Characterization of Mining-related Aromatic Contaminants in Active and Abandoned Metal(loid)s Tailings Ponds

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ABSTRACT

This study reports on the compositional diversity of organic compounds in metal(loid)-bearing tailings samples from both active and abandoned tailings ponds. Tailings samples were qualitatively analyzed by comprehensive two-dimensional gas chromatography time-of-flight mass spectrometry (GC × GC-TOFMS). In addition, the priority PAHs (16), PAEs (6) and phenols (2) were quantitatively analyzed using Gas Chromatography-Mass Spectrometry (GC-MS). We attribute the presence of some of aromatic organics in studied tailings ponds to particular sources. Mineral floatation reagents are likely the major sources of small-ring aromatics in tailings ponds, and products from metallurgical processing and burning of fossil fuels in the mining area or further afield are also possible contributors and might be the main source of large-ring aromatics. We found that tailings ponds abandoned for decades can still have organics concentrations at levels of concern. Large-ring aromatics are generally more toxic than other contaminants, and these were more abundant in abandoned tailings ponds which suggests that these large-ring organics do not readily decompose or biodegrade into less toxic byproducts, as do volatiles and many other organic compounds. Our aromatic contaminants database provides an important starting point for researchers to investigate and compare similar contaminants that might be also present in other tailings ponds and emphasizes the necessity of considering their transformations over time.

INTRODUCTION

Almost every country in the world has, or has had, a mining industry.[1] Although grinding, mineral processing, smelting and mineral refining activities cease when mining operations end, mine wastes remain a potential source of contamination that may last for years to centuries in tailings ponds.[2-4] Both active ponds (still receiving fresh tailings) and abandoned tailings ponds can continuously release metal(loid)s, flotation reagents, mine drainage and associated contaminants into neighboring soils, river sediments and groundwater, creating hazards to nearby ecosystems and humans.[5-8] Most of the characterization of tailings has focused on the geochemistry and mineralogy of their inorganic metal(loid)s such as lead, copper, arsenic, uranium and thiocyanate (SCN$^-$), and on their ability to produce acid mine drainage. The organic components of oil sand tailings have been well-studied,[9, 10] but those in tailings derived from metal mining and processing have not.

Mineral flotation reagents (MFR) are indispensable chemicals in the mining industry. MRF are widely used in the mining, processing and subsequent treatment of minerals to improve mineral grade, recovery, extraction efficiency and clean production. Flotation is the preferred and most effective method for metal recovery, especially as the quality and grade of ores declines and sustainability challenges increase.[11] The amount of ore treated by froth flotation reagents is estimated to be over 2 billion tonnes worldwide annually.[12] Therefore, a large number of MFR, including collectors (xanthate, fuel oil, naphthalene, etc.), dispersants (acrylate, methacrylate, olefinic oxide, etc.), frothers (pine oil, cresol, alkoxy, etc.), solvent extractors (phosphine, amine phosphate, oxime, etc.) and scale preventors (amino-methylene phosphonate, polyphosphates, etc.) have been used in mineral processing over the past 100 years.[12, 13] Many of organic MFR contain

24   persistent organic pollutants (POPs) such naphthalene or endocrine disruptors (EDCs) such as

25   nonylphenols. If not recovered and handled, these naturally-occurring and synthetic organic

26   reagents may become potential sources of anthropogenic contaminants, and may ultimately be

27   discharged to, and may accumulate in, tailings ponds. This is particularly true of China, where

28   larger volumes of MFR are used in mineral processing and hydrometallurgical industries compared

29   to other areas in the world.[14]

30

31   Tailings ponds are usually constructed in open-air environment and filled with large volumes of

32   tailings, in some cases up to 10 billion tons.[14, 15] Thus, tailings ponds are complex reactors that

33   have sufficient oxygen, sunlight, rainfall, metal(loid)s, and organic compounds to allow

34   photochemically, surface photocatalytic and biochemical reactions to occur, which makes the

35   organics in tailings more complicated. In addition, as the ponds age, the tailings organics could

36   undergo chemical reaction and transformations or biodegradation, resulting in the formation of

37   secondary products or complexes with the metal(loids), potentially making them mobile. The

38   potential for widespread variable organic contamination is tremendous and the size of the tailings

39   pond and volume of the contaminants can greatly complicate sampling and analysis efforts.

40

41   In this work, we characterized, for the first time, the quantities and distribution of organic

42   compounds from metal(loid)-bearing tailings in space and time by using comprehensive two-

43   dimensional gas chromatography time-of-flight mass spectrometry (GC $\times$ GC-TOFMS). We

44   quantified 16 priority PAHs, 6 PAEs and 2 Phenols using Gas Chromatography-Mass

45   Spectrometry (GC-MS). The distribution of aromatic contaminants was compared in the active

46   and abandoned tailings ponds and their possible sources considered. We aimed to test the

47   hypothesis that aromatic and other organic contaminants are extensively present in tailings ponds,

48   and aromatics profiles are different between abandoned and active tailings ponds. This knowledge

49   will help to better understand the character, concentrations, migration, transformation and

50   biogeochemical reactions of organic contaminants in tailings ponds, to enable predictions to be

51   made of their fate, potential complexation with metal(loids) and toxicity, and to develop

52   management and restoration schemes.

53

54   **MATERIALS AND METHODS**

55   **Field site.** The nonferrous metal mining areas of Nandan, Guangxi Province, China, have a long

56   history, with the extraction of silver, tin, lead and zinc beginning in the Song Dynasty (970-1127

57   A.D.), flourishing during the Tang Dynasty (618-907 A.D.) and continuing to the present day. The

58   Nandan area presently includes eight producing mines, of which seven are nonferrous, producing

59   more than 300 million tons of ore annually.[16] In Nandan, as in other parts of China, large quantities

60   of flotation chemicals (in China approximately 1.2-1.5 billion m^3 annually) are used in mineral

61   processing due to their low cost, and these are discharged to tailings ponds with little or no

62   treatment.[17, 18] Asia's largest tin processing facility (the Chehe Concentration Plant), several large-

63   scale metal smelting plants, more than ten tailings ponds, a paper mill, a fertilizer plant, and intense

64   transportation of mining products and raw materials also occur in the Nandan area. The area hosts

65   a population of 260,000 people, 11 townships, and agricultural land.[19]

66

67   **Field sampling.** A total of 60 tail sand (tailings) samples were taken from seven active (A-G) and

68   five abandoned (K-L) tailings sites from tailing ponds with different compositions and service ages

69   throughout the nonferrous metal mining area in Nandan (23°41′39″–5°37′31″N, 106°34′22″–

70   109°092′9″E) as shown in Figures S1&2. The tailings were mainly derived from antimony (Sb),

71   tin (Sn) and lead (Pb)-zinc (Zn) mining and smelting operations without any environmental

72   treatment or remediation. During sample processing, procedural blanks consisting of extraction

73   method, matrix, field, instrument and reagent blanks (n = 6) were included to ensure that the

74   analytical scheme did not introduce contamination. All tailings samples were collected from the

75   surface (0-10 cm). Ten subsamples of 30 ± 5g were collected from an area of approximately 100

76   m^2 and homogenized. Samples were stored in brown glass bottles at 4 °C during transport to the

77   laboratory. After being freeze-dried and sieved through a stainless steel sieve (100-mesh), samples

78   were stored in a freezer (−20 °C) until further preparation and analysis.[20]

79

80   **Chemical reagents.** All solvents (methanol, methylene chloride, acetone, etc.) used for sample

81   processing and analysis were HPLC grade and purchased from Fisher Scientific (Fairlawn, NJ,

82   USA). Merck Reagents silica gel (particle size 0.063–0.200 mm, 70–230 mesh ASTM) was used

83   in a cleanup step for quantitative analysis. All the standard solutions (Tables S1 and S2) were

84   purchased from Sigma (Sigma-Aldrich, St. Louis, MO). TMS reagents [N,O-bis(trimethylsilyl)

85   trifluoroacetamide(BSTFA) and trimethylchlorosilane (TMCS)] (99:1, v/v) were used as

86   derivatization reagents. All glassware was soaked in a 50% nitric acid solution for at least 48 h,

87   rinsed thoroughly with Milli-Q (18.2 MΩ·cm), and heated at 400 °C for 6 h. Plastic was avoided

88   during the sampling and the execution of experiments.

89

90   **Sample treatment.** An Accelerated Solvent Extractor (ASE300, Dionex Corporation, Sunnyvale,

91   CA, USA) was used for the treatment of samples and mixtures, and n-hexane–dichloromethane

92   (1:1 v/v) was used as an extraction solvent. Briefly, a 15 g sample was mixed with diatomite, and

93 activated copper was extracted at 105 °C and 10 MPa. Each tailings sample was extracted in

94 triplicate. Before extraction, all samples and blanks were spiked with labeled reference compounds

95 (SI-2). The extracts were evaporated to near dryness by rotary evaporation and a 99.999% purity

96 N_2 stream, and dissolved with 100 μl of hexane. To analyze organic compounds that were not

97 amenable to GC, tailing sample fractions were derivatized with 100 μl of derivatization reagent

98 (BSTFA:TMCS (99:1, v/v) at 65 °C for 30 min before chromatographic separation analysis.

99

100 **GC × GC-TOFMS analysis.** GC × GC-TOFMS is a powerful tool for the analysis of complex

101 mixtures, greatly enhancing the resolution power and detection and providing an order-of-

102 magnitude greater separation capacity than traditional one-dimensional GC-MS. The extracted

103 solutions were analyzed utilizing a two-dimensional gas chromatography coupled with Time of

104 Flight Mass Spectrometry (GC × GC-TOFMS; Pegasus 4D, LECO, St. Joseph, MI, USA). The

105 first-dimension (1D) column was a Rxi-5SilMS (30 m × 0.25 mm ID × 0.25 μm), and the second

106 dimension (2D) column was a Rtx-200 (1.5 m × 0.18 mm ID × 0.20 μm). The oven temperature

107 for the 1D column was initiated at 80 °C for 2.0 min, increased to 300 °C at a rate of 5 °C/min,

108 and held at 300 °C for 10 min. The injection port temperature was 280 °C and an injection volume

109 of 1 μL was used in splitless mode. The helium carrier gas (N_2 99.999%) was kept at a constant

110 speed of 1 mL/min. The second dimension (2D) column oven temperature was maintained at 20 °C

111 higher than the first-dimension (1D) column oven temperature. For GC × GC, the modulation

112 period was 5 s with a 1 s hot pulse duration, and the modulator temperature offset was 20 °C. MS

113 transfer line and ion source temperatures were maintained at 280 °C and 250 °C, respectively. The

114 TOFMS was operated in the electron ionization (EI) mode. The detector voltage was 1650 V with

115   a filament bias voltage of -70 eV, and the stored mass range 30-500 m/z as scanned at a rate of

116   100 spec/s.[21]

117

118   **Data processing.** All data were processed and analyzed using LECO® ChromaTOF® software,

119   version 4.51. (St. Joseph, MI, USA).[22] Only peaks having a signal-to-noise ratios (S/N) greater

120   than 200 were considered. Peak finding (MS deconvolution) and Classification were performed

121   automatically as a functional of the ChromaTOF® software. Mass spectra generated by the

122   GC×GC−TOFMS were compared to mass spectra in the National Institute for Standards and

123   Technology (NIST 2011) library to tentatively identify the compounds present. Spectra that

124   matched with a mass spectral similarity value greater than 750 were assigned tentative compound

125   names and used to identify compound class information[23]. Then, the S/N, retention times and

126   indices of referenced analytes of peaks were manually reviewed, rationalized and the

127   fragmentation pattern of the compound was ensured to be the same as the EI mass spectral library

128   suggested to increase confidence in the identification[23]. In order to identify the compounds

129   accurately, two automated approaches for GCXGC-TOFMS data analysis were used to check the

130   manual analysis. Classification was performed by ChromaTOF® software combined with the

131   method for rapid screening of environmental contaminants developed by Hilton et al.[24]

132   Quantitative structure activity relationship (QSAR) analysis was used to assess the acute and

133   chronic toxicity of identified organics based on the Ecological Structure Activity Relationships

134   (ECOSAR) predictive model. In our study, many organic MFR are artificially synthesized

135   chemicals, and their standard products are not commercially available. Thus, QSAR was

136   considered to be a feasible alternative to experimentally derived toxicity data on detected organics

137   for fish, algae and daphnia.[25] Hierarchical cluster analysis (HCA) and principal component

138 analysis (PCA) were used to investigate the variation between the normalized abundance profiles

139 of active and abandoned tailings ponds. More details of data processing can be found in the

140 Supplementary Information.

141

142 **RESULTS**

143 **Qualitative analyses.** The quantity and complexity of GC × GC-TOFMS data generated in

144 complex tailings matrices could be processed and effectively viewed in a visual multidimensional

145 fashion.[26] The results of chromatographic analysis clearly shown the advantages of GC × GC-

146 TOFMS analysis (Figure 1). For example, the pyrene (red square in Figure 1) was not detected

147 using 1D GC–MS (Figure 1A) but was successfully separated using a polar column in the 2D

148 system (TIC Figure 1C, m/z = 202 Figure 1D). These pyrene peaks, which are normally hidden by

149 those of more abundant organic compounds, were detected through deconvolution and spectrum

150 software library comparisons, yielding a match with compound 833 (Figure S6). Thousands of

151 individual chemicals in the tailings samples were matched with the NIST library (2011) spectra at

152 mass spectral similarity values greater than 750 (S/N > 200) (e.g., Tailings pond E, Figure S3).

153 These accounted for an average of 72% of the total TIC signal after excluding the influence of the

154 reagent artifacts (solvent, derivatization reagent and impurities) and column bleeding.[27]

155

156 The spatial distribution of compounds in the TIC chromatogram was broadly similar in nature

157 among the same type of tailings ponds (abandoned vs. active), although individual differences for

158 each tailings pond were observed (Figure S4). A comparison of active (A-G) and abandoned (K-

159 L) tailings is shown in Figure S5. The peaks in active tailings were more complicated and had

160 higher concentrations (in yellow circle, Figure S5) compared to the abandoned tailings. This is

161   further confirmed by the number of identified peaks from the ChromaTOF® software. An average

162   of 563 peaks was detected in each tailings pond (Table 1), but overall, there were more organic

163   compounds in the active tailings (average 612 peaks, n = 7) than in the abandoned tailings (average

164   493 peaks, n = 5). Nonetheless, we recognize that it is not enough to get an accurate comparison

165   of different tailing ponds only on a visual basis and from peak abundances due to the large amount

166   of organic compounds in tailings.[28]

167

168   A summary of the detected organic compounds classified according to their chemical and

169   functional groups (i.e., alkynes, alkanes, ketones, alcohols, acids/esters, phenols, carbon structures,

170   PAHs, PAEs, etc.) is shown in Figure 2. S-compounds were mainly composed of sulfide (C=S=C),

171   thiols (R-SH), thioesters(R-C(O)-S-R), thiophenes. Oxygenated compounds mainly comprised

172   furanoic compounds, phenolic compounds and organophosphorus (Dimethyl methylphosphonate,

173   tributyl phosphate and Tris (2-ethylhexyl) phosphate). Halogenated hydrocarbons, ketones and

174   esters/acids were also frequently identified compound classes. The aromatic compounds, both

175   monoaromatic aromatic hydrocarbons and PAHs showed higher content in active tailings rather

176   than abandoned tailings (Figure 2). Notably, not only parent PAHs but also a wide variety of PAH

177   derivatives were detected in tailings ponds such as alkylated PAHs, S-containing PAHs, O-

178   containing PAHs and mixed heterocycles (e.g., containing both O and S). Some aromatic

179   compounds, like PAHs, are toxic, cancerogenic, mutagenic, and ubiquitous environmental

180   contaminants of great concern.[29] Meanwhile, mining activity has been considered as an emerging

181   source of PAHs.[30] Thus, we focus on the aromatic contaminants including PAHs, PAEs, and other

182   aromatic contaminants in the following discussion.

183

184   Hundreds of aromatic compounds (111) were identified by qualitative analysis and their toxicities

185   are listed in Table S4 (structures given in Figure S7). The 66 aromatic compounds were further

186   verified using their authentic standards to ensure the accuracy of qualitative analysis. Sixty-two

187   (approximately 94%) of the 66 aromatic compounds could be accurately identified after manual

188   review (see Table S4.). The qualitative results for aromatic compounds showed that compounds

189   containing one (39.6%) and two (48.6%) benzene rings markedly dominated compared to those

190   having three (9.0%) and four aromatic rings (2.7%). In addition, the long-chain alkylbenzene

191   including (e.g., *dodecylbenzene* and *benzene, (1-methyldodecyl)-)* were the most toxic of the

192   aromatic compounds in tailings ponds (Top 9 in Table S4).

193

194   **Quantitative analyses.** For quantitative analysis we focused on the distribution patterns of 16

195   priority PAHs which have been categorized by the US Environmental Protection Agency (USEPA)

196   as high-priority contaminants, 6 PAEs, phenol, and m-Cresol in the twelve tailings ponds were

197   arranged by descending total concentrations of 16 priority PAHs (left) and 6 PAEs + 2 phenols

198   (right) in Figure 3. Total concentrations of the 16 priority PAHs ranged from 20 to 1800 μg/kg dw

199   (dry weight) in the tailings ponds, varying three orders of magnitude, and were dominated by

200   naphthalene (NAPH) and phenanthrene (PHEN) at all sites. Levels of the 16 priority PAHs in

201   active tailing ponds were highly variable among different sites, and ranged from 138 to 1800 μg/kg

202   dry wt (average and median values: 590 μg/kg dw and 324 μg/kg dw), while those in abandoned

203   tailings ponds ranged from only 20 μg/kg dw to 165 μg/kg dw (average and median values: 97.6

204   μg/kg dw and 89 μg/kg dw). The average and median values of the 16 priority PAHs in active

205   tailings were 6 and 3.6 times higher than in the abandoned tailings ponds, respectively.

206

207 As shown in Figure 3, the contaminant patterns in active tailings ponds varied with total

208 concentrations of the16 priority PAHs. A lower proportion of low molecular weight PAHs, such

209 as NAPH, was observed in active tailings having higher concentrations of the 16 priority PAHs

210 (e.g., 1800 μg/kg in site A and 981 μg/kg in site B), whereas tailings samples with a lower

211 concentration of the 16 priority PAHs, such as those from sites F (230 μg/kg) and G (138 μg/kg),

212 had a higher proportion of low molecular weight PAHs and a lower proportion of high molecular

213 weight PAHs (e.g., PHEN and B(a)A). To the contrary, patterns of the 16 priority PAHs in

214 abandoned tailings ponds were independent of concentration. For example, patterns of the 16

215 priority PAHs were 165 μg/kg at site B and at 89 μg/kg at site H. This suggests that the 16 priority

216 PAHs in active tailing ponds are likely derived from different sources and affected by point sources,

217 whereas in abandoned tailings ponds, the 16 priority PAHs are affected by nonpoint sources and

218 the history of contamination. The distribution patterns of the 16 priority PAHs in active and

219 abandoned tailings ponds agree with results from a previous study comparing the PAHs in early-

220 and newly- industrialized countries.[31]

221

222 The total concentration of 6 PAEs are more evenly distributed in different tailings ponds than

223 PAHs, varying from 237 to 362 μg/kg dw and the concentrations of 2 phenols (phenol and m-

224 cresol) varied from 21.4 to 77.0 μg/kg dw. There is no significant difference in the distribution of

225 PAEs and phenols in active versus abandoned tailings ponds. The average concentrations of

226 individual PAEs declined in the following order (μg/kg dw): DIOP (95.4) > DEHP (73.2) > DBP

227 (63.8) > DEP (30.3) > DMP (26.3) > BBP (9.5). Similar results were obtained for the eight PAEs

228 detected in the qualitative analysis; percent ratios of individual PAEs to Σ8 PAEs declined in the

229 following order (%): DEHP (33.8) >DIOP (23.4) > DBP (21.4) > DEP (8.8) > DMP (7.9) > DINP

230   (3.9) >DNOP (0.24) >BBP (0). At the present time, PAEs are still widely used as ester foaming

231   agents in China, despite evidence that they pose hazards to the environment and to humans.[32, 33]

232

233   **Multivariate Statistical analysis.** The quali-quantitative distribution of aromatic contaminants

234   helps in the discrimination and differentiation of possible geographical origin and manufacturing

235   stage. In order to better classify different groups of samples, a two-dimensional HCA heat map

236   (based on Euclidian distance) that summarized the relations between qualitative aromatic

237   compounds and tailings ponds as a dendrogram was used. The variables with poor differentiation

238   in samples, low toxicity, and narrow distribution were removed in order to improve the

239   classification power of the heat map.[28] Finally, 52 normalized aromatic contaminant data sets were

240   used for HCA (Table 2). HCA helped to discriminate the organics based on their distribution

241   profiles and grouped them into four main clusters, whereas the dendrogram and variational blue

242   mosaic allowed us to identify class-specific compounds at a glance in Figure 4. Some key aromatic

243   contaminants in cluster 1 (Benzene, Naphthalene (NAPH, 46), Dimethyl phthalate (DMP, 47),

244   1,1'- Biphenyl, 4-Methyl- (48), Dissobutyl Phthalate (49), 1,2,3- Trichloro- (50), Dibutyl Phthalate

245   (51), Phenanthrene (PHEN, 52) show a homogenous trend across all tailings ponds with relative

246   higher concentrations than other contaminants. Cluster one, with a large proportion of 3-4 rings

247   compounds, was abundant in the abandoned tailings, and clusters 3 and 4, with more 1-2 rings

248   compounds, were dominant in the active tailings ponds. The physico-chemical properties of the

249   organic contaminants in the different clusters also showed significant differences between the

250   abandoned and active tailings ponds. As shown in Table 2, the mean values of saturate vapor

251   pressure (mmHg at 25°C), log Kow (Octanol-water partition coefficient), and water solubility

252   (mg/L) in Cluster 4 (predominantly present in active tailings ponds) were 0.04, 3.78, and 5.81

253 compared to 0.14, 5.24, and 9.95 for compounds in Cluster 1 (predominantly present in abandoned

254 ponds).

255

256 Clustering of the samples was further assessed using PCA enable the discrimination between active

257 and abandoned tailings ponds based on the concentrations of PAHs, PAEs and phenols. As shown

258 in Figure 5, the first two principal components were extracted with eigenvalues > 1, which

259 explained 95.3% of the total variance. All of the tailings ponds plotted in the PCA corresponded

260 to positive values of the PC1 axis and were characterized by NAPH, DEP, DBP, DEHP, DIOP,

261 phenol, and m-Cresol. The PCA biplot also illustrated the differences between active and

262 abandoned tailings ponds (Figure 5), suggesting that the aromatic contaminants profiles of fresh

263 and aged tailings were dissimilar. This is consistent with the HCA results that the same type of

264 tailing ponds (active A-K; abandoned H-L) grouped or clustered together.

265

266

267 DISCUSSION

268 **Origin.** Using the qualitative and quantitative analysis results, we can attribute the presence of

269 some of the organics in studied tailings ponds to particular sources. The active tailings ponds have

270 higher contents of aromatic contaminants and more complex chemical compounds. This is likely

271 due to the continuous discharge of fresh tailings containing MFR into the active tailings ponds.

272 Many of the detected organic contaminants are consistent with organic MFR and their intermediate

273 degradation products. For example, the small-ring (1-2) aromatic contaminants and heterocyclic

274 compounds that predominated in the active tailings ponds are characteristic of most flotation

275 chemicals that contain low-quantity benzene rings (e.g., PAEs).[34] Similarly, the sulfur compounds

276 identified (Figure 2) likely come from widely used organic sulfur reagents such as xanthates

277 $(ROCS_2^-)$.[45] Of these, one of the most widely used groups are sulfhydryl collectors that are used

278 for sulfide ores. A similar spatial distribution has been found between the concentrations of

279 phenolic compounds and PAEs (Figure 5), indicating that both might be derived from similar

280 sources (e.g., used as MFR for the same types of ore).[35] This may be because phenolic compounds

281 are also used as flotation reagents and may be a degradation product or secondary contaminant of

282 flotation agents with benzene-rings.[36, 37] The MFR are likely the major sources of aromatic

283 contaminants in tailings ponds, but products from metallurgical processes and from the burning of

284 fossil fuels in the mining area or further afield are also possible contributors.[38, 39] For example,

285 PAHs and other organic and organometallic compounds in As-Hg mining-affected soils have been

286 attributed to pyrometallurgical processes that caused fossil fuels to be in contact with roasted

287 ores.[40] The highest concentration of the 16 priority PAHs and of high molecular weight benzene-

288 containing compounds ($\geq$3 benzene rings) were recorded in tailings ponds A and B (1800 and

289 981 µg/kg), which are located near metallurgical industries (Figure 3). This is consistent with

290 previous research describing high concentrations of high molecular weight PAHs in mining and

291 metallurgy areas.[40-42] Thus, coal and smelting combustion and metal smelting may be the main

292 sources of high molecular weight (large rings) PAHs in tailings. In the same vein, diesel exhaust

293 from mining and transport equipment, as well as airborne particulate matter from hauling roads

294 and mining operations, have been considered as a source of heterogeneous aromatic compounds

295 detected in the oil sands region.[43] Ferrous and nonferrous metal production (104.2-6648.3 g TEQ

296 and 2.6-33389.8 g TEQ, respectively) are considered the major sources of the polychlorinated

297 dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/Fs) that are produced in thermal

298 processes in the mining industry as unintentionally produced POPs (unintentional POPs).[44, 45]

299 Fossil fuel burning could be one of the other sources of tailings organic contaminants in tailings[46],

300 but we have not detected any compounds that could be directly linked with this source.

301

302 **Fate.** Some of the mining-related organics, such as organic sulfur, are likely to degrade. Xanthate

303 (alkyl dithiocarbonate, $R\text{-}OCS_2^-$) is an organic salt highly soluble in water and one of the most

304 widely used organic compounds in metal processing.[17, 47] Xanthate easily decomposes and

305 generates secondary toxic compounds such as carbon disulfide (CS_2).[48] The proportions of organic

306 sulfur are higher in the active ponds compared to the abandoned ponds, reflecting the fact that the

307 former are still receiving MFR that contain the sulfur. In the abandoned ponds, the sulfur will

308 likely degrade to CS_2 and H_2S. [49, 50] In addition, the proportions of alkanes are significantly higher

309 in the abandoned tailings ponds compared to the active ponds. This is likely because a large

310 number of alkanes are produced during the degradation and mineralization (to CO_2 and H_2O) of

311 flotation reagents.[51]

312

313 Some of the tailings pond aromatic compounds, such as the POPs, are unlikely to degrade. POPs

314 are neurotoxic, carcinogenic, mutagenetic and endocrine disruptors.[52, 53] Therefore, it is likely that

315 the toxicity of the organic MFR increases as they oxidize and transform into secondary POPs. For

316 instance, the most toxic long-chain alkylbenzene found in tailings ponds are likely to have a strong

317 correlation with sodium alkylbenzene sulfonate (a commonly used MFR).[54, 55] The qualitative and

318 quantitative analyses described above both show that there are still significant POPs in the

319 abandoned tailings ponds, even though the content was lower than in active tailing ponds (such as

320 pyrene and anthracene). However, tailings ponds abandoned for decades can still have organics

321 concentrations at levels of concern. Meanwhile, large ring aromatics are generally more toxic than

322   other contaminants, (Table 2), and these were more abundant in the abandoned tailings ponds.

323   These observations suggest that these large-rings organics do not readily decompose or biodegrade

324   into less toxic byproducts as do volatiles and other organic compounds. The long-term persistence

325   of other organic contaminants is also evident, as shown by the detection of POPs such as phthalates

326   in the L tailings pond, even though it has been discontinued for up to 30 years.

327

328   In addition, there are differences in the chemical reagents used in the processing of the different

329   types of minerals. This may be one of the reasons for the differences in organics between individual

330   active tailings ponds. The physical and chemical properties of organic contaminants are likely to

331   influence their fate and transport in the tailings pond. This reflected in the significant different on

332   the physicochemical properties as well as the number of organic contaminants between active and

333   abandoned tailings ponds. The higher value log-Kow of organic contaminants (easily trapped in

334   the tailings sand) and the lower saturated vapor pressure (non-volatile) and water solubility (hardly

335   soluble in water) indicated that fewer volatiles and biodegradable or short half-life organic

336   contaminants are present in the abandoned tailings ponds than in the active tailings ponds. Also,

337   the content and speciation of metals (Figure S2) in the different tailings pond could be a key factor

338   impacting the fate of the organic chemicals due to their reaction properties.

339

340   **Environmental Implications and Limitations.** Although qualitative analysis by GC $\times$ GC-

341   TOFMS has been shown to be effective for analyzing complicated environmental samples, it is

342   possible that some organic compounds, such as thermally labile organics as well as large molecular

343   weight compounds (e.g., polymers and adducts), were present in the mine tailings but were not

344   detected. The reason for not finding these compounds could be due to the sample cleaning,

345 preparation and extraction processes. The different organic solvents used to extract the samples

346 can cause different polarities of unknown organics, making them undetectable. There are still

347 hundreds of 'unknown' peaks (Table 1) without structures due to low intensities and/or unknown

348 MS/MS spectra. Thus, evidence for the identification of these compounds was insufficient.

349

350 However, we successfully identified hundreds of aromatics including toxic contaminants such as

351 PAHs, and endocrine-disrupting chemicals such as PAEs. Our results show that mine tailings

352 ponds can contain both metal(loid) and organic contaminants. Aromatic and other organic

353 contaminants in tailings ponds may pose risks to human health and the surrounding environment

354 as a persistent source of organic chemicals to humans, groundwater, river and local arable land. In

355 addition to potential contamination of water and soil, the atmosphere could also be affected. Some

356 of the detected aromatic contaminants are volatile or semi-volatile organic compounds, and these

357 could disperse into the ambient air resulting in formation of secondary organic aerosol and air

358 pollution.[56] It is necessary to conduct further research regarding the toxicology and environmental

359 fate of organics in mining areas, especially to develop appropriate methodologies for real-time

360 monitoring, risk assessment, and public policy.[57]

361

362 **Supporting Information**

363 Information on details of analytical chemical standards and quality control, samples maps, data

364 processing and toxicity of aromatic compounds. This material is available free of charge via the

365 Internet at http://pubs.acs.org.

366

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371 **Notes**

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373

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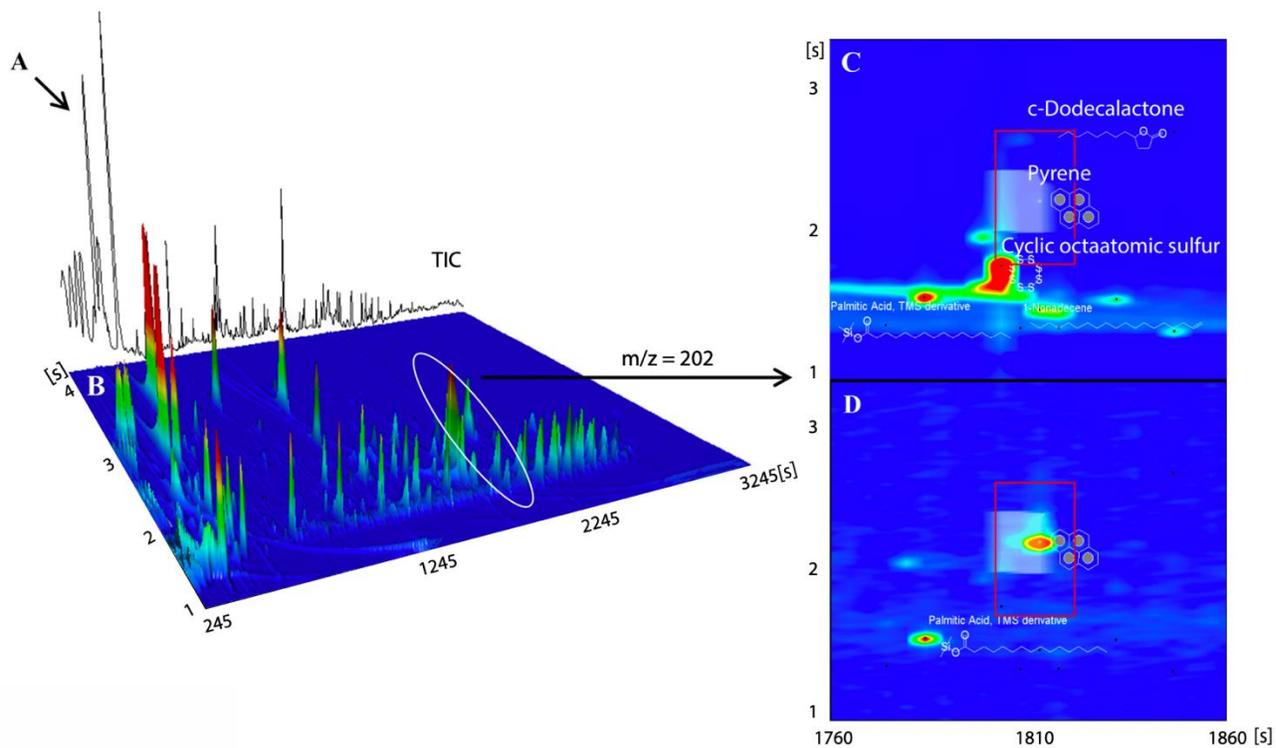
545

546

547 **Figure 1.** Total ion chromatogram (TIC) of the sample from tailings pond (H) obtained from GC-
548 MS and GC × GC-TOFMS. (A) 1D, GC-MS; (B) 3D, GC x GC-TOFMS; (C) 2D, GC × GC-
549 TOFMS; (D) 2D, GC × GC-TOFMS, key ions m/z = 202.
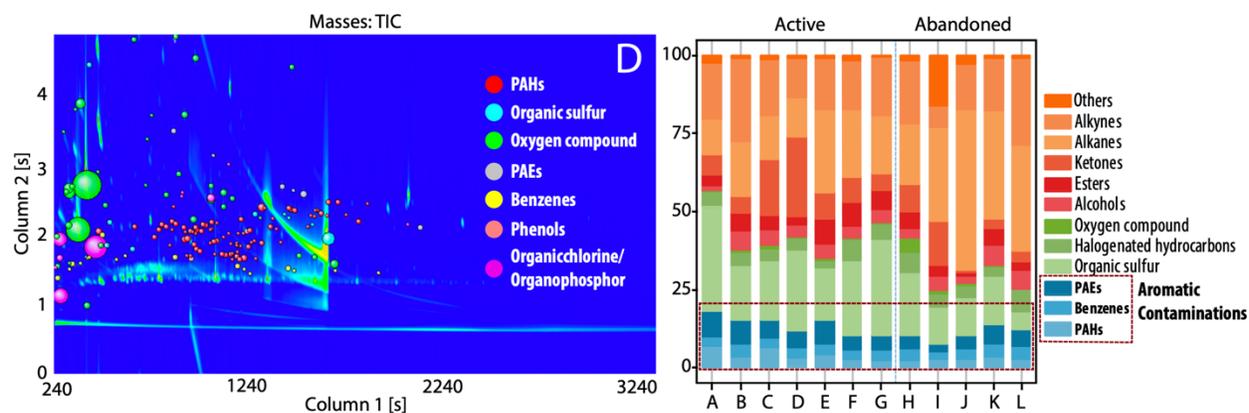
Figure 2. Classes of the detected organic compounds in the tailings samples, separated according to chemical and functional grouping, and the relative contents of the different classes of organic contaminants in active tailings pond D.
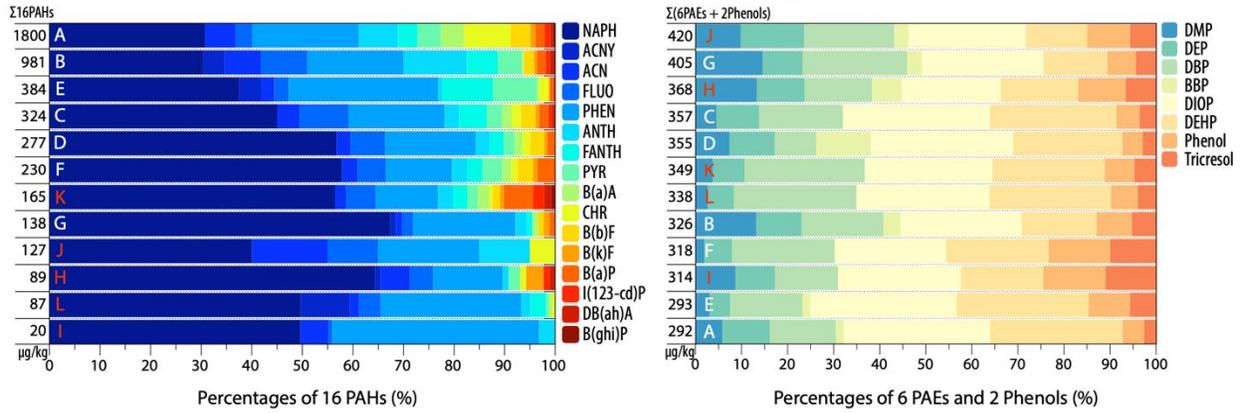
Figure 3. Percentage compositions of $\sum$16PAHs (left) and $\sum$ 6PAEs +2 phenols (right) in the active (A-G, white) and abandoned (K-I, red) tailings ponds, arranged by descending total concentration.

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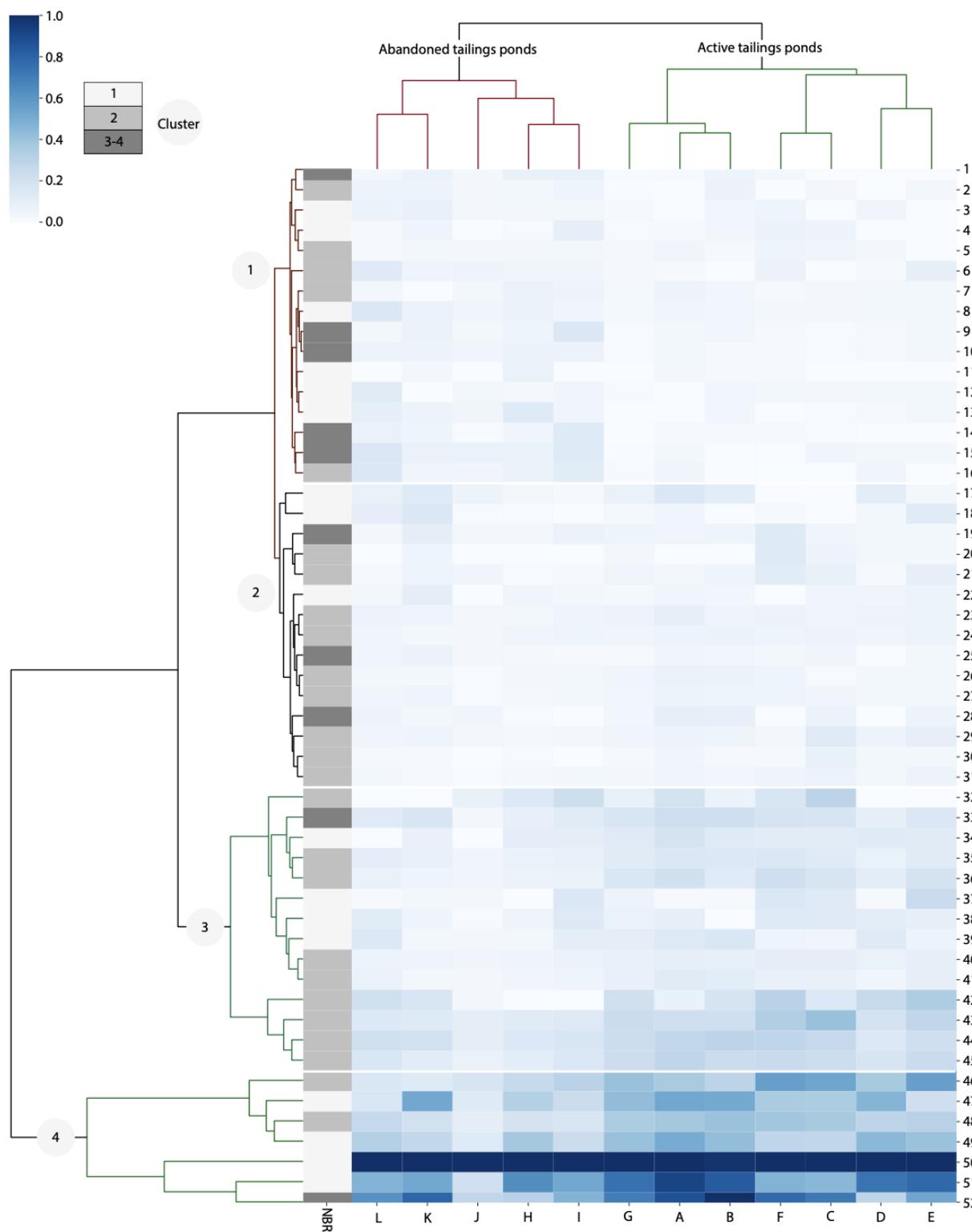
Figure 4. Heat map of tailings data set (using 52 peak areas). The blues color gradient represents
values of highest to lowest intensity. The greys gradient represents the number of benzene rings
(NBR). Numbering corresponds to chemical compounds shown in Table 2.

562
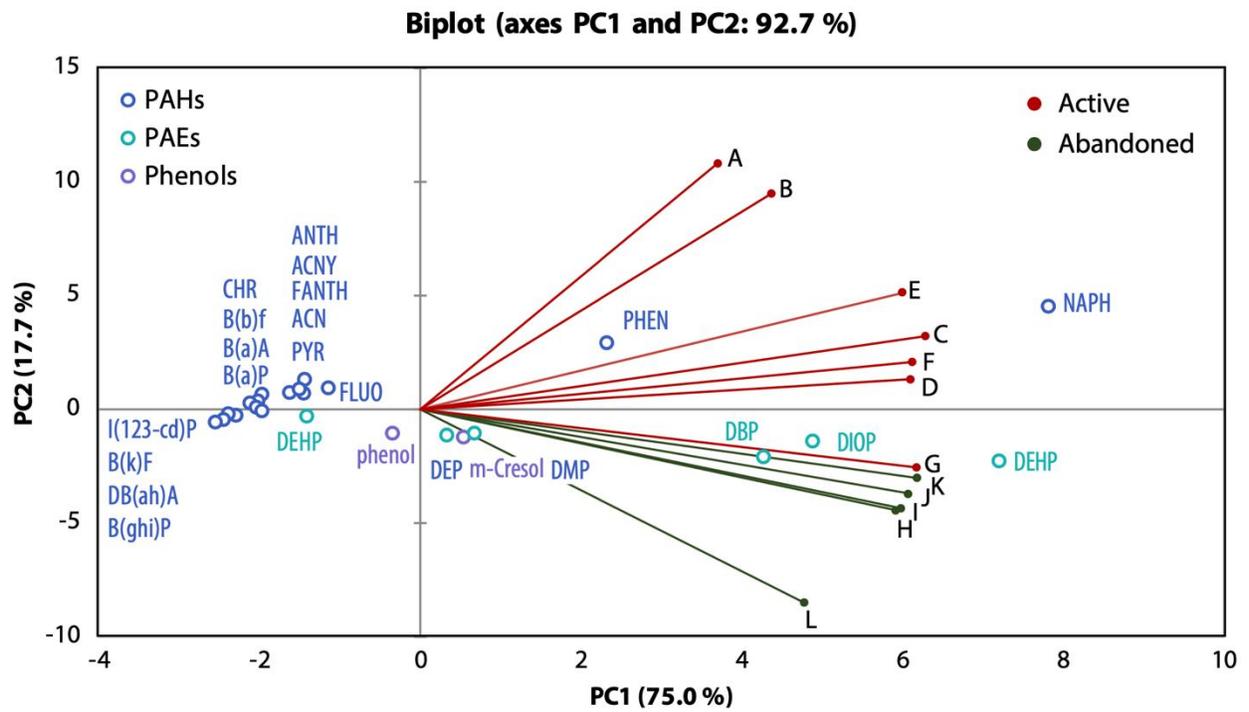
Figure 5. PCA biplot of 16 PAHs, 6PAEs and 2 phenols concentrations in active and abandoned tailings ponds.

565 **Table 1. General information for studied tailings ponds.**

	Information on tailings ponds			Number of GC x GC-generated peaks		
Site	Status	Dominant ore	Abandoned years	Peaks	Qualitative	Unknow[2] peaks
A	active	Pb–Zn	0	589	568	91
B	active	Pb–Zn	0	701	400	51
C[1]	active	Mixed	0	635	345	39
D	active	Pb–Zn, Sb	0	621	346	44
E	active	Unknown	0	624	352	39
F	active	Unknown	0	649	321	61
G	active	Pb–Zn	0	466	266	26
H	abondaned	Unknown	3	521	300	21
I	abondaned	Pb-Zn	8	567	319	35
J	abondaned	Unknown	10	389	216	17
K	abondaned	Sb	20	500	300	21
L	abondaned	Sn	32	489	292	22

566 [1] C tailings pond covers an area of approximately 50,000 m^2, altitude 726 m, established in 1976. The surface crust
567 cracks, white salt and alkali is precipitated and acidic wastewater is dark purple. The pH value is less than 2.0,
568 conductivity more than 9000 μs/cm. [2] 'Unknown' in the GC x GC-generated peak tables meaning the peaks were
569 observed that did not yield sufficiently high mass spectral similarity values (750), due to the low S/N ratio of many of
570 the compounds.

Table 2. Toxicity Results of 52 selected aromatic contaminants in metal(loid)s tailing ponds using ECOSAR Program.

No.[a]	Compounds	CAS	Sites	Formula	log-Kow[b]	Water solubility[c] (mg/L)	Vapor pressure mm Hg (25 °C)	Acute toxicity (mg/L)			Chronic toxicity (mg/L)		
								Fish (LC50)	Daphnid (LC50)	Green Alage (EC50)	Fish	Daphnid	Green Alage
1	Phenanthrene, 4,5-Dimethyl-	3674-69-9	8	C16H14	5.44	0.0713	-	0.138	0.108	0.298	0.02	0.025	0.158
2	Naphthalene, 1,4,6-Trimethyl-	2131-42-2	10	C13H14	4.81	4.78	4.84E-03	0.418	0.308	0.67	0.055	0.062	0.313
3	*Benzene, Decyl-*	104-72-3	6	C16H26	6.96	0.0100	1.28E-03	0.0063	0.0057	0.028	0.0011	0.002	0.02
4	*Benzene, Hexamethyl-*	87-85-4	11	C12H18	5.28	0.235	8.60E-04	0.152	0.177	0.304	0.021	0.026	0.156
5	Naphthalene, 1-Methyl-7-(1-Methylethyl)-	490-65-3	11	C14H16	5.17	2.01	5.00E-03	0.214	0.163	0.408	0.03	0.036	0.205
6	9H-Fluorene, 2-Methyl-	1430-97-3	9	C14H12	4.56	0.541	-	0.739	0.532	1.05	0.096	0.1	0.467
7	*Benzene, Heptyl-*	24157-81-1	10	C16H20	6.08	0.242	5.00E-04	0.038	0.031	0.11	0.0057	0.0087	0.067
8	Benzoic Acid, 2-Ethylhexyl Ester	5444-75-7	11	C15H22O2	5.19	1.06	1.00E-03	0.428	0.632	0.162	0.016	0.173	0.117
9	*Retene*	483-65-8	11	C18H18	6.35	0.0342	2.64E-06	0.024	0.02	0.08	0.0038	0.0061	0.051
10	*4H-Cyclopenta[Def]Phenanthrene*	203-64-5	11	C15H10	4.60	1.10	3.12E-05	0.717	0.518	1.04	0.093	0.099	0.466
11	1,2-Benzenedicarboxylic Acid, Butyl Methyl Ester	34006-76-3	7	C13H16O4	3.14	59.0	-	6.85	12.6	4.48	0.406	6.22	1.66
12	Benzene, (1-Methyldodecyl)-	4534-53-6	6	C19H32	8.36	0.00067	2.29E-04	0.00042	0.00042	0.0036	8.10E-05	0.00021	0.0035
13	*Benzene, 1,4-Dichloro-*	106-46-7	7	C6H4Cl2	3.28	81.3	1.74E+00	8.52	5.45	6.62	0.958	0.738	2.26
14	*Naphthalene, 2-Phenyl-*	612-94-2	7	C16H12	4.93	0.802	3.50E-05	0.39	0.29	0.662	0.052	0.06	0.317
15	*9,10-Dimethylanthracene*	781-43-1	6	C16H14	5.44	0.0560	2.74E-06	0.138	0.108	0.298	0.02	0.025	0.158
16	Naphthalene, 2-Ethyl-	939-27-5	6	C12H12	4.21	8.01	3.16E-02	1.34	0.93	1.61	0.166	0.16	0.664
17	*2,4-Di-Tert-Butylphenol*	96-76-4	9	C14H22O	5.33	35.0	2.10E-03	0.144	0.281	0.014	0.02	0.055	0.067
18	*Diethyl Phthalate*	84-66-2	9	C12H14O4	2.65	1080.00	2.10E-03	12.5	24.2	9.3	0.819	13.7	2.94
19	*Pyrene*	129-00-0	12	C16H10	4.93	0.135	4.50E-06	0.386	0.287	0.656	0.052	0.06	0.314
20	Naphthalene, 2,3,6-Trimethyl-	829-26-5	6	C13H14	4.81	1.70	2.52E-03	0.418	0.308	0.67	0.055	0.062	0.313
21	*Naphthalene, 1-Ethyl-*	1127-76-0	11	C12H12	4.21	10.7	2.52E-02	1.34	0.93	1.61	0.166	0.16	0.664
22	*Benzene, Dodecyl-*	123-01-3	9	C18H30	7.94	0.0100	5.11E-05	0.00093	0.00092	0.0066	0.00017	0.00041	0.0059
23	*4,4'-Dimethylbiphenyl*	613-33-2	11	C14H14	4.85	0.175	8.13E-04	0.411	0.304	0.673	0.055	0.062	0.317
24	*Bibenzyl*	103-29-7	11	C14H14	4.74	4.30	7.28E-03	0.519	0.38	0.805	0.068	0.075	0.37
25	*Phenanthrene, 3,6-Dimethyl-*	1576-67-6	8	C16H14	5.44	0.110	1.82E-05	0.138	0.108	0.298	0.02	0.025	0.158
26	Methane, Di-P-Tolyl-	4957-14-6	11	C15H16	5.11	2.73	3.85E-03	0.26	0.196	0.48	0.036	0.043	0.238
27	*Dibenzothiophene*	132-65-0	11	C12H8S	4.17	1.47	2.50E-04	1.72	1.19	2.03	0.213	0.203	0.83
28	*Fluoranthene*	206-44-0	7	C16H10	4.93	0.260	9.22E-06	0.386	0.287	0.656	0.052	0.06	0.314
29	Naphthalene, 2-(1-Methylethyl)-	2027-17-0	12	C13H14	4.63	8.90	5.18E-03	0.614	0.444	0.902	0.08	0.085	0.405

No.	Compound	CAS		Formula	log-Kow	WS	VP						
30	*9H-Fluorene, 9,9-Dimethyl-*	4569-45-3	9	C15H14	4.60	0.425	-	0.733	0.529	1.06	0.095	0.101	0.476
31	*Acenaphthene*	83-32-9	12	C12H10	2.94	3.90	2.15E-03	1.48	1.03	1.74	0.183	0.174	0.708
32	*Naphthalene, 2-Methyl-*	91-57-6	8	C11H10	3.72	24.6	5.50E-02	3.36	2.23	3.2	0.396	0.339	1.19
33	Naphthalene, 1,2,3-trimethyl-4-propenyl-, (E)-	26137-53-1	12	C16H18	6.13	0.227	-	0.034	0.028	0.102	0.0052	0.008	0.062
34	*N-Propyl Benzoate*	2315-68-6	9	C10H12O2	2.81	351	1.36E-01	7.38	14.1	5.27	0.468	7.62	1.76
35	Fluorene	86-73-7	12	C13H10	4.02	1.69	6.00E-04	2.11	1.45	2.33	0.257	0.237	0.922
36	Naphthalene, 1,4,5-Trimethyl-	2131-41-1	12	C13H14	4.81	2.10	2.52E-03	0.418	0.308	0.67	0.055	0.062	0.313
37	*O-Cymene*	527-84-4	10	C10H14	4.00	23.3	1.50E+00	1.78	1.21	1.94	0.216	0.198	0.764
38	*Benzene, 1,3-Dichloro-*	541-73-1	11	C6H4Cl2	3.28	125	2.15E+00	8.52	5.45	6.62	0.958	0.738	2.26
39	Dehydro-4-Epiabietal	24035-50-5	11	C20H28O	6.27	0.0669	2.15E+00	0.158	0.096	0.091	0.0027	0.0024	0.071
40	*Biphenyl*	92-52-4	11	C12H10	3.76	7.48	8.93E-03	3.35	2.24	3.26	0.396	0.342	1.22
41	9H-Xanthene	92-83-1	11	C13H10O	4.31	4.23	8.47E-04	1.27	0.89	1.6	0.159	0.157	0.673
42	*Naphthalene, 1-Methyl-*	90-12-0	10	C11H10	3.72	25.0	6.70E-02	3.36	2.23	3.2	0.396	0.339	1.19
43	*Naphthalene, 2,6-Dimethyl-*	581-42-0	12	C12H12	4.26	2.00	4.30E-03	1.19	0.833	1.47	0.149	0.145	0.614
44	*Dibenzofuran*	132-64-9	12	C12H8O	3.71	3.10	2.48E-03	3.99	2.65	3.8	0.47	0.402	1.42
45	Naphthalene, 1,2,3,4-tetramethyl-	3031-15-0	7	C14H16	4.07	-	-	-	-	-	-	-	-
46	**Naphthalene**	91-20-3	10	C10H8	3.17	31.00	8.50E-02	9.39	5.94	6.91	1.04	0.782	2.3
47	*Dimethyl phthalate*	131-11-3	12	C10H10O4	1.66	4000	3.08E-03	40.8	88	39.5	3.3	66.3	9.08
48	*1,1'-Biphenyl, 4-Methyl-*	644-08-6	12	C13H12	4.30	4.05	6.42E-03	1.18	0.827	1.49	0.148	0.146	0.625
49	*Diisobutyl Phthalate*	84-69-5	12	C16H22O4	4.46	6.20	4.76E-05	1.36	2.17	0.624	0.061	0.729	0.356
50	*Benzene, 1,2,3-Trichloro-*	87-61-6	11	C6H3Cl3	3.93	18.0	2.10E-01	2.77	1.88	2.93	0.334	0.301	1.14
51	*Dibutyl Phthalate*	84-74-2	12	C16H22O4	4.61	11.2	2.01E-05	1.11	1.75	0.492	0.048	0.565	0..295
52	*Phenanthrene*	85-01-8	11	C14H10	4.35	1.15	1.21E-04	1.15	0.809	1.147	0.145	0.144	0.625

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573 [a] Corresponds to the chemical compound numbering within Figure 4. [b, c] The value of log-Kow (Octanol-water partition coefficient), water solubility (mg/L), and
574 vapor pressure mm Hg (25 °C) obtained from ECOSA. The predicted toxicity value from ECOSAR are classified base on the system established by the Golbally
575 Harmonized System of Classification and Labeling of Chemicals (GHS)[25, 58]: white boxes, not harmful: LC_{50} / EC_{50}/ ChV >100; light grey boxes, harmful: 100 $\geq$
576 LC_{50}/ EC_{50}/ Ch $\geq$10; medium grey, toxic, 10 $\geq$ LC_{50}/ EC_{50}/ Ch $\geq$1; grey, very toxic, LC_{50}/ EC_{50}/ Ch $\leq$ 1 (0.1 $\geq$ LC_{50}/EC_{50}/ Ch $\geq$ 0 was highlight in dark grey).
577 Compounds that have been accurately identified by authentic reference standards are shown in italics with emphasis.

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