

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

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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}Cl and ^{37}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).

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CAPTIONS

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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.

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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	<i>H1+H2</i>	<i>H1+H2+H3</i>	<i>P1+P2</i>	<i>P1+P2+P3</i>
	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
Total	255.14	199.9	764.37	50.2

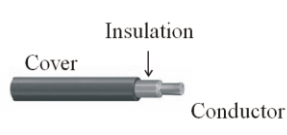
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412 **Table 2. Total emission of chlorobenzenes (CBzs) and chlorophenols (CPhs) in the**
413 **four runs performed (emission/kg plastic fraction)..**

	<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
CBzs	0.051	0.044	0.444	20.8
CPhs	12.1	13.5	43.0	141.9

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 %

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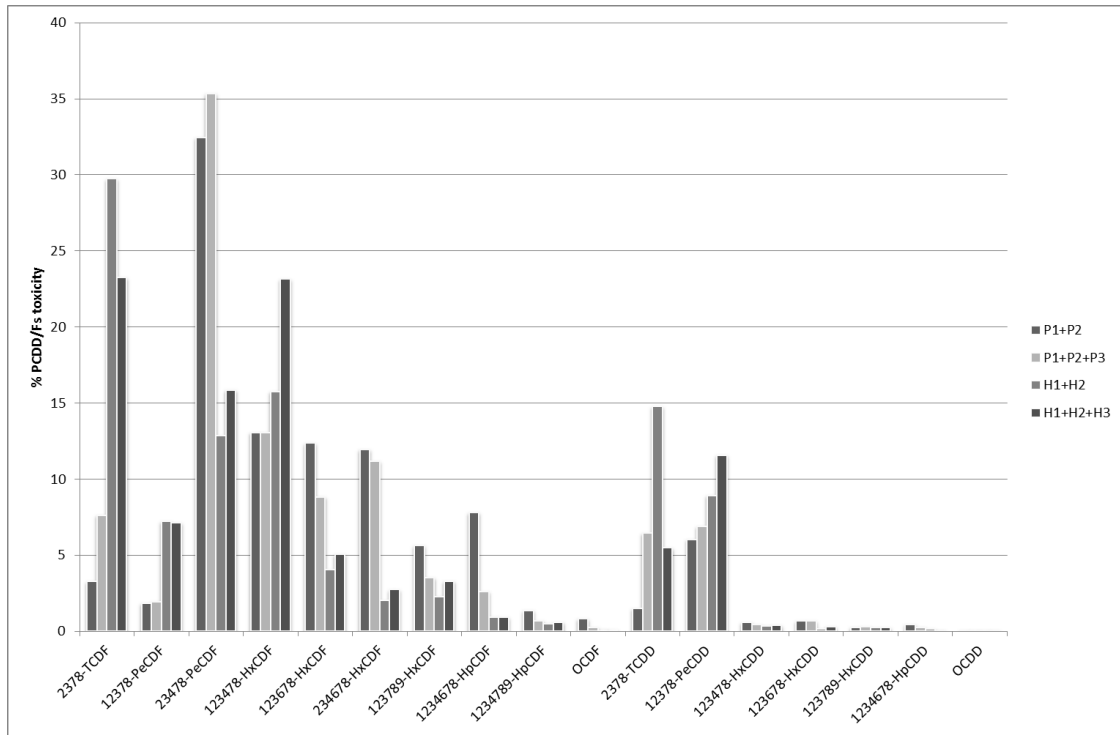
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 418 each part.

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

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

