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1 **Comparison of Polycyclic Aromatic Compounds in Air Measured by Conventional Passive**

2 **and Passive Dry Deposition Samplers and Contributions from Petcoke and Oil Sands Ore**

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8

9 **Abstract**

10   Conventional passive air samplers (PAS) and passive dry deposition (PAS-DD) samplers

11 were deployed along a 90 km south-north transect at five sites in the Athabasca oil sands region

12 during October to November 2015. The purpose was to compare and characterize the

13 performance of the two passive sampling methods for targeted compounds across a range of site

14 types. Samples were analyzed for polycyclic aromatic compounds (PACs), nitrated polycyclic

15 aromatic hydrocarbons (NPAHs), and oxygenated PAHs (OPAHs). ΣPAC and ΣNPAH

16 concentrations were highest in PAS and PAS-DD samplers at site AMS5, which is the closest

17 sampling site to surface mining and upgrading facilities. The OPAHs were elevated at site

18 AMS6, which is located in the town of Fort McMurray, approximately 30 km south of the main

19 mining area. The PAS-DD was enriched relative to the PAS in particle associated target

20 chemicals, which is consistent with the relatively more open design of the PAS-DD intended to

21 capture particle- (and gas-phase) deposition. Petroleum coke (petcoke) (i.e. the carbonaceous by-

22 product of bitumen upgrading) and oil sands ore (i.e. the material mined in open pit mines from

23 which bitumen is extracted) were assessed for their potential to be a source of PACs to air in the

24 oil sands region. The ore samples contained ~8 times and ~40 times higher ΣPACs

25 concentrations (dry weight basis) than delayed and fluid petcoke, respectively. The residue

26 analysis of ore and petcoke samples also revealed that the chemical 4-nitrobiphenyl (4-NBP) can

27 be used to track gas-phase emissions to air. A comparison of chemical residues in ore, petcoke

28 and air samples revealed that the ore is likely a major contributor to volatile PACs present in air

29 and that both ore and petcoke are contributing to the particle-associated PACs in air near open pit

30 mining areas. The contribution of petcoke particles in passive air samples was also confirmed

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31   qualitatively using scanning electron microscopy coupled with energy dispersive X-ray

32   spectroscopy.

33

1 Introduction

35   Application of passive air sampling techniques has become widespread due to their

36   simplicity, convenience, and cost-effectiveness. It enables us to routinely monitor air pollutants

37   at a larger scale and to extend air monitoring networks to strategic sites that are not feasible for

38   active air sampler installation. Conventional double-domed polyurethane foam (PUF) disk

39   passive air samplers (PAS) have been commonly used in several air monitoring programs,

40   including the Athabasca oil sands air monitoring network, which uses the Global Atmospheric

41   Passive Sampling (GAPS) Network-type sampler (Harner et al., 2006; Pozo et., 2004; Klánová.,

42   2006; Jaward., 2004; Schuster et al., 2015). A recent study demonstrated that the GAPS-type

43   polyurethane foam (PUF)-PAS sampler was capable of accumulating particles, ranging in size

44   from 250 to 4140 nm, with no discrimination compared to conventional PS-1 type active air

45   samplers (Markovic et al., 2015). The geometry of the PUF-PAS allows it to capture fine

46   particles (aerodynamic diameter $< 2.5\ \mu m$) in addition to gas-phase compounds which makes it

47   suitable for investigating semi-volatile organic compounds (Deng et al., 2007; Albinet et al.,

48   2008b; Chrysikou et al., 2009). However, coarse particles (aerodynamic diameter $>10\ \mu m$) are

49   excluded from collection since the overlapping double-dome design of the PUF-PAS does not

50   allow direct flow of bulk air through the sampler (Thomas et al., 2006). The coarse particle

51   component is the major contributor to the particle deposition flux, particularly in the settling

52   zone near emission sources (Holsen et al., 1992). As such, a prototype passive dry deposition

53   (PAS-DD) sampler was introduced in our recent study to assess dry deposition of polycyclic

54   aromatic hydrocarbons (PAHs) and related compounds (Eng et al., 2013). The design of the

55   PAS-DD, which incorporates a PUF disk as the collection substrate, positioned between two

56   open parallel flat plates that are shielded above, allows for dry particle deposition from bulk air

57   as well as dry gas-phase deposition (Figure S1).

58   Starting in October 2015, PAS-DD samplers were co-deployed with PAS samplers at 5

59   sampling sites in the Athabasca oil sands region (AOSR) in order to compare the performance of

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60   the two samplers. These sampling sites are part of a larger 16-site passive air monitoring network

61   that has been operating since 2010 (Schuster et al., 2015) under the Canada/Alberta Oil Sands

62   Monitoring (OSM) plan and reporting on polycyclic aromatic compounds (PACs) (i.e. parent and

63   alkylated PAHs, dibenzothiophene (DBT), alkylated DBTs, retene (RET)), PAH derivatives,

64   including nitrated polycyclic aromatic hydrocarbon (NPAH) and oxygenated PAH (OPAH), as

65   well as an assessment of the toxicity potential of the chemical mixture (Schuster et al., 2015;

66   Jariyasopit et al., 2016).

67   As a result of an increase in oil sands production, there has been growing concern over

68   impacts of organic constituents in air, their transport and deposition, and the associated impact

69   on the health of the environment and on humans. One of the important classes of organic

70   pollutants in this context is the PACs. PACs are emitted from a variety of sources such as

71   combustion processes (e.g. forest fires, trash burning) and also petrogenic sources; they are

72   present in the bitumen-containing ore that is mined in the AOSR (Yang et al., 2011). Information

73   on PAC sources can be obtained from the National Pollutant Release Inventory (NPRI) and

74   Environmental Impact Assessment (EIA), but these are limited to PACs which do not account

75   for compounds produced by transformation reactions (NPRI, http://ec.gc.ca/inrp-npri/donnees-

76   data/index.cfm?lang=En; Government of Alberta,

77   https://exts2.aep.alberta.ca/DocArc/EIA/Pages/default.aspx). The major mining-related

78   emissions of PACs include stacks, mining fleet vehicles, open mine pits, exposed ore deposits,

79   and fugitive dusts such as petroleum coke (petcoke) (Zhang et al., 2016). Secondary and

80   evaporative sources of PACs (e.g. tailings ponds) have also been suggested through

81   measurements and models (Galarneau et al., 2014; Parajulee et al., 2014). The atmospheric

82   deposition of PACs across the oil sands region has also been investigated using snow and lichens

83   and estimated through modeling (Zhang et al., 2015; Studabaker et al., 2012; Kelly., 2009).

84   Zhang et al., 2016 have also investigated the role of petcoke particle deposition to snow as a

85   mechanism of the transport and deposition of PACs to terrestrial surfaces.

86   Petcoke is a solid residue and is a byproduct of the upgrading of bitumen after lighter

87   hydrocarbon molecules have been fractionated. There are two major types of coking in the

88   AOSR referred to as "delayed" and "fluid" coking processes. The majority of petcoke produced

89   in the AOSR has been stockpiled while only a small percentage is re-used on-site as fuel (Alberta

90   Energy Regulator, 2014). Recently petcoke has been used for capping decommissioned tailings

91   ponds, which greatly enhances its surface area available for erosion and evaporation (Alberta

92   Energy Regulator, https://www.aer.ca/documents/sts/ST98/ST98-2014.pdf). We hypothesize that

93   secondary emissions to air of PACs from oil sands ore (open pit mines) and/or petcoke

94   stockpiles, either through evaporation or particle suspension in air (e.g. wind transport)

95   contribute substantially to PAC burdens in air, especially in areas nearby sources. Therefore in

96   addition to comparing the performance of PUF-PAS and PAS-DD samplers, a secondary

97   objective of this study is to assess the extent to which oil sands ore and petcoke contribute to the

98   PAC burden of air in the AOSR.

99   **2 Materials and methods**

100   **2.1 Sampling**

101   Five sampling sites (Figure 1) are part of the passive air monitoring network in the

102   AOSR. Details regarding site locations, sampling media preparation, and sample deployment

103   have been previously described (Schuster et al., 2015). The samplers were mounted

104   approximately 3 m above the ground. In brief, PUF disks were pre-cleaned with accelerated

105   solvent extraction (Dionex ASE 350) using acetone, petroleum ether, and acetonitrile, prior to

106   use. Since October 2015, the PAS-DD samplers have been deployed alongside the PAS samplers

107   at a subset of 5 sites (Figure 1 and Figure S1). The PAS-DD sampler was previously

108   demonstrated to collect gas-phase PAHs (i.e. dry gas-phase deposition) at similar rates as the

109   PAS sampler (Eng et al., 2013). A sampling rate of about 5 m^3 d^{-1} was derived previously using

110   co-located PAS and high volume samplers for the gas- and particle-phase PACs (Harner et al.,

111   2013). Concentrations measured by PAS-DD sampler were expressed as ng m^{-3} for comparison

112   with PAS sampler, using the PAS sampler effective air sample volume, corrected for reduced

113   exposure surface of the PAS-DD sampler. Two field blanks were included in the sampling. Oil

114   sands ore was collected from an open pit mine and provided through the cooperation of COSIA

115   and samples of delayed and fluid petcoke were obtained from the University of Alberta and were

116   the same samples previously characterized and reported by Zhang et al., 2016.

117   **2.2 Chemicals and Materials**

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118 The monitored PACs, NPAHs, and OPAHs are listed in Table S1. Standards for the

119 target analytes were purchased from Cambridge Isotope Labs (Andover, MA) and Chiron

120 (Trondheim, Norway), and AccuStandard (New Haven, CT), Chiron (Norway). Deuterium-

121 labeled recovery and internal standards were purchased from Cambridge Isotope Labs (Andover,

122 MA) and CDN Isotopes (Point-Claire, Quebec, Canada). The deuterated recovery surrogates

123 included 2,6-dimethylnaphthalene-d_{12}, acenaphthene-d_{10}, anthracene-d_{10}, benzo(b)naphtho(2,1-

124 d)-thiophene-d_{10}, 1-nitronaphthalene-d_7, 2-methyl-1-nitronaphthalene-d_9, 5-nitroacenaphthene-

125 d_9, 9-nitroanthracene-d_9, 3-nitrofluoranthene-d_9,1-nitropyrene-d_9, and 6-nitrochrysene-d_{11}. The

126 deuterated internal standards included fluorine-d_{10} and benz(a)anthracene-d_{12}, 2-nitrobiphenyl-

127 d_9, and 2-nitrofluorene-d_9. PUF disks (TE-1014, 14 cm diameter × 1.35 cm thick) were

128 purchased from Tisch Environmental (Village of Cleves, OH).

129 **2.3 Sample Preparation and Analyses**

130 *2.3.1 Chemical analyses.* PUF disk, fluid petcoke (~0.5 g), delayed petcoke (0.2 g), and

131 oil sands ore (~0.15 g) samples were spiked with the labeled recovery PAC and NPAH

132 surrogates (250 ng) prior to extraction by accelerated solvent extraction (Dionex ASE 350) using

133 petroleum ether and acetone (75:25, v:v; 2 cycles). For the passive air and petcoke samples, the

134 extracts were purified using 5 g silica columns (Mega BE-SI, Agilent Technologies, New Castle,

135 DE), eluted with dichloromethane. The oil sands ore samples were purified using 20 g silica

136 columns (Mega BE-SI, Agilent Technologies, New Castle, DE), eluted with dicholoromethane.

137 Following solvent reduction under a purified N_2 stream with a Turbovap II (Biotage, NC), the

138 sample extracts were spiked with the labeled PAC and NPAH internal standards (250 ng). PAC

139 analysis was carried out using gas chromatography mass spectrometry (GC-MS, Agilent 6890

140 coupled with an Agilent 5975 MSD), by electron impact ionization in selected ion monitoring

141 mode, on a DB-XLB column (30 m × 0.25 mm I.D., 0.25 μm film thickness, Agilent

142 Technologies). NPAH and OPAH analysis was conducted using a GC-MS (Agilent 7890A

143 coupled with and Agilent 7000 MSD), in electron capture negative ionization (ECNI), on a DB-5

144 column (30 m × 0.25 mm I.D., 0.25 μm film thickness, Agilent Technologies) (Jariyasopit et al.,

145 2016).

146 *2.3.2 Scanning Electron Microscopy.* Analysis using SEM-EDS (Zeiss Sigma 300 VP-

147 FESEM) was carried out at the University of Alberta Earth and Atmospheric Sciences SEM lab.

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148 A pie-shaped wedge section of PUF disk (2 cm base) was used for the SEM-EDS analysis.

149 Particles entrained in the PUF wedges were removed by ultrasonication in dichloromethane,

150 which was subsequently dried by nitrogen gas. A portion of the dried particles was transferred to

151 double sided adhesive conductive tape for SEM-EDS analysis. The EDS spectra were acquired

152 by a Bruker energy EDS system with dual silicon drift detectors each with an area of 60 mm^2 and

153 a resolution of 123 eV. Additional details on the SEM-EDS approach are provided in Zhang et

154 al., 2016.

155 *2.3.3 Quality Assurance and Quality Control.* Results were corrected to account for the

156 wedge portion removed for the SEM analysis and also for the area of the PUF disk covered by

157 the open plate and perforated support that holds the PUF in place (representing about ~36% of

158 the PUF area). All data were recovery and blank corrected. Average surrogate recoveries for

159 PACs, PAC derivatives were 80% (±27%) and 65% (±15), respectively. The instrumental and

160 method detection limits (IDL and MDL) are given in Table S1. Values below MDL were

161 replaced by 2/3 of MDL for statistical purposes (Schuster et al., 2015).

162 **3 Results and Discussion**

163 **3.1 Ambient concentrations of PACs, NPAHs, and OPAHs.** The highest

164 concentrations in air for ΣPACs_PAS and ΣPACs_PAS-DD were 58 and 150 ng m^{-3}, respectively

165 (Table S2), and observed at site AMS5, which is in close proximity to upgrading facilities. The

166 lowest concentrations of ΣPACs_PAS and ΣPACs_PAS-DD were 14 and 24 ng m^{-3}, respectively, and

167 were observed at AMS14, which is ~35 km southeast of Fort McMurray and adjacent to a near-

168 lake residential settlement (Anzac) that is well-removed from the open-pit mining (Table S2) but

169 within several kilometers of a bitumen upgrading facility. For all the sites, the PAS and PAS-DD

170 samples exhibited similar relative PAC compositions, with C1 Phenanthrenes/Anthracenes (C1-

171 PHEs/ANTs) and PHE being the most abundant alk-PAH and parent PAH, respectively (Figure

172 S2). For both PAS and PAS-DD samplers, the PAC chemical compositions were dominated by

173 the 2-3 ring PAHs and 2-3 ring alk-PAHs, which accounted for 65%-70% of the sum of all target

174 compounds (Figure 2). Residential sites (AMS6 and AMS14) were characterized by lower

175 concentrations in air of dibenzothiophene (DBT) and alk-DBTs (compounds that are enriched in

176 bitumen) but higher retene (RET) concentrations (a marker of wood combustion) (Ramdahl et

177 al., 1983), compared to other sampling sites that are closer to the main oil sands activities. This

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178   suggests reduced influence of petrogenic sources and an increased contribution from wood

179   combustion at sites AMS6 and AMS14, which is consistent with their greater distance from open

180   mining areas and greater proximity to residential area where wood is burned for heating and

181   recreational activities. However, it should be noted that RET does not solely originate from wood

182   burning and has also been reported for stack emissions in the oil sands region during the winter

183   period, which challenges the explanation above (Watson et al., 2013). It is also possible that the

184   small (relative to main mining area) upgrading facility, which is several kilometers southeast of

185   AMS14, may play a role.

186   For all the sites, $\Sigma NPAHs\_{PAS}$ and $\Sigma NPAHs\_{PAS-DD}$ were dominated by 2 ring NPAHs,

187   (Table S2). Concentrations in air of $\Sigma NPAHs\_{PAS}$ and $\Sigma NPAHs\_{PAS-DD}$ were highest at AMS5

188   (152 pg m^{-3} and 170 pg m^{-3}, respectively) and lowest at AMS14 (8.42 pg m^{-3} and 14.2 pg m^{-3},

189   respectively). At AMS 5, 1-methyl/2-methyl-5-nitronaphthalene (1M5NN/2M1NN) was the

190   most abundant NPAH in the PAS sample, whereas 4-nitrobiphenyl (4-NBP) was the most

191   abundant NPAH in the PAS-DD sample. The nitromethylnaphthalenes are known products of the

192   gas-phase OH and NO_3 radical-initiated reactions with methylnaphthalenes (Reisen et al., 2004),

193   while 4-NBP emission sources are not well understood and it is usually not included in air

194   monitoring campaigns. Past studies reported that ambient 4-NBP concentrations were low or

195   below detection even in urban areas (Crimmins et al., 2006; Wang and Jariyasopit et al., 2011).

196   A study reported an average 4-NBP concentration in air of 45 pg m^{-3} in Texas, at a sampling site

197   close to petrochemical manufacturing plants and oil refineries (Wilson et al., 1995). Previous

198   chamber reaction experiments demonstrated that 3-nitrobiphenyl (3-NBP) was the only nitro

199   product formed by the OH-radical initiated chamber reaction of biphenyl and that no nitro

200   products were observed from the NO_3-radical initiated chamber reaction (Atkinson and Arey,

201   1994). In this study, 3-NBP was below the detection limit at all the sites, while 4-NBP was

202   detected only at AMS5 and AMS9. It should be noted that in the same sampling period, the 4-

203   NBP concentration measured in a PAS sample at site AMS11 (data not shown), designated as the

204   main oil sands source region (Jariyasopit et al., 2016), was a factor of five higher than that

205   observed at AMS5, suggesting that airborne 4-NBP is closely linked to oil sands industrial

206   activities. However, according to our previous study, 4-NBP was below the detection limit at all

207   15 passive sampling sites during the reporting period April to May 2014 (Jariyasopit et al.,

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208   2016). Long-term monitoring of NPAHs could provide insight into seasonal and temporal trends

209   of NPAHs in air in the AOSR and improve understanding of their formation and sources.

210   NPAHs have been previously measured in $PM_{2.5}$ released from stacks emissions in the

211   AOSR (Watson et al., 2013). The majority of NPAH target compounds were below detection

212   limits in the $PM_{2.5}$ collected from stacks in the oil sands region, with the exception of 9-

213   nitroanthracene (9-NAN) (Watson et al., 2013). In general, 9-NAN was dominant NPAH in

214   urban areas and present at approximately as high concentrations as 2-nitrofluoranthene (2-NF)

215   which is the major particle-associated NPAH known to be formed by atmospheric OH and NO_3

216   radical-initiated reactions (Wang and Jariyasopit et al., 2011; Bamford et al., 2003; Albinet et al.,

217   2007). In this study site AMS5, which is close to upgrading facilities, exhibited the highest

218   ΣNPAHs concentration, however 9-NAN was below detection limits. This result suggests that

219   stack emissions were not a major PM source contributing to NPAH concentrations measured by

220   passive samplers.

221   For OPAHs, highest concentration was found at AMS6 which is located in the town of

222   Fort McMurray, approximately 30 km south of the main mining area. This is consistent with our

223   previous study. The elevated OPAHs at this site are due to local primary combustion sources

224   (e.g. vehicular exhausts) as well as enhanced atmospheric transformation process which is

225   dependent on gaseous oxidants emitted from the combustion sources (Jariyasopit et al., 2016).

226   The highest concentrations for ΣOPAHs$_{PAS}$ and ΣOPAHs$_{PAS-DD}$ were 753 and 1480 pg m^{-3}.

227   The lowest concentrations for ΣOPAHs$_{PAS}$ and ΣOPAHs$_{PAS-DD}$ were 213 pg m^{-3} and 352 pg m^{-}

228   ^{3}, respectively, and were observed at AMS13. The dominant contributor was 2-3 ring OPAHs

229   (Table S2). For both sampler types 9-fluorenone (FLO) was the dominant OPAHs at all sites.

230   Different target OPAHs have been reported by various air monitoring campaigns making it

231   challenging to compare the OPAH air concentrations in the AOSR to data available in the

232   literature. On average, the ΣOPAHs concentrations derived from PAS and PAS-DD samplers in

233   this study were comparable or lower than concentrations measured at urban sites (Wang and

234   Jariyasopit et al., 2011; Ahmed et al., 2015; Albinet et al., 2008a).

235   **3.2 PUF-PAS versus PAS-DD sampler.** A key aspect of the study was to compare the

236   performance of the PAS and PAS-DD sampler to capture PACs, NPAHs, and OPAHs. Their

237   relative performance can be illustrated using the enhancement ratio which is defined as the ratio

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238　of the concentration of an analyte in the PAS-DD sampler to that in the PAS sampler. A value

239　close to 1 indicates comparable ability of the two sampler types for capturing an analyte. Figure

240　3 shows enhancement ratios for PACs for all the sampling sites. Average ratios for 2-3 ring, 4

241　ring, and 5-6 ring PACs were 2.3, 2.8, and 3.6 respectively. Similarly, the enhancement ratio

242　increased with molecular weight for the NPAHs (Figure S3) up to an average value of about 4.

243　This finding illustrates the enhanced ability of the PAS-DD to capture more of the higher

244　molecular weight target compounds that are associated with the larger depositing particles in air,

245　whereas the PUF-PAS preferentially samples the smaller airborne particles.

246　　　The enhancement ratios for the NPAHs and OPAHs were considerably more variable

247　among sites compared to the patterns observed for the PACs (Figure S3). This may be due to

248　multiple factors contributing to their presence in air, which can be by direct emission from

249　primary sources as well as production in air through transformation processes. Transformation

250　reaction rates will vary among NPAH and OPAH compounds and also spatially, depending on

251　atmospheric conditions and oxidant concentrations.

252　　　**3.3 Chemical compositions of Petcoke and Oil Sands Ore.** The composition of PACs,

253　NPAHs, and OPAHs in petcoke and oil sands ore samples was investigated in order to assess if

254　these compositions are reflected in the passive air samplers, and thereby indicating potential

255　contributions. Results of residue analysis are discussed below and summarized in Table 1.

256　Individual PAC concentrations and composition are given in Table S3 and Figure S4.

257　　　**3.4 PACs.** The levels of ΣPACs (dry weight basis) were approximately five times higher

258　in the delayed petcoke (85,300 ng g^{-1}) compared to the fluid petcoke (16,700 ng g^{-1}) (Table 1).

259　The greater abundance of PACs in delayed petcoke (vs fluid petcoke) is likely due to the lower

260　temperatures involved in the delayed coking process (Anthony et al., 1995), resulting in reduced

261　losses of PACs due to degradation/volatilization, leaving PACs more concentrated in the residue.

262　Furthermore, the residues of 2-3 ring alk-PAHs and 4-6 ring alk-PAHs were ~10 times and ~2

263　times higher than their parent PACs (Table 1). DBT and alk-DBTs concentrations in the delayed

264　petcoke were ~5 times higher than the concentrations in the fluid petcoke. Despite the difference

265　in absolute residue concentrations of PACs, the PAC profiles were similar in delayed and fluid

266　petcoke: 4-6 ring compounds accounting for ~60% of the ΣPACs (Figures 5 and S4); of which,

267　4-6 ring alk-PAHs was the dominant group. It is also noteworthy that chrysene (CHR) and the

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268   sum of alk-benzo(a)anthracenes, alk-triphenylenes, and alk-chrysenes (alk-BTCs) were major

269   components of petcoke (Table S3 and Figure S4). The oil sands ore residue concentration of

270   ΣPACs (dry weight basis) was 680,000 ng g^{-1} which was ~40 and ~8 times higher than ΣPACs

271   determined in the fluid and delayed petcoke, respectively (Tables 1 and S3). The oil sands ore

272   had the highest residue concentrations of 2-3 ring parent PAHs, alk-PAHs, RET, and alk-DBTs,

273   however, the delayed petcoke had the greatest residue concentrations of 4-6 ring parent PAHs

274   and DBT (Table 1). In contrast to the PAC compositions of the fluid and delayed petcoke, 2-3

275   ring PACs were the major component in the oil sands ore accounting for ~70% of the ΣPACs

276   (Table 1 and Figure 4). A past study reported percent contribution of 2-3 ring PACs in oil sands

277   samples ranging from 79%-94% of the ΣPACs (Yang et al., 2011). Variability in percent

278   contribution was caused by the degree of biodegradation in the samples, with greater

279   biodegradation leading to reductions in 2-3 ring alkylated PAHs (Yang et al., 2011).

280   **3.5 NPAH and OPAH.** Residues of the sum of NPAH and OPAH concentrations in the

281   oil sands ore sample were 2 to 4 orders of magnitude lower than the PAC concentrations in the

282   delayed and fluid petcoke samples, respectively (Table 1). Similar to the results for PACs in

283   petcoke samples, the oil sands ore exhibited higher ΣNPAHs (332 ng g^{-1}), which were 1.6 times

284   and 178 times higher, respectively than in the delayed (208 ng g^{-1}) and fluid petcoke (1.91 ng g^{-1})

285   (Table S3). However, the delayed petcoke was the most enriched in 4-6 ring NPAHs. The most

286   abundant NPAHs in the delayed petcoke were 6-nitrobenzo(a)pyrene (6-NBaP) (138 ng g^{-1}),

287   whereas the most abundant in the ore was 4-NBP (228 ng g^{-1}). The presence and absence of these

288   compounds in the various source samples presents an opportunity to use these as markers to

289   evaluate emission sources to air. Figure 5 summarizes the occurrence of the various NPAH

290   marker compounds by showing extracted ion chromatograms for samples of delayed and fluid

291   petcoke, ore, and two passive air samples. In the following section of the discussion, we consider

292   the implication of these profiles for indicating potential contributions to air of petcoke and ore

293   particles.

294   Despite having relatively lower residues of PACs and NPAHs, the delayed petcoke

295   exhibited higher residues of ΣOPAHs compared to fluid petcoke and ore - approximately 10

296   times and 3 times higher, respectively (Tables 1 and S3). The most abundant OPAHs in fluid

297   petcoke, delayed petcoke, and ore were 9,10-anthraquinone (ANQ, 31 ng g^{-1}),

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298   benzo(a)fluorenone (BaFL, 180 ng g^{-1}), and FLO (113 ng g^{-1}), respectively. All individual

299   OPAH concentrations measured in the delayed petcoke were higher than those measured in the

300   fluid petcoke and the oil sands ore except for FLO which was highest in the ore. The fluid

301   petcoke and ore were enriched in lower ring OPAHs, however, the delayed petcoke was enriched

302   in higher ring OPAHs. OPAHs have been identified as transformation products of biological

303   and chemical processes and reported to be abundant in soils from PAH contaminated sites in

304   Sweden and thought to be formed through PAH remediation processes including bioremediation

305   and Fenton oxidation (Lundstedt et al., 2007).

306   **3.6 Contribution of Petcoke and Oil sands ore to PAC burdens in air.** Comparisons

307   of PAC compositions for the delayed petcoke, fluid petcoke, and oil sands ore versus the PUF-

308   PAS, and PAS-DD air samples revealed interesting differences as shown in Figure 4 and Figure

309   S4. For instance, the petcoke particles exhibited enrichment in the higher molecular weight,

310   semi-volatile and particulate-associated parent PAHs and alk-PAHs, while the oil sands ore and

311   passive air samples were dominated by lower molecular weight and more volatile alk-PAHs.

312   DBT makes up a small proportion (~0.1% - 1%) in all the samples. Alk-DBTs comprise 13% of

313   the ΣPACs in the delayed and fluid petcoke but was 17% in the oil sands ore (Table S3); whereas

314   small compositions of alk-DBTs were observed in the PAS and PAS-DD air samples (mean of 6-

315   7%) (Table S4). RET accounted for 1%-3% of the ΣPACs in the oil sands ore, PAS, and PAS-

316   DD but it accounted for much smaller proportions in the fluid petcoke and delayed petcoke.

317   Furthermore, as illustrated in Figure S4, individual 2-3 ring PACs in the oil sands ore and

318   passive air samples make up similar proportions of the ΣPAC burden. Given the relatively higher

319   volatility of these 2-3 ring PACs, this suggests that oil sands ore is contributing substantially to

320   these gas-phase PACs in air, most likely through volatilization from open mine faces.

321   To assess the potential contributions of particle-associated PACs in air, stemming

322   potentially from either petcoke or the exposed ore from open pit mines, we focus on the higher

323   molecular weight compounds which exist primarily in the particle-phase. These compounds

324   dominate the PAC composition of petcoke (Figure S4), since the more volatile, lower molecular

325   weight compounds, are depleted during the high temperature coking process. If petcoke and/or

326   ore particles represent an important contributor to PACs present in air, then their compositions

327   should be reflected in PAS and especially the PAS-DD samples. The compositions of the 4-6

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328 ring PACs in delayed petcoke, fluid petcoke, oil sands ore, and passive air samples are compared

329 in Figure S5. The parent 4-6 ring PAH composition of the passive air samples did not match the

330 4-6 ring PAH compositions of the petcoke and ore, suggesting a minimal contribution of these

331 sources to parent PAH burdens in air. This implies that other source of parent PAHs (e.g.

332 combustion, vehicle emissions) were more dominant; whereas the 4-6 ring alk-PAH

333 compositions for all samples were more similar, suggesting some contribution of petcoke and oil

334 sands ore particles in the passive air samples. However, these findings for parent PAHs and alk-

335 PAHs are somewhat contradictory. If petcoke particles had contributed substantially to alk-PAHs

336 in air, then the parent PAHs contained in these same particles (and making up ~25% of the PAC

337 residue, Table S3) should have also been important contributors, especially since concentrations

338 in air of parent PAHs are much lower and therefore more sensitive to the petcoke contribution.

339 The results are less contradictory in the case of ore since ore residues are dominated by alk-

340 PAHs (~95%, Table S3). In other words, ore particles could be contributing substantially to the

341 alk-PAHs present in air but not substantially to parent PAHs in air, which is consistent with

342 Figures S4 and S5. In fact, the relative proportions of alk-PAHs to parent PAHs in ore is

343 consistent with the relative proportions observed in air, with a dominance of the alk-PAHs

344 (Figure 4, Table S2).

345   In the case of NPAHs and OPAHs, their relatively low residue concentrations in petcoke

346 and ore samples, complicates the assessment of potential contributions of these particles to air

347 samples. As shown in Figure 5, the high molecular weight and particle-associated NPAH marker

348 compounds, 2-NP, 1,6-DNP, and 6-NBaP, are detected in various petcoke and ore samples but

349 not reflected in air. However, the gas-phase marker compound 4-NBP, which is present in

350 delayed petcoke is also captured at site AMS5 and AMS9 (Table S2). These two sites are the

351 closest to open pit mines which points to the potential importance of volatilization from open pit

352 mines as a source to air of 4-NBP and other volatile PACs. This finding is supported by the

353 results of a simple ore-air partitioning experiment showing that 4-NBP was in fact detected in air

354 that has equilibrated with ore. Details of the experimental set-up which are based on Francisco et

355 al., 2017 are provided in the Supplement.

356   We conclude that oil sands ore is contributing substantially to burdens of PACs in air

357 near mining areas but not at sites further removed from open mines. This finding is consistent

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358 with air and snow monitoring studies that indicate that most of the deposition of mining related

359 particles and associated chemicals occurs within the first several kilometers of mining areas

360 (Schuster et al., 2015; Kelly et al., 2009).

361 **3.7 Qualitative SEM-EDS analysis of PUF disks.** In this aspect of the study, passive air

362 samples were screened for petcoke particles using scanning electron microscopy (SEM) and

363 energy dispersive x-ray spectroscopy (EDS). Petcoke particles can be distinguished from ore and

364 other particle types by their unique morphology (using SEM) and elemental composition (based

365 on EDS spectra). An image and EDS spectrum of an authentic delayed petcoke particle is shown

366 in Figure 6A, demonstrating the unique relative elemental abundance (excluding carbon) as S

367 (Sulfur) > Si (Silicon) ≈ Al (Aluminum). Whereas ore particles have different relative elemental

368 abundance (i.e. Si > S > Al) (Zhang et al., 2016). Based on their morphology and elemental

369 composition, petcoke particles were screened for and identified in all of the passive air samples.

370 It should be noted that elemental composition of delayed and fluid petcoke particles are

371 indistinguishable, however, they can be distinguished from each other by morphology at 1000×

372 magnification (Zhang et al., 2016). Figure 6B shows an image of petcoke-like particle in PAS-

373 DD PUF deployed at AMS5, and the elemental profile with the dominance of sulfur. The results

374 of the particle screening exercise carried out on all of the PAS and PAS-DD samples confirmed

375 the presence of petcoke particles in PUFs collected at AMS5, AMS9, and AMS13, which are the

376 sampling sites closest to mining activities (Figure 1). This indicates that surface-derived particles

377 such as petcoke and ore particles can be suspended in air and transported away from mining

378 areas, albeit over relatively short distances. Because volatile PAH residues in ore particles are

379 much greater than in petcoke particles (Table S3), it is also very likely that ore makes a larger

380 contribution to air burdens of PACs, which is consistent with the earlier discussion related to

381 marker compounds and chemical profiles.

382 **6 Summary**

383 In summary, this study demonstrated the performance of the PAS-DD in capturing

384 depositing particles that are enriched with the higher molecular weight PACs and PAC

385 derivatives. Due to the design of PAS-DD where the PUF disk is shielded from precipitation and

386 direct sunlight by a cover plate, PACs captured by PAS-DD reflects dry deposition of PACs that

387 have been protected from photolytic degradation. Alternatively, environmental passive samplers

388 such as peat and moss have been used to collect wet and dry depositions (Zhang et al., 2016).

389 These environmental passive samplers are exposed to direct sunlight but potentially collect more

390 of the dry deposited fraction, especially the very large particles which may be excluded by PAS-

391 DD due to the top cover plate. The environmental samplers also accumulate PACs deposited in

392 precipitation. Therefore we consider PAS-DD, peat and moss as complementary tools for

393 assessing ecosystem impacts through atmospheric deposition. The comparisons of chemical

394 composition of PACs in passive air samples with petcoke and oil sands ore samples

395 demonstrated an important contribution of oil sands ore to PAC concentrations in air for sites

396 that were closer to open pit mining areas. Further characterization of ore-air partitioning is

397 identified as a topic for future experimental work and modelling. Lastly, in this study we identify

398 4-NBP (4-nitrobiphenyl) as a potential marker chemical of oil sands ore and delayed petcoke.

399 *Data Availability*. Data used in this study are provided in the Supplement.

400 *Competing interests*. The authors declare that they have no conflict of interest.

401 **Acknowledgements**

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Figure 1. Passive sampling site map (110 km × 180 km). AMS5 – Mannix, AMS6 – Fort McMurray, AMS9 – Barge landing, AMS13 – Syncrude, AMS14 – Anzac. A) Conventional PUF disk passive air samplers (PAS) and B) Passive dry deposition (PAS-DD) sampler.
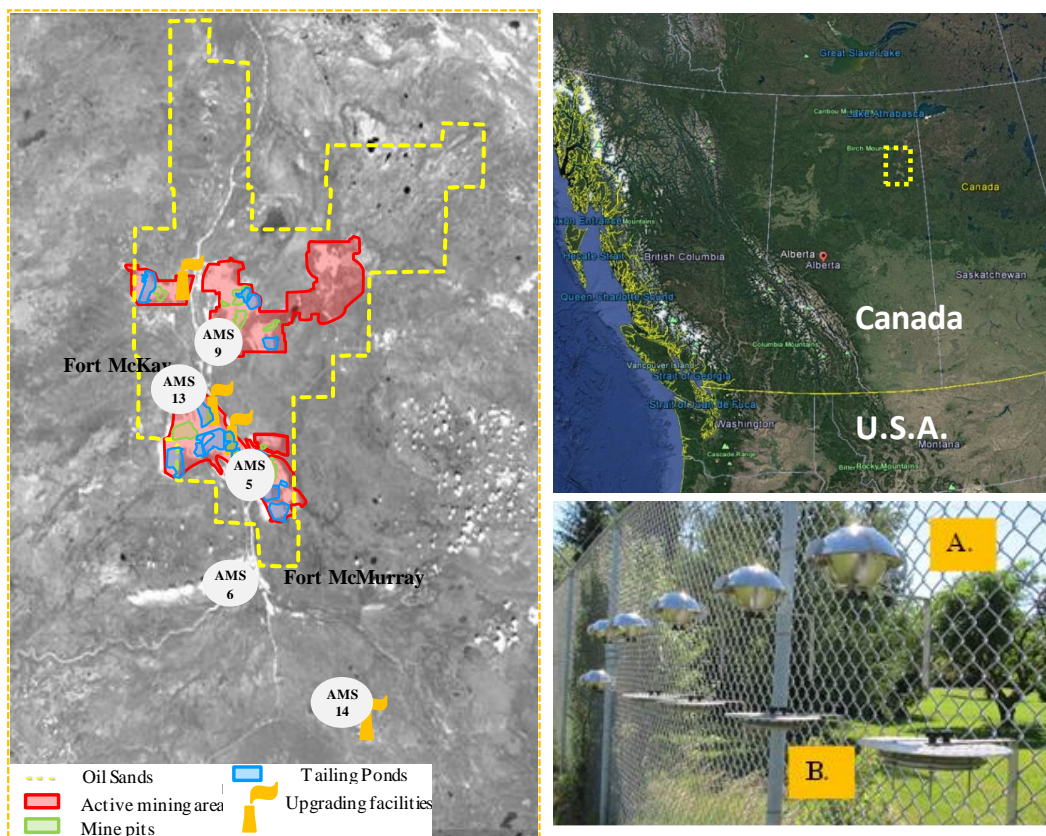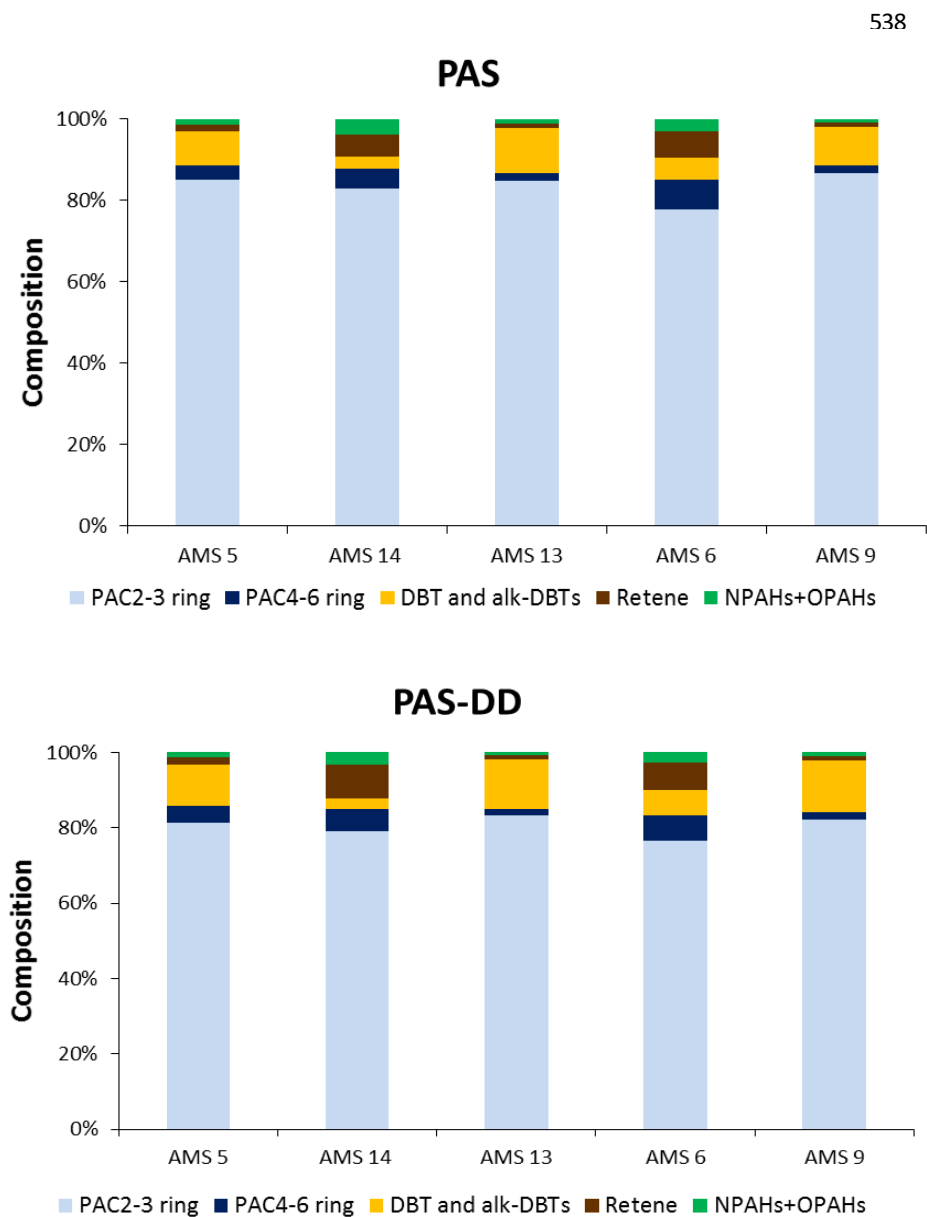
534 **Figure 2.** Composition of target compounds in air samples from five sites in the oil sands region,
535 collected using the conventional passive sampler (PAS) and the passive dry deposition (PAS-
536 DD) sampler, collected during October to November 2015. "PAC" includes parent PAHs and
537 alk-PAHs.

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Figure 3. Enhancement ratios (expressed as a ratio of the concentration of an analyte in the PAS-DD sampler to that in the PAS sampler) for A.) alk-PAHs and alk-DBTs and B.) parent PAHs, DBT, and RET during October to November 2015 across five sites in the oil sands region.
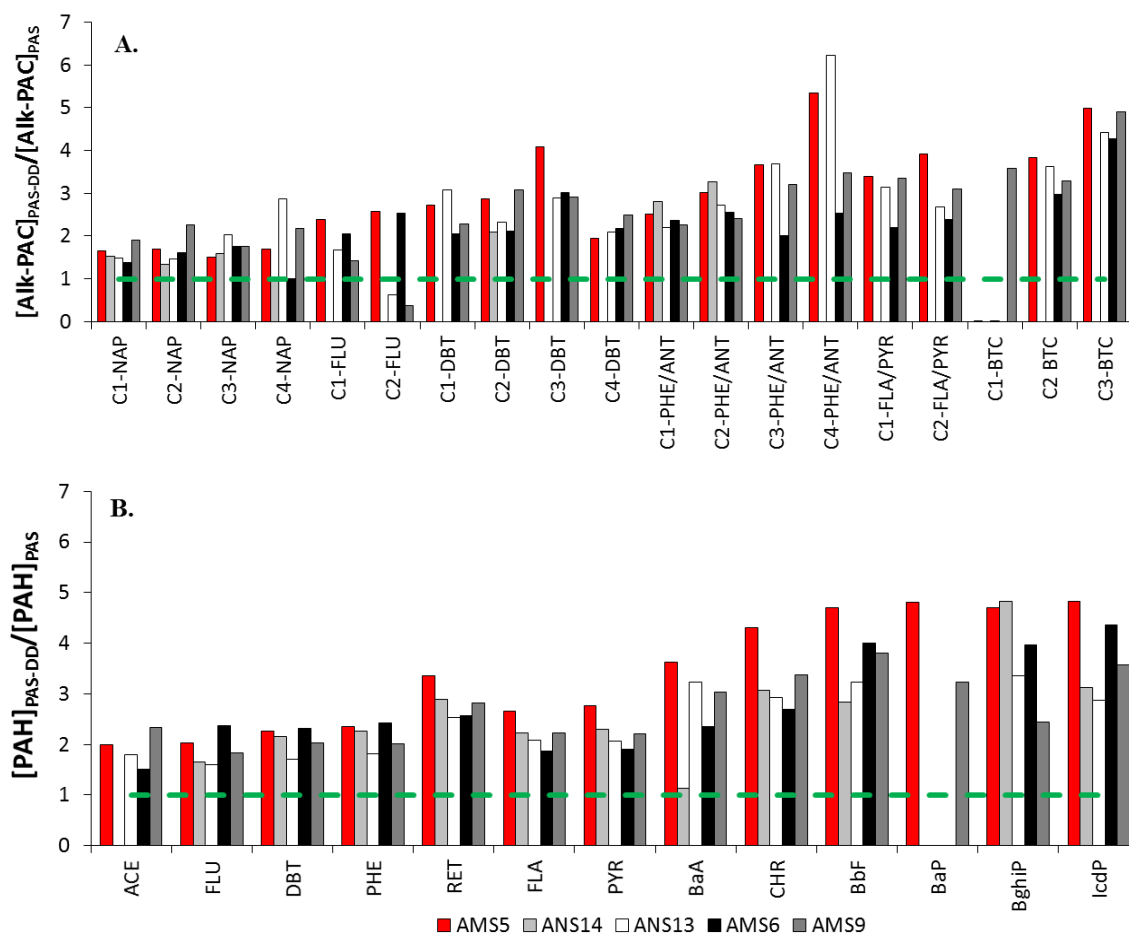
563 **Figure 4.** PAC compositions of fluid petcoke, delayed petcoke, oil sands ore, and air samples
564 (PAS and PAS-DD). PAC compositions of air samples are averages of five sites. Number at the
565 top of each bar represents the total residue concentration (ng mg^{-1}, dry weight basis) or
566 concentration in air (ng m^{-3}), for PAS and PAS-DD air samples.

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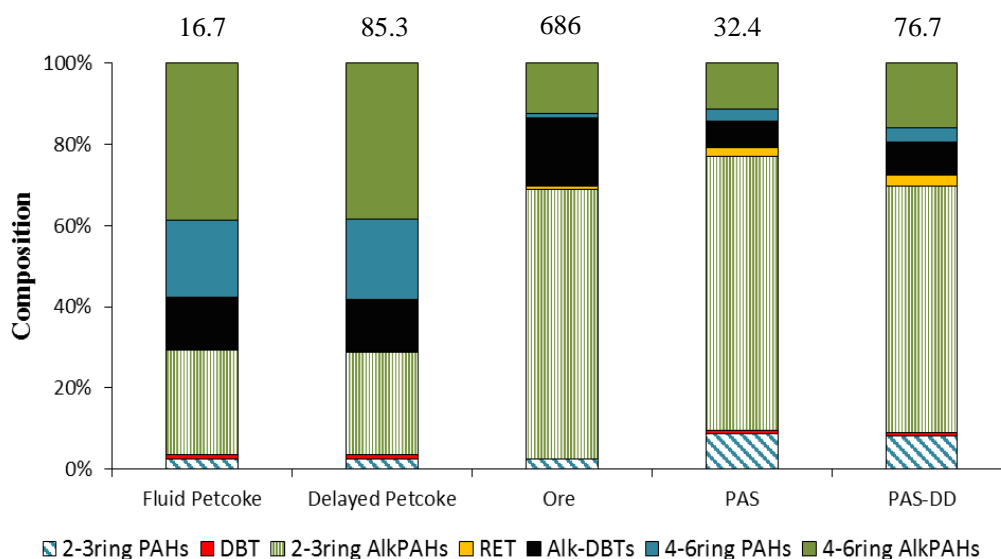
Figure 5. GC-MS extracted ion chromatograms of 4-nitrobiphenyl (4-NP), 2-nitropyrene (2-NP), 1,6-dinitropyrene (1,6-NP), and 6-nitrobenzo(a)pyrene (6-NBaP) in a selection of samples including delayed petcoke, fluid petcoke, oil sands ore, passive dry deposition sample at AMS5, passive dry deposition sample at AMS14, and air sample collected from ore-air partitioning study. The phase distribution of each marker is also indicated as gas-phase or particle-phase.

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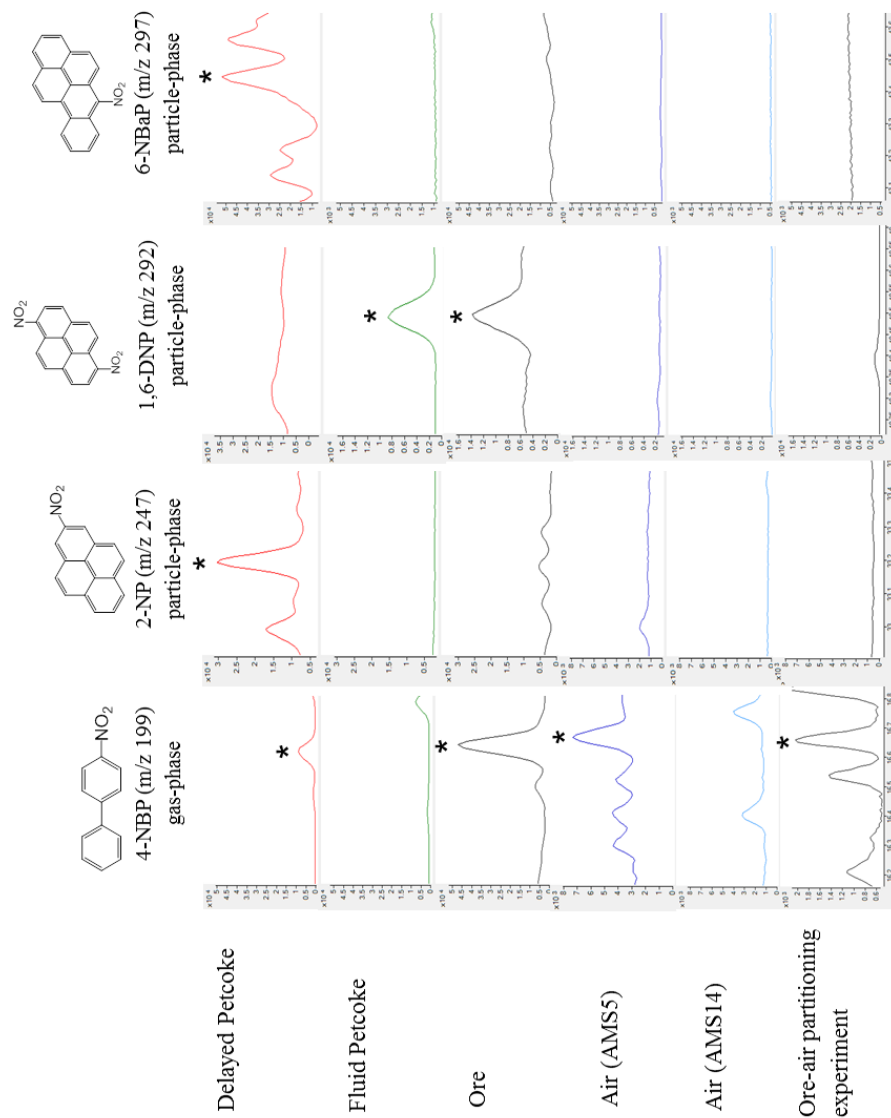
579 **Figure 6.** Scanning electron microscopy (SEM) images and energy dispersive X-ray (EDS)
580 spectra of A) authentic delayed petcoke particles and B) a petcoke particle found in a PAS-DD
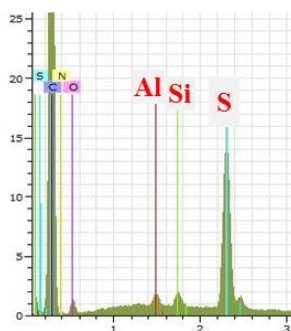581 sample collected at AMS5. Al = Aluminum; Si = Silicon; S = Sulfur.
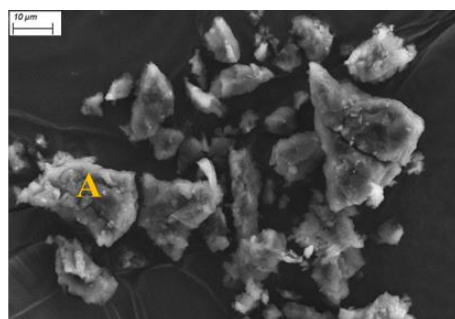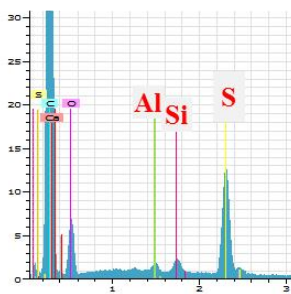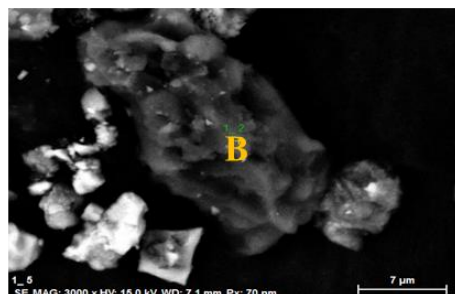
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594 **Table 1.** Concentrations of parent PAHs, dibenzothiophene (DBT), alk-PAHs, retene (RET), NPAHs, OPAHs, and potential NPAH markers in fluid petcoke, delayed petcoke, oil sands ore (ng g⁻¹ on a dry weight basis) and air samples (pg m⁻³, PAS and PAS-DD).

	parent PAHs		DBT	Alk-PAHs		RET	Alk-DBTs	ΣPACs	NPAHs		OPAHs		Potential markers			
	2-3ring	4-6ring		2-3ring	4-6ring				2-3ring	4-6 ring	2-3 ring	4-6 ring	4-NBP	2-NP	1,6-DNP	6-NBaP
	ng/g	ng/g	ng/g	ng/g	ng/g	ng/g	ng/g	ng/g	ng/g	ng/g	ng/g	ng/g	ng/g	ng/g	ng/g	ng/g
Fluid Petcoke	416	3200	184	4290	6440	1.34	2170	16700	0.514	1.35	60.8	0.742	N.D.	N.D.	1.34	N.D.
Delayed Petcoke	2148	16900	872	21500	32800	3.35	11100	85300	28.8	180	274	363	26.1	41.0	0.0	139
Oil sands ore	17015	6910	514	455000	85000	6.38	115000	680000	280	52	170	31.5	228	N.D.	52.1	N.D.
	ng/m³	ng/m³	ng/m³	ng/m³	ng/m³	ng/m³	ng/m³	ng/m³	ng/m³	ng/m³	ng/m³	ng/m³	ng/m³	ng/m³	ng/m³	ng/m³
PAS (mean of 5 sites)	2.81	1.02	0.264	21.9	3.65	0.738	2.05	32.4	0.0828	N.D.	0.443	0.0315	0.0223	N.D.	N.D.	N.D.
PAS-DD (mean of 5 sites)	6.37	2.71	0.542	46.5	12.3	2.06	6.24	76.7	0.119	N.D.	0.820	0.0809	0.0602	N.D.	N.D.	N.D.

595 N.D. = Non Detect