

1 **Exposure of polychlorinated naphthalenes (PCNs) to Pakistani populations**
2 **via non-dietary sources from neglected E-waste hubs: A problem of high**
3 **health Concern**

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5 Sidra Waheed^a, Muhammad Usman Khan^{b*}, Andrew J. Sweetman^c, Kevin C. Jones^c, Hyo-
6 Bang Moon^b, Riffat Naseem Malik^{a*}

7
8 ^aEnvironmental Biology and Ecotoxicology Laboratory, Department of Environmental
9 Sciences, Quaid-i-Azam University, Islamabad 45320, Pakistan

10 ^bHuman & Ecology Analytical Laboratory (HEAL),
11 Department of Marine Science and Convergence Engineering, Hanyang University, Ansan
12 15588, Republic of Korea

13 ^cCentre for Chemicals Management, Lancaster Environment Centre, Lancaster University,
14 Bailrigg, Lancaster LA1 4YQ, UK

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18 *Corresponding author: Muhammad Usman Khan & Riffat Naseem Malik

19 Phone: +82-5002020-1 & +92-51 9064-3017

20 Fax : 9064-3017

21 E-mail: usman_gau86@yahoo.com; r_n_malik2000@yahoo.co.uk

22 Abstract

23 To date limited information's are available concerning unintentional productions, screening,
24 profiling, and health risks of polychlorinated naphthalenes (PCNs) in ambient environment
25 and occupational environment. Literature reveals that dust is a neglected environmental
26 matrix never measured for PCNs. To our knowledge, this is the first study to investigate the
27 concentrations and health risks of PCNs in indoor dust, air, and blood of major e-waste
28 recycling hubs in Pakistan. Indoor air (n=125), dust (n=250), and serum (n=250) samples
29 were collected from five major e-waste hubs and their vicinity to measure 39 PCN congeners
30 using GC-ECNI-MS. \sum_{39} PCN concentrations in indoor air, dust, and serum (worker >
31 resident > children) samples ranged from 7.0 to 9583 pg/m³, from 0.25 to 697 ng/g, and from
32 0.15 to 401 pg/g lipid weight, respectively. Predominant PCN congeners in indoor air and
33 dust were tri- and tetra-CNs, while tetra- and penta-CNs were dominant in human serum
34 samples. The higher PCNs contribution was recorded at the recycling units, while the lower
35 was observed at the shops of the major e-waste hubs. Higher contribution of combustion
36 origin CNs in air, dust and human samples showed combustion sources at the major e-waste
37 hubs, while Halowax and Aroclor based technical mixture showed minor contribution in
38 these samples. Mean toxic equivalent (TEQ) concentrations of PCNs were 2.79E⁺⁰⁰ pg-
39 TEQ/m³, 1.60E⁻⁰² ng-TEQ/g, 8.11E⁻⁰¹ pg-TEQ/g, 7.14E⁻⁰¹ pg-TEQ/g, and 6.37E⁻⁰¹ pg-TEQ/g
40 for indoor air, dust, and serum samples from workers, residents, and children, respectively. In
41 our study, CNs- 66/67 and -73 in indoor air, dust, and human serum were the great
42 contributors to total TEQ concentrations of PCNs. This first base line data directs government
43 and agencies to implement rules, regulation to avoid negative health outcomes and suggests
44 further awareness in regard of provision of proper knowledge to the target population.

45

46 **Keywords:** Human serum; combustion activities; Halowax; Health risk; Distribution levels

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50 **Capsule:** Due to lack of data on production, screening, and profiling of PCNs, this is the first
51 study to investigate concentrations of PCNs in indoor dust, air, and blood serum at the major
52 e-waste recycling hubs in Pakistan where crude recycling methods were common and the
53 potential health risks to human via its non-dietary pathways exposure would experience. This
54 study results identified that Tri- to penta-CN_s were dominant in the environmental samples
55 and showed that higher PCNs contribution in the environmental samples was recorded by
56 Combustion based activities as compared to technical mixture based CN_s.

57

58 **1. Introduction**

59 Polychlorinated naphthalenes (PCNs) due to its wider chemical stability and flame
60 resistance properties dictate its selection for use in different products. They were
61 manufactured in different countries with different trade names (Falandysz, 1998). PCNs
62 were extensively practiced in the electric cables insulation, dielectric fluids, engine oil
63 additives, dyes production fungicides, wood preservatives and released as a result of coal
64 consumption (Kover, 1975; Falandysz, 1998; Falandysz, 2003; Helm and Bidleman, 2003;
65 Noma et al., 2004; Orlikowska et al., 2009; Wyrzykowska et al., 2009). They were also
66 produced in the industrial processes like chlor-alkali and metals (magnesium, aluminium and
67 copper) production (Kannan et al., 1998). Besides, other sources of PCNs are combustion/or
68 incineration process of e-waste and other wastes at different temperature ranges (Falandysz et
69 al., 2008; Jin et al., 2016) and to some extent use of PCNs in the PCB technical mixture
70 (Aroclor) formulation (Falandysz, 1998; Falandysz, 2003; Helm and Bidleman, 2003;
71 Falandysz et al., 2004; Taniyasu et al., 2005). Historically, 150,000 tons of PCNs have been
72 formulated worldwide and practiced extensively in variety of products since its first time of
73 production (Falandysz, 1998). But later on with the passage of time, PCNs' were considering
74 as detrimental to environment health and have been banned since 1977 and later on it was
75 deemed as persistent organic pollutants under consideration by Stockholm Convention (NRC,
76 2006). However, many studies reported the occurrence of PCNs at different environmental
77 matrices (Jaward et al., 2005; Hogarh et al., 2012; Fernandes et al., 2020) but still in most of
78 the developing countries, data on PCNs at different environmental compartments have not
79 been yet investigated or even very limited information's are available. Nowadays, e-waste
80 generation at the developed world and its import to the developing world is growing day by
81 day (Iqbal et al., 2015). Most of the developing countries even lacking safety measures for

82 the exposed population via e-waste derived toxic chemicals (such as PCNs) and no stringent
83 rules, and regulations still exist for its prevention and implementation.

84 The e-waste products have mainly their short life span and low quality materials usage (Khan
85 et al., 2019) that makes possible contaminants (PCNs) release to the associated environment.

86 Indoor dust and air has been widely used as an exposure marker, because many pollutants can
87 bind and travel through the aforementioned medium (Butte and Heinzow, 2002). Population/
88 or individual working and living at the e-waste sites or its vicinity makes a potential exposure
89 of pollutants especially PCNs via ingestion, absorption (dermal contact) and inhalation from
90 air and dust and further enhanced the risks to the intact population with havocs symptoms and
91 problems (Mercier et al., 2011; Dirtu et al., 2012; Ali et al., 2013; Khan et al., 2016, khan et
92 al., 2017). Human exposure to PCNs may lead to various chemical and physiological changes
93 (O'Connor, 1972). It has been identified that PCNs exposure to human may create detrimental
94 outcomes like skin problems, hepatotoxicity, teratogenicity, embryo-toxicity, and kidney
95 dysfunction (O'Connor, 1972; Fernandes et al., 2020).

96 In Pakistan, occupational hygiene and safety gear usage has been unnoticed, and occupational
97 exposure data were deficient at different environmental matrices (Kamal et al., 2012). As
98 PCNs exposure to human is declared as vital in regard of health concerns. Besides, the e-
99 waste materials collection: processing, burning, disposal and exposure risks and impacts on
100 human via non dietary pathways are totally unexplored. A detailed literature review disclosed
101 the absence of any structured study focussing on the investigation of potential health effects
102 associated with e-waste borne-PCNs in Pakistan. Very limited literature regarding PCNs in
103 air is available but no research on PCNs in air at the selected e-waste sites from Pakistan
104 were carried out. On the basis of past literature review, data regarding PCNs in dust
105 environment is totally lacking. In Pakistan there was not available any stringent laws on
106 safety measures to human from e-waste exposure and its implementation is totally lacking or

107 very poor. Therefore, seeing this perspectives, the current study was designed with the
108 following objectives: To evaluate the selected PCNs concentration in indoor air, indoor dust
109 and human serum (workers, residents and children's) at the five major e-waste hubs and
110 further to develop the potential linkage of dominant PCNs congeners transfer via indoor dust
111 and indoor air to human serum. The technical mixture of Halowax and Aroclor were studied
112 for and compared with PCNs origin in air, dust and human serum samples.

113

114 **2. Materials and methods**

115 *2.1. Sampling sites description*

116 Five sampling sites from major and the most populated mega cities (Karachi, Lahore,
117 Peshawar, Rawalpindi and Gujranwala) of Pakistan were selected for collection of (dust, air
118 and blood samples) based on their e-waste processing activities as shown in Fig. 1. In
119 Karachi, Shersha is a well-known e-waste site that is a huge e-waste importer and recycling
120 centre in Sindh province, Pakistan, while Misri shah is located in Lahore (Punjab) famous for
121 large scrap electronic waste market and is recognized as one of Asia's largest scrap e-waste
122 hubs. Peshawar (located in Khyber Pakhtunkhwa) has also the e-waste reserves famous for
123 dismantling activities, while the other e-waste sites located in Rawalpindi (Punjab) and
124 Kamoke-Gujranwala (Punjab) were also recognised for e waste activities in open plots, roof
125 tops and congested areas with burning, acid dipping and part salvaging activities. E-waste
126 scraps origins in the aforementioned hubs were collected from different cities and localities
127 within the country and as well as abroad viz., Afghanistan, India, Iran, China, USA, Japan
128 and Europe etc. They were comprised of war debris, engines, pipes, train parts, ship anchors
129 and all sorts of electronic goods, spare parts, computers, and plastic wastes. These hubs have
130 a large numbers of registered and nonregistered factories, iron and steel industries, and

131 warehouses along with densely packed houses. The scrap recycling network has been
132 penetrated to the surrounding residential areas too (Saeed, 2013a,b).

133

134 *2.2. Sampling approach adopted for air and dust samples*

135 For collecting air samples at different e-waste sites, a specially designed Polyurethane foam-
136 passive air samplers (PUF-PAS) were prepared. The air sampler design detail was given by
137 Jaward et al. (2005). The PUF-PAS was pre-cleaned for 24 h with DCM in a Soxhlet
138 extraction system and subsequently with acetone for 48 h. Thereafter, the PUF-PAS was
139 dried completely in desiccators and stored in amber glass bottles.

140 A total of 125 PUF-PAS were fixed for a total period of eight weeks in the indoor
141 environment at the selected sites. To check any contamination contents during transport or
142 field deployment stage, eight PUF-PAS were specified for this purpose. About 25 PUF-PAS
143 were deployed at each e-waste hub, where recycling processes were carried out in
144 warehouses (n=5), shops (n=5), and dumping areas with a small sitting office (n=5), as well
145 as, for instance, recycling kilns/units (n=5) and residential areas (n=5) were also penetrated in
146 the recycling area.

147 A total of two hundred and fifty (n= 250) indoor dust samples were collected from
148 five major e-waste hubs in Pakistan and from each site (n=50) samples were collected.
149 Furthermore, indoor dust samples were collected from the same sites from where passive air
150 samplers were deployed in the following pattern as: warehouses (n=10), shops (n=10), and
151 dumping areas with small sitting offices (n=10), recycling kilns/units (n=10) and residential
152 areas (n=10) entangled in the e-waste hubs. Pre-cleaned disposable plastic brushes and pans
153 were used regularly each time to collect the dust samples to avoid any cross-contamination
154 into the sample. Indoor dust samples were collected from floor by brushing 5 to 7 m² area in
155 each site. Furthermore, the dust sample was grounded into homogenised powder with the

156 help of mortar and pestle and then passed through 500 μm mesh sieve to avoid large particles,
157 hair and debris intrusion. All the collected dust samples were wrapped in aluminium foil to
158 protect them from any changes and packed in labelled zipper bags till further analysis.

159

160 *2.3. Blood sampling*

161 Total blood samples (n=250) were collected from adult and children's population
162 working in e-waste sites (shops/godowns), residential areas in the vicinity of five e-waste
163 sites of Pakistan. The details of the human blood sample collection were as: worker (n=95);
164 resident= (85); male child (n=70) from overall 5 e-waste sites, Pakistan. Information's
165 regarding age, body height, body mass, smoking habits, occupational history, working hours,
166 and disease history were obtained from a selected observational population in a questionnaire
167 survey. With the help of a trained medical staff, blood samples including whole blood and
168 serum were obtained in marked vials specified for collection. Afterwards, careful
169 transportation and storage was done using mobile cold kits and the samples for serum were
170 kept in refrigerator at temperature of 4°C till further analysis. Serum was collected in yellow
171 top vacutainers to assess PCNs concentrations. Approval for working on human
172 authorization was given by the ethical approval committee (EAC, QAU) Islamabad, Pakistan
173 before commencement of the study. All the samples (air, dust and human blood) for PCNs
174 analysis were transported to the Centre for Chemicals Management, Lancaster Environment
175 Centre, Lancaster University.

176

177 *2.4. Extraction and clean-up procedure for dust and air samples*

178 A 5 g dust sample and the whole PUF-PAS samples were subjected to the extraction
179 process. The Soxhlet extraction procedure was carried out by adding 100 ml of DCM solvent
180 to dust and PUF-PAS samples for total time period of 19 hours. The homogenized solution

181 for dust and PUF-PAS prior to extraction process was spiked with Surrogate Standard of
182 isotopic ^{13}C - labelled trans-chlordane. After soxhlet extraction process, the solvent volume
183 (DCM=50 ml) was reduced up to 2 ml by using rotary evaporator at temperature of 25-35°C
184 and vacuumed pressure (300-500 m Bar). The extract was transferred to an amber vial for
185 solvent exchange phase with addition of 15 ml of hexane. The volume was reduced further up
186 to 0.4 ml by blowing the extract under a nitrogen stream. The extract was cleaned by column
187 packed from bottom to top with 1 cm sodium sulphate, neutral alumina and neutral silica gel
188 (both layers of 3cm, 3% deactivated), 50 % sulphuric acid silica layer of 3 cm and anhydrous
189 sodium sulphate (1 cm). The column for each sample was eluted with 50 ml of DCM/ hexane
190 (1: 1) solution. However, the volume was further reduced up to 30 μl under a gentle nitrogen
191 stream. The polychlorinated biphenyls (PCB) congeners isotopic labelled of $^{12}\text{C}_{12}$ PCB-30 and
192 $^{13}\text{C}_{12}$ (PCB-141) were prepared in dodecane and added as internal standard. PCNs were
193 analyzed by using Agilent 7890A GC-ECNI-MS (Gas Chromatography-Electron Capture
194 Negative Ion-Mass Spectrometry) in selected ion monitoring (SIM) mode. Column
195 specifications DB-5MS with film thickness of (30 m \times 0.25 mm i.d. \times 0.25 μm) was used for
196 separation of PCNs compounds, while methane was used as a reagent gas. Initially, the oven
197 temperature was set initially at 80 °C for 0.5 minute, 15 °C per minute to 160 °C, 3 °C per
198 minute to 240 °C, and 6 °C per minute to 270 °C for 10 min. The MSD source temperature
199 was set up to 230 °C and the quadruple temperature was fixed at 150 °C. The technical
200 Halowax 1014 mixture of PCNs was used as quantification standard. The PCN congeners
201 analyzed were: CN-14, -15, -16, -17/25, -19, -24, -23 (tri-CN_s); CN-33/34/37, -42, -47, -
202 36/45, -28/43, -27/ 30, -39, -32, -35, -38/40, -46 (tetra-CN_s); CN-52/60, -58, -61, -50, -51, -
203 54, -57, -62, -53, -59, -49, -56 (penta-CN_s); CN-66/67, -64/68, -69, -71/72, -63, -65 (hexa-
204 CN_s); CN-73, -74 (hepta-CN_s); CN-75 (octa-CN).

205

206 *2.5. Extraction and clean-up for Serum*

207 The extraction and clean up procedure for PCNs analysis in human blood samples
208 (20 ml) was adopted with little modification from study of Park et al. (2010). The ECN-5102,
209 a mixture of (³C₁₀-CNs -27, -42, -52, -67, -73, and -75) (Cambridge Isotope Laboratories,
210 Inc., U.S.A.) was used as an internal standard for spiking the thawed serum. The serum
211 samples were left for about 10 hours after maintaining the equilibrium position by vortex
212 mixing. Acetone and hexane in 2:1 were used to extract the samples. The organic phase was
213 exclusively washed with sodium oxalate and hexane and the extracted volume was reduced
214 under a gentle nitrogen stream. The clean-up was done using a column layered with silica and
215 alumina at the top and bottom layered with 1 cm of sodium hydroxide. The volume was
216 reduced until 1.5 ml was left under the nitrogen stream. Recovery standard (E-D 910) named
217 as 1,2,3,4-tetrachlorodibenzo-p-dioxin (¹³C₆) (Cambridge Isotope Laboratories, Inc., U.S.A.)
218 and nonane solvent keeper were added before transfer into the final vial. The final extract was
219 dried and concentrated into 30 µl for final injection into the high resolution GC-MS (HP 6890
220 gas chromatograph coupled with a JEOL- 800 D mass spectrometer). The PCNs were
221 analyzed using a DB5-MS column with specifications (60 m length, 0.25 mm I.D. and 0.25
222 µm film thickness). The ion source was kept in 280 °C, and ionization was performed with
223 electron impact mode. ECN-5489 was used as a calibration standard. The linear relative
224 response factor (R² for linear RRF) was more than 0.99.

225

226 *2.6. Quality control and quality assurance QA/QC*

227 Analytical grade solvents; hexane, DCM, nonane, isooctane and acetone were used
228 throughout the laboratory experiments. Glassware including round bottom flasks, soxhlet
229 extractors and flasks were rinsed with acetone and backed for 8 to 10 hours at 480 °C prior to
230 analysis. The analytical procedure was examined using strict quality assurance and control

231 measures. The calibration standards were prepared in hexane for PCNs congener
232 determination and were run after every 10 samples to determine the instrument accuracy or
233 precision. Laboratory blanks and field blanks were extracted and analysed in the similar way
234 as the real material samples except the present of sample in it. All the PCNs were not
235 detected in the blank samples except for PCN-49 that was detected in both air and dust
236 blanks. Surrogate recoveries were recorded to be 69-85% and 60-81% for dust and air,
237 respectively. The method recoveries were detected with a working standard (containing all 39
238 PCN congeners) and by spiking the PUF disks and 8 dust samples. To check the instrumental
239 accuracy quality control standards after every eight samples being run on the instrument. The
240 detected peaks were only integrated where the signal to noise ratio was more than 3; if not,
241 they were measured as non-detected. For human serum samples, ECN-5489 was used as
242 calibration standard. The linear relative response factors (R^2 for linear RRF) were more than
243 0.99. The error of isotopic ratio between two selected ions was less than 13%, and the
244 recovery of all ^{13}C -labeled compounds ranged 30–110%. The limit of detection (LOD) for
245 instrument was determined with 3 times signal to noise ratio, and they were reported as 57,
246 105, 64, 192 and 227 pg/g lipid for tri- to octa- CN, respectively.

247

248 *2.7. Statistical analysis*

249 The normality of the data set was first determined by performing the K-S
250 (Kolmogorov–Smirnov) test. Descriptive statistics such as mean, range and standard
251 deviation were plotted on SPSS 19. The one way analysis of variance (ANOVA) was used for
252 comparison among different e-waste site to evaluate the degree of significance among the
253 concentration of PCNs. The values with probability ($p < 0.05$) were considered to be
254 statistically significant. Correlation analyses were performed using Statistica 7. ARC GIS
255 software was used for locating the sampling sites and localities on map.

256

257 3. Results and Discussion

258 3.1. PCNs occurrence, spatial distribution and combustion sources in indoor air

259 Indoor air contaminated with PCNs has been considered as a health risk for human
260 population via different exposure pathways living in occupational cohorts or people residing
261 near contaminated environments. Descriptive statistics of the analysed PCNs (thirty-nine
262 congeners) concentration in indoor air (overall sites) from the e-waste hubs in Pakistan are
263 summarized (Table 1). The individual congener concentrations for PCNs were ranged from 7
264 to 9538 pg/m^3 . The congeners (tri to octa CNs) analysed were detected in all of the indoor air
265 samples. Tetra-CNs were the leading one with 39% dominancy followed by tri-CNs (25%),
266 penta-CNs (22%), hexa-CNs (8%), hepta and octa-CNs (3%) (Fig. 1). Comparatively, the
267 high prevalence of tri- and tetra- chlorinated naphthalenes, totalling 64% in the studied area,
268 might indicate the breaking process of higher chlorine containing congeners at different
269 environmental conditions over there. Literatures also support emission of less chlorinated
270 CNs (tri- to tetra- homologs) that results from various industrial thermal or burning practices
271 of wastes (Liu et al., 2014). However, there is no available study regarding PCNs
272 concentration and distribution at e-waste sites or potential industrial sites (iron ore, cement,
273 and metallurgy) from Pakistan and that makes it difficult to compare with concentration
274 profile of the current study. But few studies regarding PCNs profile in air samples from
275 Pakistan showed similar homologue patterns with tetra-CNs dominancy was observed by Ali
276 et al. (2016) and Mahmood et al. (2014) from Pakistan and Hogarh et al. (2012) from Ghana.
277 Among all the studied PCNs, CN- 35, CN- 39 (tetra-CNs) and CN- 51 (penta-CNs) congeners
278 were the most dominant with average highest concentration of 5138, 4574 and 4773 (pg/m^3),
279 respectively and reflecting their origin from combustion practices. Most of the information's
280 regarding electronic gadgets, PVC coated wires, scrap collections and burning from the five

281 major e waste hubs have been observed through surveys and field sampling campaigns. Iron
282 foundries were also present within the scrap yards and could be considered as potential
283 contributors of PCNs in the environmental samples. The organic impurities in scraps could be
284 an important factor to explain the occurrence of CNs as combustion origin. Most of the
285 studies reported that high thermal processes like municipal solid waste and e-waste
286 incinerations, metal refining and iron steel sintering processes were the culprit for PCNs
287 emissions (Liu et al., 2012; Yamashita et al., 2000; Falandysz, 1998; Abad et al., 1999).

288 **Table SI- 1** provides spatial distribution of PCN congeners in indoor air at the five (5)
289 major e-waste recycling/or processing sites. But the general dominant homologue patterns of
290 PCNs at the five e-waste hubs were ranked as: tetra > tri > penta > octa (Fig. 2). The highest
291 concentration in air samples were recorded at GUJ (6126 pg/m³; CN- 51) followed by LHR
292 (6038 pg/m³; CN- 17/25), KRC (5958 pg/m³; CN- 16), PESH (5164 pg/m³; CN- 51) and
293 RWP (4940 pg/m³; CN- 17/25). The concentration of CNs at different sites mainly depend on
294 the sites characteristics regarding the waste quantity, waste composition and nature, and
295 practices like burning at different temperature. However on other hand, the CNs properties
296 (both physical and chemical) itself and the environmental factors like temperate, humidity,
297 wind etc. also influence the CNs concentration and distribution at different sites of the study.
298 All sampling sites are located in major cities that are intensely populated with a rising trends
299 in the usage of electronic gadgets and enhanced e-waste generation and industries like iron,
300 steel, aluminium, copper, zinc, carbonless copy paper, and plastic) were also present over
301 there (Raza, 2010; Iqbal et al 2015; Saeed, 2013a,b). The concentration reported in our study
302 also attributed to open burning and dumping of domestic waste as shown in **Fig. SI-1** and
303 lack of stringent regulations and implementations in our country.

304 The concentration of PCNs reported in the current study were higher than the studies
305 from Pakistan at the industrial/urban and agricultural/rural areas (4.9-140 pg/m³); river

306 Chenab (1-1588 pg/m³) and Indus River basin (1222-5052 pg/m³) (Xu et al., 2014; Mahmood
307 et al., 2014; Ali et al., 2016). The above studies conducted were not from e-waste sites but
308 due to lack of literature, it was compared with PCNs in air samples at different sites of
309 Pakistan. Our reported concentrations were also higher than studies reported from India (nd-
310 31 pg/m³); America (0.19-3.4 pg/m³) and Ghana (27-95 pg/m³) (Manodori et al., 2006; Xu et
311 al., 2014; Hogarh et al., 2012). For large e-waste hubs and indoor air samples, higher PCNs
312 concentrations were reported during waste burning and incineration in industrial processes as
313 compared to our study results (Liu et al., 2012; Nie et al., 2012 a,b; Jin et al., 2016).
314 Furthermore, a previous study from a manufacturing site (150-1400 ng/m³) and at potential
315 user site (10-33 ng/m³) in Augsburg Germany reported far higher concentrations of PCNs
316 (Dorr, 1996) than our study results. However, concentrations and emission factors reported
317 from industrial processes could be useful for understanding the PCNs formation mechanisms
318 (Ba et al., 2010; Liu et al., 2010; Hu et al., 2012). Previous studies showed that raw material
319 or waste containing (PVCs or acids) and high temperature are the factors influencing the
320 formation patterns of PCNs. The studied sites signify clear accomplishments of point to
321 potential sources of PCNs as combustion origin in the environment.

322 The combustion related PCNs, such as CN- 36/45, -39, -35, -50, -51, -54, -62, -49, -
323 66/67, -73, described by Helm et al. (2006), and Hogarh et al. (2012) were produced during
324 thermal processes. The abovementioned PCNs are true indicators of combustion attributes
325 (Lee et al., 2007; Meijer et al., 2001). In the current study, combustion origin CNs was in
326 higher percentage viz., KRC (50.9%), GUJ (50.1%), LHR (48.8%), PESH (45.6%), and RWP
327 (44.7%). However, there are congeners (CN- 23, CN- 33, CN- 59, and CN- 33, -34, -37 and
328 CN- 46) that contributed towards the technical mixture or Halowax or polychlorinated
329 biphenyls (PCB) mixtures (Falandysz, 1998; Hogarh et al., 2012; Hanari et al., 2013). The
330 percentage contribution of technical mixture based PCNs were CN- 23 (1.7%) CN- 59 (0.2%),

331 CN- 33/34 (1.2%) and CN- 46(1.46 %). Furthermore, CN- 52/60 is considered as technical
332 mixture based CNs based on their presence in Halowax 1001 and 1014. (Falandysz et al.,
333 2006; Hanari et al., 2013). In the current study technical mixture contributed by 0.3%. It is
334 clear from results that technical mixture based CNs has least contribution towards overall
335 PCNs congeners analyzed.

336 Combustion or Halowax technical mixture based source contribution can be estimated
337 by applying the formula [Σ comb (combustion) PCNs/ Σ PCNs *100] given by Lee et al.
338 (2007). It was inferred that the fractions below 11% depict the PCNs source based on
339 Halowax, whereas the fraction more than 50% reflects combustion origin, including
340 electronic, municipal, medical waste incineration and iron sintering processes and the fraction
341 lies between 11 to 50 indicating mixed sources (combustion plus technical mixtures) (Hanari
342 et al., 2013). In this study, percentage calculation based on Σ comb (combustion) PCNs/ Σ
343 PCNs *100 (detail given in (Text SI- 1), showed 44-58% in air samples. However, the
344 combustion related congeners were very high in their own homologue group and they are
345 comprised of 56 to 96% for indoor air.

346 In addition to Halowax, the PCB technical mixture (TM) viz., (Aroclor 1016, Aroclor
347 1232, Aroclor 1248, Aroclor 1254, Aroclor 1260, and Aroclor 1262; KC-400, KC-500, KC-
348 600, Sovol, Chlorofen, Clophen A40, Clophen T64, Phenoclor DP3, Phenoclor DP4,
349 Phenoclor DP5 and Phenoclor DP6 were reported in literature and as the important
350 contributors of PCNs (Yamashita et al., 2000; Orlikowska et al., 2009). Literature also
351 reported that the USA and UK were the primary users of Aroclor TM (Giesy and Kannan,
352 1998), while Clophen and Phenoclor were manufactured in Germany and Italy, respectively
353 (Falandysz and Szymczyk, 2001). PCNs input from these PCB based TM tracks the import
354 fingerprints of second hand electronic gadgets or e-waste from developed economies
355 (Nordbrand, 2009). As PCNs were present in PCB technical mixtures, and the source

356 contribution was studied by using the homologue profile of CNs verses PCB technical
357 mixtures as shown in Fig. SI- 2. The composition profiles of PCNs in the studied matrices
358 were not exactly matched with the composition profile of specific TM (technical mixtures of
359 Halowax and PCBs). It was observed that the Halowax 1013, Aroclor 1016 and 1232 profiles
360 resembled quite little with the current studied PCNs profile, as described in Fig. SI- 2. It is
361 difficult to trace the formulators or user countries of the aforementioned technical mixtures
362 that they could be either responsible for exporting polychlorinated biphenyls (PCBs)
363 encompassing equipment or other items to the developing world.

364

365 *3.2 PCNs occurrence, spatial distribution and combustion sources in indoor dust*

366 The PCNs concentrations in overall sites of indoor dust were ranged from 0.25 to 697
367 ng/g (Table 1). Among the studied congeners in dust, tetra-CNs (38%), and tri-CNs (26%)
368 were the most dominant ones with highest percentage followed by penta (22%), hexa (8%),
369 hepta (3%) and octa (3%) -CNs (Fig. 1). However, CN- 36/45 and CN- 62 were the most
370 abundant congeners with average concentrations of 164 and 141 (ng/g), respectively.
371 Different studies regarding PCNs concentration in soil revealed a similar pattern of the tetra-
372 and tri- CNs congeners' dominancy in Pakistan, China, Ghana and other countries (Helm et
373 al., 2004; Jaward et al., 2005; Herbert et al., 2005; Lee et al., 2007; Ishaq et al., 2009; Pan et
374 al., 2013; Hogarh et al., 2012; Mahmood et al., 2014; Ali et al., 2016). Dust PCNs data at the
375 e-waste sites are not available for comparison with other studies results and hence, it was
376 inferred that dust is a neglected environmental compartment for PCNs exposure studies. So,
377 this study highlights the first report on the occurrences of PCNs in the indoor dust samples
378 collected from different e-waste sites in Pakistan. Moreover, PCN profile in dust is
379 comparable or higher than the soil PCNs concentration reported from studies of the Pearl

380 River Delta (9.5-666 ng/g); Eastern Tibet, China (13-29 ng/g) by Wang et al., (2012) and Pan
381 et al. (2013), respectively. Individual concentration of PCNs in dust were far higher than the
382 reported soil content along the Indus River (0.02-23 ng/g) and Chenab River tributaries (25-
383 233 ng/g) by Ali et al. (2016) and Mahmood et al. (2014). The high level of PCNs is not
384 surprising, since these chemicals were being used in electronic gadgets long ago. During the
385 salvaging and burning processes, the aforementioned congeners get detached and find their
386 ways into the environment especially dust. So the dust provides an excellent medium for the
387 adherence of chemicals like PCNs.

388 **Table SI- 2** provides spatial distribution of PCNs congeners in dust at the five major e-waste
389 hubs. The highest mean concentration was reported from KRC (466 ng/g) followed by GUJ
390 (363 ng/g), PESH (184 ng/g), RWP (169 ng/g) and LHR (103 ng/g). The higher PCNs
391 concentration in KRC (dust) is explained by its huge scraps
392 e-waste collection and their import from other countries and neighboring cities as well
393 (Saeed, 2013a). Another reason may be the high humidity in the indoor air over there that
394 favors the deposition of the PCNs from air to dust. The highest concentration was reported by
395 CN- 36/45 and CN- 62 at KRC and GUJ, respectively, while CN- 16 was recorded by LHR,
396 RWP and PESH having their origin from combustion activities. A homologue pattern
397 observed in the studied sites was: tetra > tri > penta > hexa > hepta and octa CNs (**Fig. 2**). By
398 visualizing the whole data set of CNs in dust, it was conceded that low to medium chlorinated
399 naphthalenes (tri plus tetra congeners) contribute higher (64%) toward the compositional
400 profile. The higher percentage contribution was recorded by CN- 36/45 (5.34%), CN- 62
401 (4.58%) and CN- 16 (4.21%). The combustion related CNs (as given in detail in the Text SI-
402 1) showed 16-52% in dust samples. However, the combustion related congeners were also
403 high in their own homologue group and comprised of 45 to 69% in dust. In contrast to
404 combustion based CNs, congeners of Halowax based origin were comparatively very low in

405 their percentage contribution to the congeners analysed viz., CN- 23 (2.48%), CN- 33/34
406 (2.64%), CN- 46 (3.9%) and CN- 52/60 (2.08%). The literature revealed that combustion
407 carried out for metal refining, iron, steel production and waste incineration leads to the
408 release of PCNs (Kim et al., 2005; Ryu et al., 2013; Liu et al., 2014). Polychlorinated
409 biphenyls (PCBs) present in electronic equipment's also lead to PCNs generation in trace
410 quantities (Helm and Bidleman, 2006; Odabasi et al., 2010). Besides, household combustion
411 activities and wood preservation via chlorine were another potential CNs sources
412 (Wyrzykowska et al., 2007; Wyrzykowska et al., 2009).

413

414

415 *3.3. Site activity based PCN distribution levels in the indoor dust and air of e-waste hubs in* 416 *Pakistan*

417 Among the studied PCNs in the indoor dust at five processing units, the **highest**
418 **concentration was reported at the recycling units followed by ware houses, dumping areas,**
419 **residential areas and shops (Table SI- 3).** But the highest percentage contribution was
420 recorded by CN- 19 (9.7%) at recycling units, CN- 62 (6.5%) at shops, CN- 62 (5.7%) at
421 residential area, CN- 36/45 (11.5%) at ware houses and CN- 16 (7.9%) at dumping areas (**Fig.**
422 **SI- 3).**

423 The mean concentration of 39 CNs analysed in indoor air at the five processing units
424 of e waste are given in **Table SI- 4** , and recorded higher concentration at the recycling units
425 (6199 pg/m^3) followed by residential areas (5893 pg/m^3), dumping areas (5281 pg/m^3), ware
426 houses (5063 pg/m^3) and shops (4829 pg/m^3). The percentage contribution comparison
427 revealed that highest contribution was recorded by CN-35 (10.4%) at the recycling units, CN-
428 35 (11.8%) at residential areas, CN- 35 (9.6%) at dumping areas, CN-51 (9.56%) at shops

429 and CN- 17/25 (10.6%) at ware houses **Fig. SI- 4**. The percentage contribution of combustion
430 origin CNs was quite high as compared to the technical mixture CNs. Hence, the combustion
431 CNs were present highest at the recycling units (58%) followed by ware houses (42%),
432 residential areas (33%), dumping areas (25%) and shops (21%). The highest concentration
433 and contribution of PCNs in air and dust samples at the recycling units, reflects its higher
434 disintegration/degradation, and burning activities over there. The other reason might be the
435 presence of such huge quantities of wastes (e-waste and other wastes) as compared to other
436 processing units. According to literature, the high temperature at the processing units and raw
437 materials in the e-waste products are important factors that facilitate the formation of CNs.
438 As the recycling units or kilns were operating at different temperature ranges between 200 to
439 700 °C that can release the target CNs into the environment (Jansson et al., 2008; Jiang et al.,
440 2015; Jin et al., 2016). Different wastes may contain aromatic hydrocarbons, naphthalenes
441 and chlorphenol, coke that can act as a precursor for the formation of PCNs (Lino et al.,
442 1999; Kim et al., 2005; Liu et al., 2010; Liu et al 2013; Ryu et al., 2013). Jin et al. (2016)
443 have reported that temperature, feeding materials and chlorine contents in co-processing
444 wastes of cement kilns result in PCNs concentration variation at different stages. They also
445 identified that chlorination and de-chlorination were the key pathways for the formation and
446 decomposition of PCNs. At the residential areas of the study area, cooking and coal practices
447 were the other potential sources of PCNs.

448 Contrary to expected individual congener distribution patterns at different processing
449 units of e waste, hence the uniform patterns of CNs dominance from combustion activities
450 were observed. The possible reason for the dominance of combustion CN origin is the
451 burning of e waste, scrap metals, and PVC etc. at the recycling units, dumping areas and ware
452 houses. All the e waste hubs were penetrated in congested areas with houses and shops. Some
453 segregation of e waste processing was done in studied units but they were not far away or

454 sealed. However, different activities taken place in one processing unit could affect the other
455 unit by air currents and dust in air associated with target PCNs.

456 3.4. PCNs concentration profile and sources in serum samples

457 The PCNs concentration analysed in human population serum at the five e-waste hubs
458 are; workers (1.12 to 401 pg/g lipid), childrens (0.25 to 302 pg/g lipid) and residents (0.15 to
459 313 pg/g lipid) 3123 pg/g lipid as shown in Table 2. The highest mean PCNs concentration
460 was recorded in workers followed by residents and children highlighting their exposure time,
461 intensity and distance from the e waste sites. The tetra- and penta- CNs were dominant in all
462 the exposed subjects. The tetra CN- 38/40 being the leading congener, added 19% of the total
463 CNs detected in the human serum samples (Fig. 2). The hepta CN- 73 was the dominant
464 congener having contribution of 19% and 24% in the resident and child groups respectively,
465 shown in Fig. 2. Hepta and tetra-CN's predominancy among the other congeners in the
466 exposed populations were evident in the available studies (Park et al., 2010). The penta-,
467 hexa- and tetra- congeners were the dominant CNs detected in previous studies of human
468 biological matrices including plasma, liver, milk and fat tissue (Kunisue et al., 2009; Lunden
469 and Noren, 1998; Haglund et al., 1995; Witt and Niessen, 2000; Weistrand and Nore'n,
470 1998). Weistrand et al. (1997) also reported that penta- and hexa- CNs as the predominant
471 congeners in human serum. However, no significant variation was recorded among the
472 exposed verses control subjects. The concentrations found for CN- 52 and CN- 67 were 214
473 and 198 (pg/g lipid), respectively, in the 6 exposed and 5 control subjects. Relatively higher
474 Σ PCNs concentrations ranging from 318 to 5360 pg/g lipid in four different exposed groups
475 in the USA were reported (Horii et al., 2010; Kannan, 2015). A significantly high
476 concentration of CN- 66/67 i.e., 30,400 pg/g lipid, was reported from the subjects exposed of
477 the Yu-Cheng incident (Rayan and Masuda., 1994). The levels of PCN found in our study
478 were comparable to or lower than the abovementioned studies. However, our results were

479 higher than a study by Herman et al., (2015), who selected blood samples randomly from the
480 German population aged 20-68 years old.

481 In the human serum (worker, resident, child) there was dominance of tetra-, penta- and hepta-
482 CNs, highlighting their Halowax and Aroclor mixture origin. Out of the total CNs, the CN
483 combustion origin percentage was 67% in workers, 70% in residents and 69% in the children.
484 Significant variation was observed among the studied groups for congeners CN- 42, -38/40, -
485 50, -54, -57, -49, -69, -63, -73 and CN- 75. In the current study the elevated CNs combustion
486 percentage reflects the increased combustion activities at the e-waste processing places. The
487 potential burning sources were electrical cables, computer motherboards and electronic
488 gadgets. In addition to the CNs combustion origin, the Halowax, a stockpiled/imported and
489 mistakenly used in Japan in early 2000 as the PCNs mixture of other type (Falandysz et al.,
490 2008; Yamashita et al., 2003) and PCB technical mixtures (Aroclor 1016, Aroclor 1232,
491 Aroclor 1248, Aroclor 1254, Aroclor 1260, and Aroclor 1262) were the major contributors of
492 PCNs (Orlikowska et al., 2009; Yamashita et al., 2000). The compositional profile of PCNs
493 in the exposed subjects serum trace the unintentional CNs production and least contribution
494 via volatilization of Halowax and PCBs encompassing gadgets during combustion of e waste
495 and coal

496

497 *3.5. TEQ tendency in Environmental samples (air, dust and serum)*

498 Keeping in view that PCNs resemble dioxins based on chemical structure and the
499 same receptor triggering pathway i.e., aryl hydrocarbon (AhR), which induces biochemical
500 changes, and the toxicological implication of PCNs in the dust, air and serum were evaluated
501 (Villeneuve et al., 2000). Overall, the TEQs for dust samples from the studied area were
502 calculated by means of the PCNs CN- 17/ 25, -42, -36/45, -27/30, -38/40, -52/60, -61, -50, -
503 54, -57-53, -56, -66 / 67, -64 /68, -69, -71 72, -63, -73, -74 and CN- 75. The available toxic

504 equivalence factors (TEFs) and relative potency factors (RPFs) were used by Falandysz et al.
505 (2014); Park et al. (2010); Blankenship and Giesy, (2002); Blankenship et al. (2000); and
506 Villeneuve et al. (2000) as given in **Table SI- 5**.

507 The TEQs values for indoor air and indoor dust at different e-waste sites are presented in
508 **Table 3**. The minimum and maximum TEQ values for indoor dust and indoor air samples at
509 different e-waste sites were ranges between $3.78E^{-08}$ (CN- 61) to $3.35E^{-01}$ (CN- 69) ng-TEQ/g
510 and $2.94E^{-06}$ (CN- 61) to $1.65E^{+01}$ (CN- 73) Pg-TEQ/m³, respectively (**Table 3**). However, the
511 TEQ values for comparison with other studies in dust in regard of PCNs congeners are
512 lacking and therefore the data was compared with the existing studies on TEQs for PCNs in
513 the soil. The mean TEQ values calculated for dust in the current study ($1.60E^{-02}$ ng TEQ g⁻¹)
514 were higher than Qinghai Plateau soil in China, 0.001 pg TEQ/g), Indus River basin soil
515 ($4.6E^{+00}$ - $3.6E^{+01}$ pg TEQ/g), and the Chenab canals soil (2.6 pg TEQ g⁻¹) (Pan et al., 2013;
516 Ali et al., 2016 ; Mahmood et al., 2014).

517 Our mean TEQ values calculated (see **Table 3**) for indoor air samples ($2.79E^{+00}$ pg TEQ m⁻³)
518 from the major e-waste hubs of Pakistan were higher than studies from the Indus River basin
519 Pakistan ($2.3E^{-04}$ - $1.1E^{-03}$ pg TEQ m⁻³), Chenab River tributaries (0.5 pg TEQm⁻³), Ghana air
520 ($2.1E^{-03}$ pg TEQm⁻³) and urban zone of Dongjiang China ($6.7E^{-03}$ pg TEQ m⁻³) (Ali et al.,
521 2016; Mehmood et al., 2014; Hogarh et al., 2012; Wang et al., 2012).

522 Generally, CN- 66/67 and CN- 73 added a greater amount in air (37.14%) and dust (31.09%)
523 to the total TEQ in the case of indoor dust samples. For the major e-waste hubs of Pakistan,
524 dust contributed greater toxicity than air.

525 The average TEQ calculated in workers ranged from $3.05E^{-06}$ (CN- 17/25) to $1.21E^{+00}$ (CN-
526 73) pg TEQ /g, while for resident and child it were $1.89E^{-06}$ (CN=17/25) to $8.95E^{-01}$ (CN- 73)
527 pg TEQ /g and $1.98E^{-06}$ (CN- 17/25) to $9.07E^{-01}$ (CN- 73) pg TEQ/g, respectively (**Table 4**).

528 The CN- 66/67 contributed a higher level in the worker and resident groups of $4.75E^{+01}$ and

529 7.55E⁺⁰², whereas CN- 73 reported the highest level of 8.75E⁺⁰² to the total TEQ in the
530 children's group. Our TEQ values are also reported higher than Park et al. (2010).

531

532 **4. Conclusions**

533 It was inferred from the current study results that the indoor dust and human serum samples
534 analysed for PCNs concentration in sighted for the first time in detected levels that may
535 cause human health issues via dust and air inhalation at the 5 unexplored e-waste hubs in
536 Pakistan and furthermore, signifying its exposure and health risks for the intact population.
537 Among the studied PCNs congeners, Tetra- and tri-CNs were the most dominant CNs in air
538 and dust samples, while tetra- and penta-CNs were recorded in higher levels in the exposed
539 human subjects. Overall, prevalence of combustion origin CNs in air, dust and human
540 samples revealed combustion sources at the processing units of different e-waste hubs, while
541 the Halowax and Aroclor based TM showed minor contribution to PCNs congeners' origin
542 into these samples. But industrial thermal processes, cooking and coal use were the other
543 combustion sources of PCNs at the different processing units. Based on the TEQ values, CN-
544 66/67 and CN- 73 were the predominant congeners in air, dust, and human serum samples.
545 This study directly suggests government a potential discourage plans and rigorous policies for
546 e-waste implementation to locate the hotspot and ban the illegal transportation, recycling of
547 e-wastes and burning activities for these and other wastes in the premises. Moreover,
548 awareness among the local population should be raised to highlights the negative prevailing
549 impacts on human health from the PCNs and other toxic chemicals at the e-waste hubs. This
550 study results will provide the first base line data in the environmental matrices (air, dust and
551 human serum samples) for PCNs concentration at the e-waste sites. Detailed health impact
552 studies and eco-friendly management options and remedial techniques should be introduced

553 to minimize the health outcomes from the e-waste derived PCNs and with other suspected
554 derived toxic chemicals.

555 **Acknowledgment**

556 The first author of the manuscript highly acknowledges the efforts of “Higher education
557 commission (HEC) of Pakistan” for the financial support under the scholarship of (IRSIP)
558 that may possible her Lab analysis abroad. The experimental work of the manuscript would
559 not be accomplished without mentioning the extreme support of “Centre for Chemicals
560 Management, Lancaster Environment Centre, Lancaster University, UK” team.

561 **Conflict of interest**

562 All the authors have declared that they have no competing interest.

563

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