

2 **assessment of VOCs emitted from manufacturing industries**

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12 **Abstract**

13 In this study, a few important manufacturing industries located in Central Taiwan were
14 studied ($n = 13$) for the emission of volatile organic compounds (VOCs), relative ozone
15 formation potential (ROFP) and relative carcinogenic risk (RCR). Higher emission
16 factors of total VOCs (\sum VOCs) were observed for stencil printing (423 mg-VOC kg⁻¹)
17 compared to other emission sectors. Alkanes formed the most dominant group of VOCs
18 for steel foundry (41.6%), aluminum foundry (25.1%) and synthetic resin
19 manufacturing (25.0%). However, for the chemical sector (synthetic and polyester
20 resin), oxygenated organics like acetone (55.7%) and ethyl acetate (79.7%) were the
21 predominant VOCs. Moreover, emissions from acrylic resin manufacturing had higher
22 contributions from aromatic compounds (> 95%). Toluene was the topmost compound
23 in terms of its contribution to \sum VOCs in plastic tape manufacturing (44.4%), aluminum
24 foundry (39.6%), steel foundry (11.6%), plastic coating (64.3%) and stencil printing
25 (35.3%). Analysis of ozone formation potentials showed that the metal product &
26 machinery acrylic resin manufacturing and stencil printing had a higher normalized
27 ROFP index and belonged to level-I emission sources. However, in terms of the RCR,
28 integrated iron & steel manufacturing had the highest normalized RCR index belonged
29 to level-I emission sources. Level-I represents the most important VOC emission
30 sources.

31 **Keywords:** Volatile organic compounds; Manufacturing sources; Relative ozone
32 formation potential, Relative carcinogenic risk, Potential source comparison.

33 **1. Introduction**

34 Manufacturing industries are the important stationary emission sources of air
35 pollutants worldwide. These emission sources have become one of the major
36 contributors to air pollution due to a substantial increase in industrial production [1–3].

37 The pollutants such as particulate matter, oxides of carbon, oxides of nitrogen,
38 polycyclic aromatic hydrocarbons and volatile organic compounds (VOCs) pose threats
39 to human health and the environment [4–7]. VOCs are of interest in part because they
40 participate in atmospheric photochemical reactions that contribute to ozone formation
41 [8]. Tropospheric ozone is formed by chemical reactions involving airborne VOCs,
42 airborne nitrogen oxides, and sunlight [9]. The oxidation products of VOCs may also
43 get absorbed by the atmospheric aerosols [10]. VOC lifespan in the atmosphere could
44 range from a few minutes to several months. So, some of the VOCs may travel over
45 large distances and enter human body mainly through inhalation or skin absorption
46 causing varieties of health effects [11]. Health effects can vary by types of VOC species
47 which include cancerous illnesses, respiratory irritation, central nervous system damage,
48 eye and skin irritation [12]. Several VOCs have been classified by the International
49 Agency for Research on Cancer (IARC) as Group 1 carcinogens for human [13].
50 Benzene, a known carcinogen, has been found to be a common byproduct of the
51 chemical manufacturing, petrochemical industries, production of xylene, toluene and
52 other aromatic compounds, printing sectors and industrial solvent usage [14,15].

53 Studies regarding VOC emissions from manufacturing sectors are still limited
54 [14,16–18]. The major VOC emission sources include fossil fuel combustion,
55 petrochemical, printing and solvent usage [16,17,19,20]. Wang et al. [20] studied the
56 distribution of VOCs emitted from solvent usage in furniture paint, auto paint and
57 printing ink. Their study indicated that the largest contributing groups among the
58 measured VOCs were aromatics (51.9%) followed by alkanes (31.8%) and alkenes
59 (16.3%). Yuan et al. [17] identified alkanes and aromatic compounds as the most
60 contributing groups in the printing sector. Tsai et al. [21] reported toluene, 1,2,4-

61 trimethyl benzene, m/p-xylene, 1-butene, ethylbenzene, and benzene predominantly
62 emitted from an integrated iron and steel plant located in Southern Taiwan.

63 Stack emissions from different industries might differ greatly in the VOC species
64 compositions. Thus, the emissions from different sources might play roles in
65 atmospheric chemistry and human health hazards in different ways. It is essential to
66 characterize VOC emission sectors, not only in terms of VOC emission concentrations
67 but also their chemical reactivity and associated health hazards. However, such works
68 are still limited for industrial emission sources. In this study, a few important industrial
69 emission sources were investigated on the basis of emission factors, relative ozone
70 formation potentials and relative carcinogenic risks of VOCs.

71 **2. Materials and methods**

72 *2.1. Description of emission sources*

73 In this study, the following thirteen types of VOC emission sources were selected:
74 organic solvent manufacturing, synthetic resin manufacturing, acrylic resin
75 manufacturing, polyester resin manufacturing, plastic tape manufacturing, aluminum
76 foundry, steel foundry, metal products & machinery industries, integrated iron & steel
77 manufacturing, non-ferrous metal-based manufacturing, polyurethane (PU) leather
78 manufacturing, plastic coating and stencil printing. All of the selected emission sources
79 were located within Taichung city, Taiwan. The sample industries were selected to
80 represent the major industrial emission sources located within Taichung city. The
81 selected emission sources contributed to 72.5% of total VOC emissions within the city
82 in the year 2016 (Taiwan EPA). The selected emission sources were grouped into the
83 following five sectors on the basis of U.S. EPA's North American Industrial
84 Classification System (NAICS): chemical manufacturing sector (NAICS 325), plastics
85 products manufacturing sector (NAICS 326), metals manufacturing sector: primary

86 (NAICS 331) and fabricated metal product manufacturing (NAICS 332), leather
87 manufacturing (NAICS 313) and printing and related support activities sector (NAICS
88 323).

89 The chemical manufacturing sector covers the transformation of organic and
90 inorganic raw materials by the chemical processes and the formation of products. The
91 plastic product manufacturing sector includes facilities that make goods by processing
92 plastic materials and raw rubber. The synthetic fiber industry involves the
93 manufacturing of cellulosic, noncellulosic, and polyester fibers. The metal (primary and
94 fabricated) manufacturing sector includes iron and steel industries, metal casting
95 industries, and nonferrous metal industries. The leather/textile manufacturing sectors
96 consist of establishments engaged in synthetic leather, spinning natural and manmade
97 fibers into yarns and threads. The printing sector include plastic coating, stencil printing,
98 plate-making and bookbinding. In this study, only the sintering process of integrated
99 iron and steel industry was investigated. Detailed information about selected emission
100 sources can be found in Table 1.

101 [Add Table 1]

102 2.2. VOCs sampling and analysis

103 VOC emissions from manufacturing industries can be categorized into fugitive
104 emissions and stack emissions. The current study was conducted only for stack
105 emissions. Emission samples were collected using 6 L fused silica stainless steel
106 canisters (Entech Instruments, Catalog# 29-10622) that had been pre-cleaned with high
107 purity-nitrogen and evacuated with an automated canister cleaner. A flow controller
108 and teflon tubing were used to extract the exhaust gas from emission stacks to the
109 evacuated canisters. The collected samples were analyzed with the Gas
110 Chromatography (7890) Mass Spectroscopy (5977B) system (GC/MS, Agilent

111 Technologies). The details of the GC/MS analysis is described elsewhere [22]. Internal
112 calibration method was applied for the quantification of the VOCs. A total of 72 VOC
113 species were quantified in this study (Table S1). Taiwan NIEA (National Institute for
114 Environmental Analysis) standard (A715.15B) was used as the external standard.
115 Bromochloromethane, 1,4-difluorobenzene, chlorobenzene-d5 and 4-
116 bromofluorobenzene (BFB) were used as the internal standards. Based on the functional
117 groups, these VOCs were classified as alkanes, alkenes, aromatics, oxygenated VOCs
118 and halocarbons. Emission factors of the detected VOC species were calculated for each
119 of the emission sources by using Eq. (1).

120

$$Emission\ factor = \frac{VOC\ con. \times Exhaust\ volume\ (dry\ basis)}{Raw\ material\ unit \times Sampling\ duration} \quad (1)$$

121

122 The calculated emission factor of each VOC species was normalized ($x_{i,j}$) to the
123 \sum VOCs emission factors in the source sample for each emission sources. The detailed
124 concentrations and emission factors can be found in Additional file 1 (Table S1 and
125 Table S2).

126 2.3. *Quality assurance and quality control (QA/QC)*

127 The canisters were pre-cleaned before sampling with ultra-pure nitrogen (99.999%)
128 to remove water vapor and contaminants. Canisters were cleaned for 12 cycles of filling
129 and evacuation using a canister cleaning system (3100A, Entech). Two replicate
130 measurements were done for each sample. The blank analysis was run before each
131 sample analysis.

132 2.4. *Relative ozone formation potential (ROFP)*

133 The absolute ozone formation potential (OFP) of VOC species is usually calculated
134 by multiplying the its concentration by its maximum incremental reactivity (MIR)

135 [23,24]. However, it is usually the relative importance of each VOC species in
 136 comparison with the other emission sources that is of more practical significance.
 137 Knowing the relative importance of different VOCs allows for targeting more reactive
 138 VOCs sources, hence more efficient and flexible for sources comparing strategies.
 139 Therefore, ROFP was calculated on the basis of the VOC emission factor (normalized
 140 to 1) and the MIR value of each VOC (Eq. 2).

$$ROFP_j = \sum_{i=1}^n x_{i,j} \times MIR_i \quad (2)$$

141 where, $ROFP_j$ is the relative ozone formation potential of VOCs for source j (g-O_3
 142 g-VOCs^{-1}), $x_{i,j}$ is the ratio of EF of VOC species i to ΣVOCs for source j , and MIR_i
 143 is the maximum incremental reactivity value of species i as proposed by Carter [25].

144 2.5. Relative carcinogenic risk (RCR)

145 The absolute carcinogenic risk is usually estimated by multiplying the actual VOC
 146 concentration and its carcinogenic risk factor [26]. However, to ensure comparability
 147 among different emission sources, carcinogenicity was calculated for each emission
 148 sources on a relative basis (Eq. 3).

$$RCR_j = \sum_{i=1}^n x_{i,j} \times UR_i \times f_i \quad (3)$$

149 where, RCR_j is the relative carcinogenic risk of source j (mg m^{-3})⁻¹, $x_{i,j}$ is the ratio
 150 of emission factor of VOC species i to ΣVOCs for source j , UR_i is the carcinogenic
 151 risk factor for VOC species i ($\mu\text{g m}^{-3}$)⁻¹, and f_i is the unit conversion factor. The U.S.
 152 EPA developed Integrated Risk Information System (IRIS) to provide carcinogenic risk
 153 factors for VOCs (Table S3).

154 2.6. Normalized ROFP and RCR

155 After obtaining the ROFP and RCR values for different emission sources, they were
156 sorted from high to low. The normalized ROFP (NROFP) index and normalized RCR
157 (NRCCR) index were calculated using the Eqs. (4) and (5).

$$NROFP_j = \frac{ROFP_j - ROFP_{min}}{ROFP_{max} - ROFP_{min}} \quad (4)$$

$$NRCCR_j = \frac{RCR_j - RCR_{min}}{RCR_{max} - RCR_{min}} \quad (5)$$

158 where, $NROFP_j$ is the normalized ROFP index of source j , $ROFP_{min}$ is the
159 minimum $ROFP_j$ among VOC sources, $ROFP_{max}$ is the maximum $ROFP_j$ among VOC
160 sources, $NRCCR_j$ is the normalized RCR index of sources j . RCR_{min} is the minimum
161 RCR_j among VOC sources, RCR_{max} is the maximum RCR_j among VOC sources.

162 3. Results and discussion

163 3.1. Emission factors

164 The \sum VOCs emission factors of manufacturing sectors are shown in Fig. 1. The
165 \sum VOCs emission factors of manufacturing sectors were observed to be ranging from
166 0.00267 mg-VOC/kg to 423 mg-VOC/kg. Among all sectors, the maximum emission
167 factors of \sum VOC were observed for stencil printing (423 mg-VOC kg⁻¹) followed by
168 plastic tape (24.9 mg-VOC kg⁻¹), metal product & machinery (10.3 mg-VOC kg⁻¹) and
169 organic solvent (4.42 mg-VOC kg⁻¹). For synthetic resin, acrylic resin, polyester resin,
170 integrated iron & steel, aluminum foundry, steel foundry, non-ferrous metal, PU leather
171 and plastic coating, \sum VOCs emission factors were found ≤ 1 mg-VOC kg⁻¹. Stencil
172 printing had the highest emission factor which could be due to the presence of large
173 amount of organic compounds, including, xylene, ethyl benzene and ethyl acetate in
174 printing inks [19]. Some other organic compounds such as acetate, glycolic acid butyl
175 ester, butyl glycol were also used in printing inks [27]. Printing inks are made up of
176 pigments, dyes, additives and carrier solvents. Different types of printing sectors have

177 variable ink flow properties, which range from extremely thin watery through highly
178 viscous to dry powder.

179 [Add Figure 1]

180 3.2. VOC species compositions

181 The VOCs emission factors have been expressed as the percentage of each species
182 relative to \sum VOCs emission factors. The identified VOCs were classified into the
183 following five categories: alkanes, alkenes, aromatics, halocarbons and oxygenated
184 VOCs. As presented in Fig. 2, alkanes formed the dominant VOC group in steel
185 foundry (41.6%), aluminum foundry (25.1%) and synthetic resin (25.0%). The higher
186 proportion of alkenes were observed for metal product & machinery (59.7%) followed
187 by other emission sectors. Zhao et al. [18] observed a high percentage of alkanes (25.6%)
188 followed by alkynes (15.5%), aromatics (13.6%) and alkenes (11.2%) in the emissions
189 from iron and steel sectors.

190 [Add Figure 2]

191 The higher proportion of alkanes and alkenes emissions indicates insufficient
192 oxidation of volatile components released from the fuels [23]. Chemical sectors such
193 as organic solvent and polyester resin manufacturing were found to have more than 75%
194 \sum VOCs contributed by oxygenated VOCs. Acrylic resin, plastic tape, integrated iron &
195 steel, plastic coating and stencil printing sectors showed the major fraction of \sum VOCs
196 contributed by aromatics (65.1% – 98.9%). Tsai et al. [21] reported the high abundance
197 of aromatic species, including, toluene, 1,2,4 trimethylbenzene, xylene and benzene in
198 the emissions from an integrated iron and steel industry. Yuan et al. [17] reported that
199 the aromatics were the most abundant VOC group in the emissions from solvent usage
200 in auto-painting, architectural painting and printing. The results provide only the
201 functional groups of VOCs for different manufacturing sectors. Detailed profiles of the

202 VOCs (top 5 contributors) for each manufacturing sector are presented in Table 2 and
203 discussed in the following subsections.

204 [Add Table 2]

205 3.2.1. *Chemical manufacturing*

206 The top five VOC species emitted from four chemical manufacturing sectors,
207 such as, organic solvent, synthetic resin, polyester resin and acrylic resin industries are
208 shown in Table 2. The VOC species emitted from organic solvent manufacturing were
209 mainly oxygenated VOCs, such as ethyl acetate and acetone, accounting for > 65% of
210 Σ VOCs. Methyl isobutyl ketone, toluene and isopropyl alcohol, accounted for a minor
211 fraction of Σ VOCs. Synthetic and polyester resin manufacturing sectors predominantly
212 emitted oxygenated VOCs like acetone (55.7%, 0.0228 mg-VOC kg⁻¹) and ethyl acetate
213 (79.7%, 0.0260 mg-VOC kg⁻¹). However, the acrylic resin industry had higher
214 contributions from aromatics (> 95% of Σ VOCs) such as *m,p,o*-xylene, ethylbenzene,
215 and toluene. Most organic resins are solvent-borne, which contain a mixture of organic
216 solvents, many of which are VOCs. The common solvents used in resins contain toluene,
217 xylene, benzene, ethyl ketone, and methyl isobutyl ketone. Acrylic resin is widely used
218 in paint formulations, and the paints emit predominantly aromatics compounds, such as
219 benzene, toluene, ethylbenzene and xylene [28,29]. However, polyester resin was found
220 to have the emission contributions mainly from oxygenated VOCs, as it is formed by
221 the reaction of dibasic organic acids and polyhydric alcohols [30]. The difference in
222 VOC emissions was probably related to the raw materials and products originating from
223 the chemical manufacturing sectors.

224 3.2.2. *Plastic tape manufacturing*

225 The VOC species emitted from the plastic tape manufacturing industry were
226 mainly aromatics such as toluene, ethyl acetate, *m,p*-xylene and ethylbenzene,

227 accounting for 44.4% (11.1 mg-VOC kg⁻¹), 16.2% (4.04 mg-VOC kg⁻¹), 10.1% (2.52
228 mg-VOC kg⁻¹), 10.1% (2.50 mg-VOC kg⁻¹) and 5.24% (1.30 mg-VOC kg⁻¹) of \sum VOCs
229 emission factors, respectively. Tsubaki et al. [31] found toluene to be the major VOC
230 species emitted from the double-sided pressure-sensitive adhesive tape. Adhesive
231 plastic tape products included petroleum, petroleum by-products, natural rubber, acrylic
232 resins, silicone rubber, dispersions, polymers, solvents and other chemicals. Solvent-
233 based adhesive tape applications require high stress resistance. There is no solvent-free
234 adhesive tape available that show equivalent properties. Therefore, there is no
235 alternative to solvent-based adhesives in the high quality range. All stages of the tape
236 manufacturing process included hot melt that release VOCs into the atmosphere.

237 3.2.3. *Metal manufacturing*

238 Toluene, ethyl acetate, acetone, 1-butene, *n*-butane, cis-2-butene, benzene, and
239 ethanol were the main VOC species emitted from the metal-based manufacturing
240 industries. Toluene was the most abundant VOC species in the emissions from both
241 aluminum and steel foundries, accounting for 39.6% (0.0116 mg-VOC kg⁻¹) and 11.6%
242 (0.000285 mg-VOC kg⁻¹) of the \sum VOCs emission factors, respectively. Benzene had
243 the highest contribution (40.8%, 0.0243 mg-VOC kg⁻¹) in the integrated iron & steel
244 sector. Samples from metal product & machinery and non-ferrous metal showed the
245 major fractions of 1-butene and ethyl acetate emissions, accounting for 40.1% (4.15
246 mg-VOC kg⁻¹ and 38.3% (0.00408 mg-VOC kg⁻¹) of the \sum VOCs emission factors,
247 respectively (Table 2). VOC compositions in the emissions from the integrated iron &
248 steel manufacturing sector were similar to those reported by the previous work [21] for
249 four processes of integrated iron & steel industries. The study reported benzene, toluene,
250 xylene, *n*-butane and 2-methyl pentane for the sintering process as the major VOCs.
251 Toluene, 1,2,4-trimethyl benzene, isopentane, *m/p*-xylene, 1-butene, ethylbenzene,

252 benzene, trichloroethylene, *n*-hexane and *n*-pentane were the major VOC species in
253 coke making exhausts [21].

254 3.2.4. *Leather manufacturing*

255 The major VOCs emitted from PU leather industry were methyl ethyl ketone,
256 toluene and methyl methacrylate, accounting for 60.0% (0.402 mg-VOC kg⁻¹), 24.0%
257 (0.161 mg-VOC kg⁻¹) and 12.6% (0.0847 mg-VOC kg⁻¹) of \sum VOCs, respectively. The
258 contributions of major VOC species detected in this study were similar to those reported
259 in the earlier studies. Chang and Lin [32] obtained a higher amount of toluene and
260 methyl ethyl ketone in the emissions from coating, drying and surface treating processes
261 of the PU leather industry. Wang et al. [33] reported a high quantity of 2-butanone,
262 toluene and ethyl acetate in different areas of the manufacturing facility such as
263 manufacturing department, semi-finished raw material department, resin warehouses and
264 outside vicinity of the industries. Organic solvents are widely used in the PU industries
265 which could be a potential source of VOCs. The species of organic solvents include
266 toluene, methyl ethyl ketone and dimethylformamide. Some solvents are added as
267 thinners and additives to avoid excessive viscosity of polyurea-formaldehyde in PU
268 industry [32]. These results showed that the VOC species compositions were
269 attributable to the organic solvent and other raw materials used in PU industries.

270 3.2.5. *Printing sectors*

271 The printing sector in the present study included plastic coating and stencil printing
272 (Table 2). Toluene was the most abundant species in the emissions of plastic coating
273 and stencil printing, accounting for 64.3% (0.00990 mg-VOC kg⁻¹) and 35.3% (149 mg-
274 VOC kg⁻¹) of \sum VOCs emission factors, respectively. However, methyl methacrylate,
275 ethyl acetate, acetone, methyl ethyl ketone and 2-methyl hexane accounted for a minor
276 fraction of \sum VOCs for both sectors. Organic solvents are widely used in the plastic

277 coating and ink printing [17] which could make an important source of aromatic
278 compounds. Li et al. [19] obtained a higher percentage of alkanes (44.8%) and
279 aromatics (47.4%) in printing ink. The study reported that VOC species emitted from
280 the ink printing sectors were mainly, alkanes and aromatics. Some other studies found
281 that toluene, benzene, and some oxygenated organics are the typical species emitted
282 from printing sectors [19,29,34]. Zheng et al. [29] reported aromatics (e.g., benzene and
283 toluene) as the major species of letterpress printing, while ethyl acetate and isopropyl
284 alcohol were important VOCs in offset printing and gravure printing processes. Raw
285 materials and derivatives might be the responsible factor for the observed differences
286 in the emissions from different printing sectors.

287 3.3. Relative ozone formation potential

288 The top five VOCs in terms of their contributions to ROFP in different emission
289 sectors are shown in Fig. 3. The top five VOC species for organic solvent included ethyl
290 acetate, toluene, 1,2,4-trimethylbenzene, *m*-xylene and *m*-ethyl toluene that together
291 accounted for 75.1% of the total ROFP. In synthetic resin industries, the top five ROFP
292 VOCs accounted for 71.7% of the total ROFP. They included aromatics (toluene and
293 *m*-xylene), alkanes (methylcyclohexane), and oxygenated VOCs (acetone and methyl
294 ethyl ketone). In the polyester resin industry, oxygenated and aromatic species were
295 predominant contributors to the total ROFP, whereas in the acrylic resin industry, the
296 aromatic VOCs (*m,p,o*- xylene, ethylbenzene and toluene) were the major contributors
297 to ROFP. 1-butene and ethyl acetate were the dominant contributors to the total ROFP
298 for metal product & machinery and non-ferrous metal sectors, respectively. Similarly,
299 toluene was the highest contributor followed by *m,p*-xylene and ethyl acetate in the
300 plastic tape manufacturing sector. Likewise, toluene was the dominant contributor of
301 total ROFP for the aluminum foundry, steel foundry, integrated iron & steel, PU leather

302 and plastic coating sectors. For the stencil printing sector, 1,2,3-trimethyl benzene was
303 the major contributor of the total ROFP. Moreover, several aromatic VOCs including
304 1,3,5-trimethyl benzene, 1,2,3-trimethylebenzene and *m*-ethyltoluene were also
305 obtained as the top five VOCs contributing to the total ROFP in the stencil printing
306 sector.

307 [Add Figure 3]

308 The ROFPs of VOCs varied widely across different emission sectors (Fig. S1). The
309 total ROFP of metal product & machinery emission was the highest (7.61 g-O₃ g-VOCs⁻¹)
310 among all emission sources, followed by acrylic resin manufacturing (7.40 g-O₃ g-
311 VOCs⁻¹), stencil printing (6.50 g-O₃ g-VOCs⁻¹), and plastic tape manufacturing (4.56 g-
312 O₃ g-VOCs⁻¹). In the metal product & machinery sector, alkenes were the main
313 contributors, accounting for 88.0% of total ROFP. However, in acrylic resin
314 manufacturing, printing and plastic tape sectors, aromatics contributed to 99.9%, 99.8%
315 and 85.3% of total ROFP, respectively. The major aromatic VOCs for these emission
316 sources were 1-butene, *m*-xylene, 1,2,4-trimethylbenzene and toluene. The total ROFP
317 for synthetic resin manufacturing emissions were lowest because the oxygenated VOCs
318 with low reactivity accounted for the major fraction of \sum VOCs. The ROFP
319 contributions for acrylic resin, plastic tape, metal manufacturing (integrated iron & steel,
320 aluminum and steel foundries) and printing (plastic coating and stencil printing)
321 emissions were mainly from aromatic VOCs. However, oxygenated VOCs was the
322 major contributing group to the ROFP for other manufacturing sectors (i.e., organic
323 solvent, polyester resin, non-ferrous metal and PU leather). Li et al. [19] also reported a
324 similar VOC emission pattern for iron & steel and printing sectors. It should be noted
325 that the ozone formation potential depends on the speciated VOC emission factors and

326 their MIR values. Thus, VOCs with high emission factors may not always be the major
327 contributors to ozone formation.

328 *3.4. Relative carcinogenic risk*

329 The RCR of each of the emission sources investigated in this study have been
330 presented in Fig. S2. The RCR of emissions from the integrated iron & steel sector was
331 the highest among all tested emission sources with the risk value of 40.6×10^{-8} (mg m^{-3})
332 $^{-1}$, followed by steel foundry (4.0×10^{-8} (mg m^{-3}) $^{-1}$) and non-ferrous metal industry
333 (9.2×10^{-9} (mg m^{-3}) $^{-1}$). RCR values of other emission sectors such as organic solvent,
334 synthetic resin, acrylic resin, plastic tape, aluminum foundry, PU leather, plastic coating
335 and stencil printing ranged from 1.2×10^{-10} – 9.1×10^{-9} (mg m^{-3}) $^{-1}$. The RCRs were not
336 calculated for polyester resin and metal product & machinery because of the
337 unavailability of the carcinogenic risk factor values for the VOCs detected in the
338 emissions of those sources. The highest relative RCRs were observed for the integrated
339 iron & steel manufacturing sector and steel foundry because those sources emitted high
340 amount of benzene. Several VOC species, including benzene, chloroform,
341 trichloroethylene, bromoform and 1,3-butadiene are classified as carcinogenic
342 compounds according to the Integrated Risk Information System. Industrial
343 manufacturing sectors are reported as the major VOC emission sources [21,29]. Several
344 previous studies have assessed cancer risks for the inhalation exposure to VOCs in
345 industrial areas, but most of them focus on the ambient VOCs [35–37].

346 *3.5. Specific potential emission sources*

347 A comparison of potential VOC emission sources based on ROFP and RCR
348 between different emission sectors is presented in Fig. 4. NROFP and NRCCR were
349 categorized into four levels: level-I (0.75 – 1.00), level-II (0.50 – 0.75), level-III (0.25
350 – 0.50) and level-IV (0 - 0.25) where, Level-I represents the most important VOC

351 emission sources and Level-IV represents the least important emission source in terms
352 of NROFP and NRCR. Metal product & machinery, acrylic resin and stencil printing
353 sectors belonged to the level-I emission sources (NROFP index: > 0.75). However, in
354 terms of the NRCR, it was found that the integrated iron & steel had the highest NRCR
355 index that belonged to level-I emission sources. Therefore, it can be concluded that not
356 only the single factor such as OFP, but also the cancer risk should be taken into the
357 consideration for the identification of potentially important VOC emission sources.

358 [Add Figure 4]

359 **4. Conclusions**

360 In this study, 13 types of stationery emission sources were investigated for the
361 emission factors of speciated VOCs and associated ROFPs and RCRs. ROFPs and
362 RCRs were used for the identification of potentially important VOC emission sectors.
363 The results showed that the maximum \sum VOCs emission factors were observed for
364 stencil printing (423 mg-VOC kg⁻¹) among all tested emission sources. Alkanes formed
365 the dominant VOC group in the steel foundry (41.6% of \sum VOCs emission factors),
366 aluminum foundry (25.1% of \sum VOCs emission factors) and synthetic resin (25.0% of
367 \sum VOCs emission factors). However, in the chemical sector (synthetic and polyester
368 resin), oxygenated VOCs such as acetone (55.7% of \sum VOCs emission factors) and
369 ethyl acetate (79.7% of \sum VOCs emission factors) were the major contributors to total
370 VOCs. However, *m,p,o*-xylene, ethylbenzene, and toluene formed > 95% of \sum VOCs
371 emission factors in the emissions from acrylic resin manufacturing. Analysis of ROFP
372 showed that metal product & machinery sector, acrylic resin manufacturing and stencil
373 printing were potentially important emission sources in terms of OFP. However, in term
374 of the NRCR, integrated iron & steel sector was the potentially important source with
375 the highest NRCR index.

376 **Competing interests**

377 The authors declare that they have no competing interests

378 **Availability of data and materials**

379 All data generated or analyzed during this study are appear in the submitted article.

380 **Authors' contributions**

381 HHY contributed to study design, data analysis, drafting and editing the manuscript.

382 SKG and NBD led sampling, analysis, modeling and contributed to the study design,

383 data analysis, drafting and editing the manuscript. All authors read and approved the

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