in order to study the pollutant production in different  
274 conditions. PAHs, CBs, CPhs, mono to octa-chlorinated dioxins and furans and PCBs  
275 were determined for each run.

276 PAHs emission decreases in the presence of the metal conductor, whereas the emission  
277 of chlorinated species dramatically increases, by using both kinds of wires.

278 PVC wire presents very much higher emissions than halogen-free wire, and, as  
279 expected, the emission of chlorinated species is also much higher. In this sense, total  
280 dioxin equivalent toxic emissions were approx. 60 pg/g in the case of halogen-free  
281 wire, regardless of the presence of metal. For PVC wire the emission was 5690 pg/g  
282 with no metal and 6 times higher in the presence of copper.

283 PCDD/Fs maximum emissions is of species with a high chlorination degree, except for  
284 samples with a high copper and calcium content, where the maximum is displaced to  
285 lower chlorine content (2 or 3 chlorine atoms).

#### 286 5. ACKNOWLEDGMENTS

287 Support for this work was provided by the Generalitat Valenciana (Spain) with projects  
288 PROMETEO/2009/043/FEDER, and by the Spanish MCT CTQ2008-05520.

## 289 REFERENCES

- 290 Directive 2002/95/EC of the European Parliament and of the Council on the restriction of the  
291 use of certain hazardous substances in electrical and electronic equipment. Official Journal of  
292 the European Commission, Brussels. 2003.
- 293 *European Commission* webpage on electrical and electronic equipment.  
294 [http://ec.europa.eu/environment/waste/weee/index\\_en.htm](http://ec.europa.eu/environment/waste/weee/index_en.htm).
- 295 *US EPA* webpage. Wire and Cable Insulation and Jacketing: Life-Cycle Assessments for Selected  
296 Applications. <http://www.epa.gov/dfe/pubs/wire-cable/lca.htm>.
- 297 2003. Directive 2002/96/EC of the European Parliament and of the Council on Waste Electrical  
298 and Electronic Equipment. Official Journal of the European Commission, Brussels.
- 299 Altarawneh, M., Dlugogorski, B.Z., Kennedy, E.M., Mackie, J.C., 2009. Mechanisms for  
300 formation, chlorination, dechlorination and destruction of polychlorinated dibenzo-p-dioxins  
301 and dibenzofurans (PCDD/Fs). *Prog. Energy Combust. Sci.* 35, 245-274.
- 302 Andersson, P., Rosell, L., Simonson, M., Emanuelsson, V., 2004. Small and Large Scale Fire  
303 Experiments with Electric Cables under Well-Ventilated and Vitiated Conditions. *Fire*  
304 *Technology* 40, 247-262.
- 305 Aracil, I., Font, R., Conesa, J.A., 2005. Semivolatile and volatile compounds from the pyrolysis  
306 and combustion of polyvinyl chloride. *J. Anal. Appl. Pyrolysis* 74, 465-478.
- 307 Ballschmiter, K., Braunmiller, I., Niemczyk, R., Swerev, M., 1988. Reaction pathways for the  
308 formation of polychloro-dibenzodioxins (PCDD) and --dibenzofurans (PCDF) in combustion  
309 processes: II. Chlorobenzenes and chlorophenols as precursors in the formation of polychloro-  
310 dibenzodioxins and --dibenzofurans in flame chemistry. *Chemosphere* 17, 995-1005.
- 311 Barneto, A.G., Carmona, J.A., Gálvez, A., Conesa, J.A., 2009. Effects of the composting and the  
312 heating rate on biomass gasification. *Energy Fuels* 23, 951-957.
- 313 Blomqvist, P., McNamee, M.S., Andersson, P., Lönnemark, A., 2012. Polycyclic Aromatic  
314 Hydrocarbons (PAHs) Quantified in Large-Scale Fire Experiments. *Fire Technology* 48, 513-528.
- 315 Born, J.G.P., Louw, R., Mulder, P., 1989. Formation of dibenzodioxins and dibenzofurans in  
316 homogenous gas-phase reactions of phenols. *Chemosphere* 19, 401-406.
- 317 Conesa, J.A., Font, R., Fullana, A., Martín-Gullón, I., Aracil, I., Galvez, A., Molto, J., Gomez-Rico,  
318 M.F., 2009. Comparison between emissions from the pyrolysis and combustion of different  
319 wastes. *Journal of Analytical and Applied Pyrolysis* 84, 95-102.
- 320 Conesa, J.A., Fullana, A., Font, R., 2002. De novo synthesis of PCDD/F by thermogravimetry.  
321 *Environ. Sci. Technol.* 36, 263-269.
- 322 Conesa, J.A., Fullana, A., Font, R., 2005. Dioxin production during the thermal treatment of  
323 meat and bone meal residues. *Chemosphere* 59, 85-90.
- 324 Conesa, J.A., Galvez, A., Font, R., Fullana, A., 2007. Formation of pollutants at intermediate  
325 oxygen level in sewage sludge combustion. *Organohalogen Compd.* 69, 1317-1320.
- 326 Conesa, J.A., Moltá, J., Font, R., Egea, S., 2010. Polyvinyl chloride and halogen-free electric  
327 wires thermal decomposition. *Industrial and Engineering Chemistry Research* 49, 11841-11847.
- 328 Conesa, J.A.G., A.; Martín-Gullón, I.; Font, R., 2011. Formation and Elimination of Pollutant  
329 during Sludge Decomposition in the Presence of Cement Raw Material and Other Catalysts.  
330 *Advances in Chemical Engineering Science* 1, 183-190.
- 331 Chaala, A., Darmstadt, H., Roy, C., 1997. Vacuum pyrolysis of electric cable wastes. *Journal of*  
332 *Analytical and Applied Pyrolysis* 39, 79-96.

333 Christmann, W., Kasiske, D., Kloppel, K.D., Partscht, H., Rotard, W., 1989. Combustion of  
334 polyvinylchloride - An important source for the formation of PCDD/PCDF. *Chemosphere* 19,  
335 387-392.

336 Fiedler, H., Lau, C., Eduljee, G., 2000. Statistical analysis of patterns of PCDDs and PCDFs in  
337 stack emission samples and identification of a marker congener. *Waste Management and*  
338 *Research* 18, 283-292.

339 Gullett, B.K., Linak, W.P., Touati, A., Wasson, S.J., Gatica, S., King, C.J., 2007. Characterization of  
340 air emissions and residual ash from open burning of electronic wastes during simulated  
341 rudimentary recycling operations. *J. Mater. Cycles Waste Manage.* 9, 69-79.

342 Hagstrom, B., Hampton, R.N., Helmesjo, B., Hjertberg, T., 2006. Disposal of cables at the "end  
343 of life"; some of the environmental considerations. *Electrical Insulation Magazine*, IEEE 22, 21-  
344 30.

345 Hirschler, M.M., 1994. Comparison of large- and small-scale heat release tests with electrical  
346 cables. *Fire and Materials* 18, 61-76.

347 Hull, T.R., Lebek, K., Pezzani, M., Messa, S., 2008. Comparison of toxic product yields of burning  
348 cables in bench and large-scale experiments. *Fire Safety Journal* 43, 140-150.

349 Kantarelis, E., Donaj, P., Yang, W., Zabaniotou, A., 2009. Sustainable valorization of plastic  
350 wastes for energy with environmental safety via High-Temperature Pyrolysis (HTP) and High-  
351 Temperature Steam Gasification (HTSG). *J. Hazard. Mater.* 167, 675-684.

352 Kim, K.S., Hong, K.H., Ho, Y.H., Kim, M.G., 2004. Emission Characteristics of PCDD/Fs, PCBs,  
353 Chlorobenzenes, Chlorophenols, and PAHs from Polyvinylchloride Combustion at Various  
354 Temperatures. *J. Air Waste Manage. Assoc.* 54, 555-562.

355 Li, Y., Jiang, G., Wang, Y., Wang, P., Zhang, Q., 2008. Concentrations, profiles and gas-particle  
356 partitioning of PCDD/Fs, PCBs and PBDEs in the ambient air of an E-waste dismantling area,  
357 southeast China. *Chin. Sci. Bull.* 53, 521-528.

358 Lundin, L., Aurell, J., Marklund, S., 2011. The behavior of PCDD and PCDF during thermal  
359 treatment of waste incineration ash. *Chemosphere* 84, 305-310.

360 Moltó, J., Egea, S., Conesa, J.A., Font, R., 2011. Thermal decomposition of electronic wastes:  
361 Mobile phone case and other parts. *Waste Manage. (Oxford)* 31, 2546-2552.

362 Ryu, J.-Y., 2008. Formation of chlorinated phenols, dibenzo-p-dioxins, dibenzofurans,  
363 benzenes, benzoquinones and perchloroethylenes from phenols in oxidative and copper (II)  
364 chloride-catalyzed thermal process. *Chemosphere* 71, 1100-1109.

365 Ryu, J.-Y., Mulholland, J.A., Takeuchi, M., Kim, D.-H., Hatanaka, T., 2005. CuCl<sub>2</sub>-catalyzed  
366 PCDD/F formation and congener patterns from phenols. *Chemosphere* 61, 1312-1326.

367 Sidhu, S.S., Maqsood, L., Dellinger, B., Mascolo, G., 1995. The homogeneous, gas-phase  
368 formation of chlorinated and brominated dibenzo-p-dioxin from 2,4,6-trichloro- and 2,4,6-  
369 tribromophenols. *Combust. Flame* 100, 11-20.

370 Stanmore, B.R., 2004. The formation of dioxins in combustion systems. *Combust. Flame* 136,  
371 398-427.

372 Thibert, E., Gautier, B., 1999. Combustion of an electrical cable insulation: thermal study and  
373 modelling at EDF. *Polym. Degrad. Stab.* 64, 585-593.

374 Tuppurainen, K.A., Ruokojärvi, P.H., Asikainen, A.H., Aatamila, M., Ruuskanen, J., 2000.  
375 Chlorophenols as Precursors of PCDD/Fs in Incineration Processes: Correlations, PLS Modeling,  
376 and Reaction Mechanisms. *Environmental Science & Technology* 34, 4958-4962.

377 Van den Berg, M., Birnbaum, L.S., Denison, M., De Vito, M., Farland, W., Feeley, M., Fiedler, H.,  
378 Hakansson, H., Hanberg, A., Haws, L., Rose, M., Safe, S., Schrenk, D., Tohyama, C., Tritscher, A.,  
379 Tuomisto, J., Tysklind, M., Walker, N., Peterson, R.E., 2006. The 2005 World Health  
380 Organization Reevaluation of Human and Mammalian Toxic Equivalency Factors for Dioxins  
381 and Dioxin-Like Compounds. *Toxicol. Sci.* 93, 223-241.

382 Weber, R., Nagai, K., Nishino, J., Shiraiishi, H., Ishida, M., Takasuga, T., Konndo, K., Hiraoka, M.,  
383 2002. Effects of selected metal oxides on the dechlorination and destruction of PCDD and  
384 PCDF. *Chemosphere* 46, 1247-1253.

385 Xhrouet, C., Pirard, C., De Pauw, E., 2001. De novo synthesis of polychlorinated dibenzo-p-  
386 dioxins and dibenzofurans on fly ash from a sintering process. *Environ. Sci. Technol.* 35, 1616-  
387 1623.

388 Zhang, Y.F., Zhang, H., Xu, M.Z., 2011. Transfer behavior of PAHs and PCBs from sewage sludge  
389 in the thermal treatment process. *Zhongguo Huanjing Kexue/China Environmental Science* 31,  
390 933-937.

391

392



393

## CAPTIONS

394

### 395 **Tables**

396 Table 1. Emission of 16 EPA priority PAHs in the four runs performed.

397 Table 2. Total emission of chlorobenzenes (CBzs) and chlorophenols (CPhs) in the four

398 runs performed.

399

### 400 **Figures**

401 Figure1. Scheme of the electrical cables, their composition (supplied by manufacturer)

402 and % weight of each part.

403 Figure 2. Toxic congener profiles in the emission of PCDD/Fs for H (halogen-free) and

404 P (PVC) wires.

405 Figure 3. Mono to octachloro dioxins and furans in the emission for H (halogen-free)

406 and P (PVC) wires.

407

408 **Table 1. Emission of 16 EPA priority PAHs in the four runs performed**  
 409 **(emission/kg plastic fraction).**

Compound	H1+H2+H3		P1+P2+P3	
	mg compound/kg consumed material		mg compound/kg consumed material	
naphthalene	142.6	102.8	410.0	39.8
acenaphthylene	54.8	42.4	113.3	3.83
acenaphthene	2.26	2.35	6.61	nd
fluorene	nd	4.86	34.1	0.71
phenanthrene	19.1	13.7	89.1	3.37
anthracene	2.29	1.25	13.0	nd
fluoranthene	6.01	4.86	28.8	0.93
pyrene	12.7	10.8	36.2	0.67
benzo(a)anthracene	1.19	0.90	5.48	0.20
chrysene	3.50	3.07	10.6	0.73
benzo(b)fluoranthene	nd	nd	nd	nd
benzo(k)fluoranthene	4.69	5.80	13.0	nd
benzo(a)pyrene	1.94	2.85	1.39	nd
indeno(1.2.3-cd)pyrene	1.14	1.09	0.43	nd
dibenz(a.h)anthracene	nd	nd	nd	nd
benzo(g.h.i)perylene	2.69	3.13	2.08	nd
<b>Total</b>	<b>255.14</b>	<b>199.9</b>	<b>764.37</b>	<b>50.2</b>

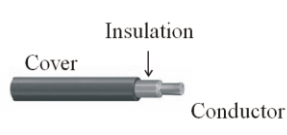
410

411

412 **Table 2. Total emission of chlorobenzenes (CBzs) and chlorophenols (CPhs) in the**  
413 **four runs performed (emission/kg plastic fraction)..**

	<i>H1+H2</i> mg compound/kg consumed material	<i>H1+H2+H3</i> mg compound/kg consumed material	<i>P1+P2</i> mg compound/kg consumed material	<i>P1+P2+P3</i> mg compound/kg consumed material
<b>CBzs</b>	<b>0.051</b>	<b>0.044</b>	<b>0.444</b>	<b>20.8</b>
<b>CPhs</b>	<b>12.1</b>	<b>13.5</b>	<b>43.0</b>	<b>141.9</b>

414  
415



Part	PVC cable (P) wt. %	Halogen free cable (H) wt. %
1 (Cover)	P1: PVC, 41 %	H1: Thermoplastic polyolefin (PE-TPE-ATH), 36 %
2 (Insulation)	P2: Reticulated polyethylene, 9 %	H2: Silicone rubber, 20 %
3 (Conductor)	P3: Copper, 50 %	H3: Copper, 44 %

416

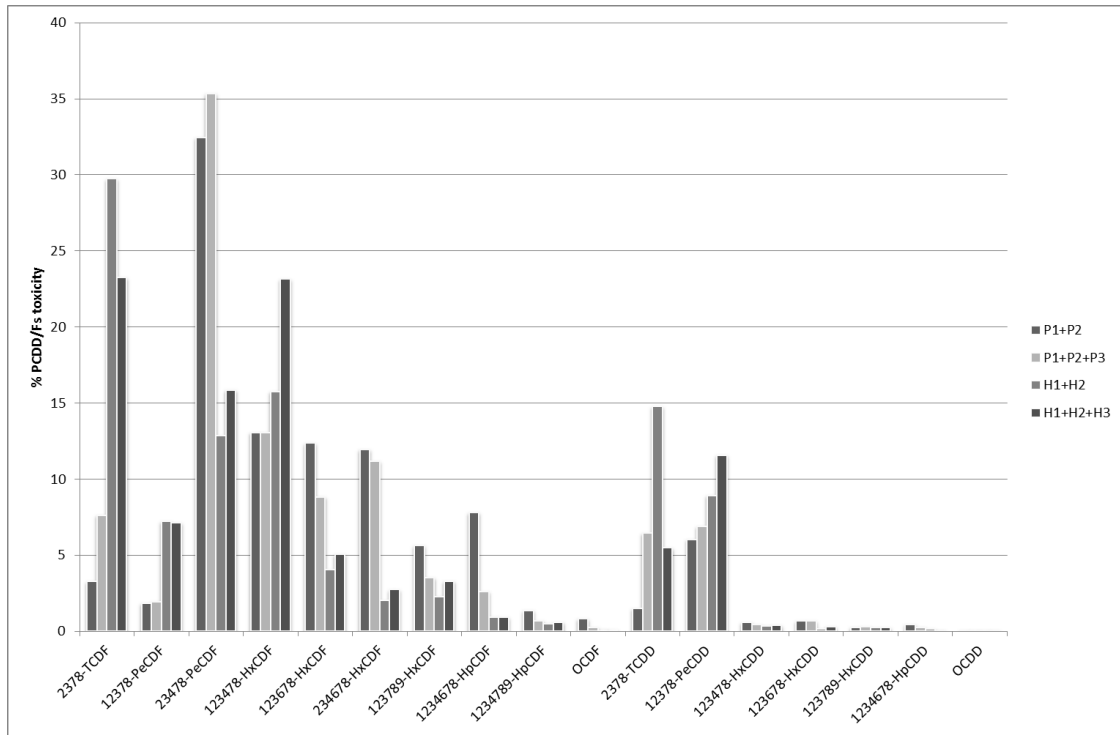
417 Figure 1. Scheme of the electrical cables, their composition (supplied by manufacturer) and % weight of  
 418 each part.

419

420

421 **Figure 2. Toxic congener profiles in the emission of PCDD/Fs for H (halogen-free)**  
 422 **and P (PVC) wires.**

423



424

425

426 **Figure 3. Mono to octachloro dioxins and furans in the emission for H (halogen-**  
 427 **free) and P (PVC) wires.**

