RELATIVE INFLUENCE OF TRANS-PACIFIC AND REGIONAL ATMOSPHERIC TRANSPORT OF PAHS IN THE PACIFIC NORTHWEST, USA

RELATIVE INFLUENCE OF TRANS-PACIFIC AND REGIONAL ATMOSPHERIC TRANSPORT OF PAHS IN THE PACIFIC NORTHWEST, USA

SCOTT LAFONTAINE[1], JILL SCHRLAU[2], JACK BUTLER[3], YULING JIA[2], BARBARA HARPER[3¥,4], STUART HARRIS[3¥], LISA M. BRAMER[5], KATRINA M. WATERS[6], ANNA HARDING[4], STACI L. MASSEY SIMONICH[1,2 *]

[1]*Department of Chemistry, Oregon State University, Corvallis, Oregon USA 97331;* [2]*Environmental and Molecular Toxicology, Oregon State University, Corvallis, Oregon, USA, 97331;* [3]*Confederated Tribes of the Umatilla Indian Reservation, Pendleton, Oregon, USA, 97801;* [4]*School of Biological and Population Health Sciences, College of Public Health and Human Sciences, Oregon State University, Corvallis, Oregon, USA, 97331,* [5]*Computational and Statistical Analytics, Pacific Northwest National Laboratory, Richland, Washington 99352, United States,* [6]*Computational Biology and Bioinformatics, Pacific Northwest National Laboratory, Richland, Washington 99352, United States*

[¥]Affiliation at the time of the study.

*Corresponding author e-mail: staci.simonich@orst.edu; phone: (541) 737-9194; fax: (541) 737-0497

ABSTRACT

The relative influences of trans-Pacific and regional atmospheric transport on measured concentrations of polycyclic aromatic hydrocarbons (PAHs), PAH derivatives [Nitro- (NPAH) and Oxy-(OPAH)], organic carbon (OC), and particulate matter (PM) less than 2.5 μm in diameter ($PM_{2.5}$) were investigated in the Pacific Northwest, USA in 2010-2011. Ambient high volume $PM_{2.5}$ air samples were collected at two sites in the Pacific Northwest: 1.) Mount Bachelor Observatory (MBO) in the Oregon Cascade Range (2763 m above sea level (asl)) and 2.) Confederated Tribes of the Umatilla Indian Reservation (CTUIR) in the Columbia River Gorge (CRG) (954 m asl). At MBO, the 1,8-dinitropyrene concentration was significantly positively correlated with the time a sampled air mass spent over Asia, suggesting that this NPAH may be a good marker for trans-Pacific atmospheric transport. At CTUIR, NOx, CO_2, and SO_2 emissions from a 585 MW coal fired power plant, in Boardman OR, were found to be significantly positively correlated with PAH, OPAH, NPAH, OC, and $PM_{2.5}$ concentrations. By

35   comparing the Boardman Plant operational time frames when the plant was operating to when it

36   was shut down, the plant was found to contribute a large percentage of the measured PAH

37   (67%), NPAH (91%), OPAH (54%), $PM_{2.5}$ (39%) and OC (38%) concentrations at CTUIR and

38   the CRG prior to Spring 2011 and likely masked trans-Pacific atmospheric transport events to the

39   CRG. Upgrades installed to the Boardman Plant in the spring of 2011 dramatically reduced the

40   plant's contribution to PAH and OPAH concentrations (by ~72% and ~40%, respectively) at

41   CTUIR and the CRG, but not NPAH, $PM_{2.5}$ or OC concentrations.

42   **Introduction**

43   Polycyclic Aromatic Hydrocarbons (PAHs) are formed during incomplete combustion

44   and are emitted directly into the gas-phase, as well as sorbed onto particulate matter of 2.5 µm

45   in diameter ($PM_{2.5}$), composed of black carbon (BC) and organic carbon (OC).[1-3] Incomplete

46   combustion sources include anthropogenic sources, such as coal combustion[4] and vehicular

47   emissions[5], as well as natural sources, such as forest fires[6] and volcanoes[7]. PAHs are a human

48   health concern because some PAHs are mutagenic components of $PM_{2.5}$.[8,9]

49   Previous studies have determined that there is significant outflow of particulate-phase

50   PAHs from Asia,[10] as well as the trans-Pacific atmospheric transport of polluted dust[11],

51   mercury[12], ozone[13], PM[14] and particulate phase PAHs[6, 15, 16] to the western U.S. Zelenyuk et al.[17]

52   recently explained the relatively high PAH concentrations measured during trans-Pacific

53   atmospheric transport events by rationalizing that, during particle formation, PAHs become

54   entrapped in a semi solid secondary organic aerosol and protected from evaporation or oxidation

55   during transport. In addition, Timonen et al.[14] estimated that, during the spring (March-May),

56   Asian sources account for approximately 50 – 80% of the total $PM_{2.5}$ measured in clean

57   background areas of the Pacific Northwest (PNW) and approximately 36% - 50% in urban areas

58 of the PNW. Given that $PM_{2.5}$ and PAHs are often co-emitted from the same sources, the

59 percentages may be similar for PAHs.

60 PAH derivatives (nitro-PAH (NPAH) and oxy-PAH (OPAH)) form directly during

61 incomplete combustion processes, as well as from gas phase reaction and heterogeneous

62 reactions of PM-bound parent PAHs with other atmospheric pollutants, such as OH radical, O_3,

63 NO_2, and NO_3 radical. Based on the behavior of their analogous parent PAHs, NPAHs and

64 OPAHs may undergo trans-Pacific atmospheric transport bound to $PM_{2.5}$.[18, 19] Previous studies

65 have measured PAH derivatives at remote and rural sites far from point sources,[20] as well as

66 urban sites[21].

67 The primary objectives of this research were to 1.) measure the PAH and PAH derivative

68 (NPAH and OPAH) concentrations on $PM_{2.5}$ in ambient air masses in the Pacific Northwest and

69 2.) determine the relative influence of trans-Pacific and regional transport at a remote mountain

70 site in the Oregon Cascade Range (Mt. Bachelor Observatory) and at a regional, rural site on the

71 Confederated Tribes of the Umatilla Indian Reservation (CTUIR) located on the Columbia

72 Plateau and bordering the Columbia River Gorge (CRG) national scenic area in 2010 and 2011.

73 Understanding the relative influence of these transport pathways will help to formulate regional,

74 national, and international air quality regulations.

75 **Experimental**

76 *Chemicals.*

77 All of the PAHs, NPAHs and OPAHs analyzed for in this study, and their abbreviations,

78 are listed in Table 1. PAHs, NPAHs and OPAHs were purchased from AccuStandard (New

79 Haven, CT), Chem Service (West Chester, PA), Chiron AS (Trondheim, Norway) and Sigma-

80 Aldrich (St. Louis, MO). Deuterium-labeled PAHs and NPAHs were purchased from CDN

81 Isotopes (Point-Claire, Quebec, Canada) and Cambridge Isotope Laboratories (Andover, MA).

82   These isotopically labeled standards were used as recovery surrogates and internal standards as

83   previously described in detail by Wang et al.[2]   Only HR-GC OmniSolv® grade solvents

84   (Reagents, Charlotte, NC) were used.

Sampling Sites and Sample Collection

86   Two sampling sites, in Oregon, were chosen for this study (Figure 1B). The mountain top

87   sampling site at Mount Bachelor Observatory (MBO) (43.98°N 121.69°W, 2783 m above sea

88   level (asl)) is located ~180 km east of the Pacific Ocean in Oregon's Cascade Range and was

89   established to observe trans-Pacific atmospheric transport events.[12] Previous studies at MBO

90   have measured the trans-Pacific and regional atmospheric transport of particulate phase PAHs[15]

91   and PM^{14}. Episodic trans-Pacific atmospheric transport is most likely to occur at MBO in the

92   spring of the year, from March to May.[15] $PM_{2.5}$ samples were collected at MBO from March to

93   May 2010 (27 samples collected) and March to May 2011 (16 samples collected). The specific

94   dates sampled at MBO are shown in Figure 2.

95   The other sampling site was on the CTUIR on Cabbage Hill (45.60°N 118.61°W, 929.34

96   m asl) (see Figure 1B) and was selected because it was a representative site for the CRG and the

97   CRG Plateau. This sampling site lies ~302 km northeast of MBO and ~179 km from the eastern

98   edge of the CRG National Scenic area in the rolling hills of the Columbia Plateau. PM_{10} and

99    $PM_{2.5}$ concentrations were observed by Vaughan et al. to increase by 370% and 134%

100   respectively, from the trans-Pacific transport of Asian dust to sites on the Columbia Plateau.[23]

101   The Cabbage Hill sampling site lies ~20 km south east of Pendleton, OR (estimated 2013

102   population ~16,935)[24] and ~2 km from a section of I-84, with an annual daily traffic volume of

103   ~10,000 vehicles/day,[25] including diesel and personal automobiles. $PM_{2.5}$ samples were collected

104   at the Cabbage Hill site on the CTUIR from March to December 2010 (43 samples collected) and

105 March to September 2011 (43 samples collected). The specific dates sampled at CTUIR are

106 shown in Figure 3. $PM_{2.5}$ samples were collected at both MBO and CTUIR from March to May

107 in 2010 and 2011.

108   At both MBO and Cabbage Hill, $PM_{2.5}$ was collected a High Volume Cascade Impactor

109 (Series 230, Tisch Environmental, Cleves, OH) which was operated in accordance to the

110 procedures established by the U.S. Environmental Protection Agency (CFR40, Part 50.11,

111 Appendix B, July 1, 1975) and ASTM Specification D2009.[26] We cannot eliminate the potential

112 for both positive[27] and negative[28-30] sampling artifacts. However, given that both sites are

113 relatively rural and remote, we have assumed that the measured PAH, NPAH and OPAH

114 concentrations at the sites are representative. Quartz fiber filters (QFFs) were used and were

115 prebaked at $350^{o}C$ prior to sample collection. Field blanks were also collected over the sampling

116 time periods (10 field blanks at CTUIR and 4 field blanks at MBO) along with lab blanks and

117 were analyzed for the PAH, NPAH, and OPAH listed in Table 1 following the procedure

118 outlined in both Wang et al. and Jariyasopit et. al.[2, 19]

119   During the sampling periods, direct mass measurements of $PM_{2.5}$ were also made at

120 CTUIR's Mission sampling site ($45.68^{o}N$ $118.65^{o}W$, 391.7 m asl, ~10 km from Cabbage Hill

121 site) (see Figure 1) using a Thermo Scientific Taper Oscillating Microbalance (TEOM) monitor

122 (Thermo Scientific, Franklin, MA, USA). Direct $PM_{2.5}$ mass measurements were also made

123 during the sampling periods at the Oregon Department of Environmental Quality (ODEQ) air

124 quality monitoring station in Pendleton, OR ($45.65^{o}N$ $118.82^{o}W$, 318.8 m asl, ~18 km from the

125 Cabbage Hill Sampling site) using a nephelometer (see Figure 1B). Additional information on

126 sample collection is provided in the SI.

127 ***Sample Extraction and Chemical Analysis.***

128   The sample extraction and analysis procedures have been previously validated[2, 15, 19] and

129   are described in the SI. In brief, the samples were extracted using a pressurized liquid extraction

130   (PLE) method outlined by in Wang et al. and Jariyasopit et al.[2, 19]After extracting the filters twice

131   with dichloromethane (DCM), the resulting extract was split in half by weight for chemical

132   analysis using GC/MS and toxicological analysis using the Ames assay.[2] A signal-to-noise ratio

133   of 10:1 was used to define the limit of quantitation. Site specific estimated detection limits

134   (EDLs) were calculated from EPA-method 8280A,[31] and were defined as a signal-to-noise ratio

135   of 3:1 in the sample matrix.

Organic Carbon and Black Carbon Analysis

137   A Sunset EC/OC analyzer (Sunset Lab, Tigard, OR) was used to analyze for organic

138   carbon (OC) and black carbon (BC),[32] concentrations on the ambient $PM_{2.5}$ samples collected at

139   MBO and Cabbage Hill using a 1"x 1" section cut from the filters. We focus on OC here

140   because PAHs are a component of the OC on PM.

Back Trajectory Analysis and Calculation of Source Region Impact Factors

142   The methods used to conduct the back trajectory analysis and calculation of source region

143   impact factors (SRIFs) have been described in detail by Primbs et al.[15] and are given in the SI.

144   In brief, ten day air mass back-trajectories were calculated using NOAA's ARL HYSPLIT online

145   model[33] and data from the GDAS (Global Data Assimilation System) archive and were

146   calculated at three arrival elevations above model ground level (1300, 1500, and 1700 m for

147   MBO and 400, 600 and 800 m for CTUIR), every 3 h, over the 24 h sampling period (including

148   the start and stop time), for a total of 27 trajectories per sample. The 10 day back trajectories

149   were used to determine the impact of different source regions (Oregon, Washington, California,

150   Asia, Siberia, British Columbia, Alaska, West and East) on the air masses sampled (Figure 1A)

151   and the calculation of SRIFs was based on Primbs et al.[10]

152   *Ames Assay*

153   The method reported by Maron et al.[34] was used as described by Wang et. al[2] and the

154   details are provided in the SI. Salmonella strain TA98 (Xenometrix, Inc, Allschwil, Switzerland)

155   was used and the test was conducted, with and without metabolic activation, by using rat S9 mix.

156   **Results and Discussion**

157   *Pollutant Concentrations and Sources to MBO*

158   Figure 2 shows the $\sum PAH_{32}$, $\sum OPAH_{10}$, $\sum NPAH_{27}$ concentrations on $PM_{2.5}$ measured at

159   MBO. Significant positive correlations ($p < 0.05$) between $\sum PAH_{32}$ and $\sum OPAH_{10}$

160   concentrations, as well as between $\sum OPAH_{10}$ and $\sum NPAH_{27}$, were measured. However, $\sum PAH_{32}$

161   and $\sum NPAH_{27}$ concentrations were not significantly correlated with each other. Overall, the

162   individual PAH and $\sum PAH_{32}$ concentrations were relatively low (pg/m^3) at MBO in 2010 and

163   2011 compared to other studies that identified trans-Pacific transport of PAHs[6, 16], including at

164   MBO[15]. This suggests that the trans-Pacific transport of PAHs was not particularly strong in the

165   spring of 2010 and 2011 and is consistent with Fischer et. al.[35, 36] who found that anomalous

166   meteorology (such as cloud scavenging of aerosols and a more persistent wind flow from the

167   south) reduced the aerosol concentration at MBO during this time period. It is unclear why the

168    $\sum PAH_{32}$, $\sum OPAH_{10}$, $\sum NPAH_{27}$ concentrations were significantly elevated at MBO on March 26

169   and 27, 2011 (Figure 2). However, the mean $\sum PAH_{32}$, $\sum OPAH_{10}$, $\sum NPAH_{27}$ concentrations at

170   MBO were not statistically different between 2010 and 2011.

171   PM_1, and not $PM_{2.5}$, mass concentration was measured at MBO, during the sampling

172   periods[14] and is shown in Figure S1. The difference between PM_1 and $PM_{2.5}$ concentrations has

7

173   been shown to be ~10-40%[37-40]. However, we assumed that the fluctuations in PM_1

174   concentration at MBO would be representative of fluctuations in the $PM_{2.5}$ concentrations at

175   MBO. No statistical difference in the mean PM_1 concentration was found between 2010 and

176   2011. The OC, $\sum PAH_{5,6ring}$, and individual PAH (RET, BaA, CHR+TRI, BbF BkF, BeP, BaP

177   DcaA, IcdP and BghiP) concentrations were positively correlated with the PM_1 concentrations

178   ($p < 0.05$) at MBO. However, there were no statistically significant correlations between

179    $\sum PAH_{32}$, $\sum OPAH_{10}$, $\sum NPAH_{27}$, and PM_1 concentrations at MBO.

180   *Source Region Impact Factors and Meteorological Conditions at MBO*

181   The source regions to MBO have been previously defined[15] and include regional/urban

182   sources regions (Oregon, Washington, Urban Oregon, Urban Washington, British Columbia,

183   Alaska, and California), as well as source regions in Asia and Siberia (Figure 1A). Figure S2

184   shows the calculated SRIFs for MBO for the sampling days. Similar to Primbs et al. in 2004-

185   2006 at MBO,[15] elevated SRIFs for California, Oregon and Washington were observed during

186   the spring sampling periods in 2010 and 2011. There were minimal correlations between the

187   individual PAHs and PAH derivative concentrations and SRIFs (Table S1). There were

188   significant positive correlations ($p < 0.05$) with 6-NCH and OC concentrations and CA %, with

189   BenzANT and OC concentration and Urban WA % and with 1-NP concentration and Alaska%

190   and BC%. These correlations indicate that these compounds may be a result of regional

191   atmospheric transport.

192    $\sum NPAH_{27}$ and 1,8-DNP concentrations were significantly positively correlated with the

193   Asia SRIF% ($p < 0.05$). 1,8-DNP was found to form in chamber reaction studies under simulated

194   atmospheric conditions with Beijing PM under exposure to NO_3/N_2O_5 and expected to lead to

195 increased mutagenicity.[19] This indicates that 1,8-DNP may be a potential marker for trans-Pacific

196 atmospheric transport.

197   Table S2 shows the statistically significant correlations between the PAH, NPAH, and

198 OPAH concentrations at MBO and HYSPLIT model output ($\sum$precipitation during the trajectory

199 (ppt (mm/hr)) and the amount of time the trajectories spent above or below the boundary layer

200 (% above and % below, respectively)[41]), weather conditions (water vapor (WV) (g/kg), relative

201 humidity (RH) and ambient pressure (mbar) and 1000/Temperature (K^{-1})), and atmospheric

202 pollutant concentrations (O_3 (ppbv) and CO (ppbv))[12, 42]. At MBO during the spring, increased

203 CO and O_3 concentrations have been shown to be associated with Asian air masses.[15, 42]

204 Significant negative correlations ($p < 0.05$) between CO concentrations and 2-MNAP, 1-MNAP,

205 2,6-DMNAP, 1,3-DMNAP, 2-MPHE, 1-MPHE, NAP, ACY, and ACE concentrations at MBO

206 (Table S2 and S3) suggest that these PAHs may be indicators of regional transport. Primbs et al.

207 attributed these same PAHs to regional transport from the Western U.S.[15] There was a significant

208 positive correlation ($p < 0.05$) between BghiP and CO concentrations (Table S2), suggesting that

209 BghiP concentrations at MBO may be a marker for trans-Pacific air masses.

210   Significant negative correlations, between many PAH and PAH derivative concentrations

211 and O_3 concentrations were observed at MBO (Table S2). Recently, Jariyasopit et al.[19] found

212 that, under simulated trans-Pacific transport conditions, O_3 exposure resulted in significant

213 degradation of PAHs bound to Beijing PM. This may suggest that some PAHs, including BbF,

214 BkF, BeP, BaP, IcdP, degrade during trans-Pacific transport due to reaction with O_3. However,

215 we cannot eliminate the possibility that this result may be due to a sampling artifact from

216 drawing O_3 over the PM-bound PAHs on the filter, resulting in their degradation.

217 ***Ames Assay Results at MBO***

218   There were 10 sampling days (3/6/10, 3/7/10, 3/19/10, 4/9/10, 4/15/10, 4/19/10, 4/30/11,

219   5/2/11, 5/9/11, and 5/12/11) out of 43 sampling days at MBO with direct acting mutagenicity (-

220   S9 rat liver enzyme) statistically different ($p < 0.05$) from the negative control (Figure S3). Of

221   these 10 days, 2 days were previously identified by Timonen et al. as trans-Pacific events at

222   MBO (4/19/10 and 5/12/11).[14]   NPAHs and OPAHs have been shown to be direct acting

223   mutagens[2]. However, no correlations were found between OPAH and NPAH concentrations at

224   MBO and revertants/(plate·m^3), likely because of the low OPAH and NPAH concentrations

225   measured. There were no sampling days at MBO in which the indirect acting mutagenicity (+S9

226   rat liver enzyme) was statistically different from the negative control.

227   ***Pollutant Concentrations and Sources to CTUIR***

228   Figure 3 shows the $\sum PAH_{32}$, $\sum OPAH_{10}$, $\sum NPAH_{27}$ concentrations measured at the

229   CTUIR Cabbage Hill site. The $\sum PAH_{32}$, $\sum OPAH_{10}$, $\sum NPAH_{27}$ concentrations were significantly

230   positively correlated ($p < 0.05$) with each other. In addition, the mean $\sum PAH_{32}$, $\sum OPAH_{10}$, and

231    $\sum NPAH_{27}$ concentrations were significantly higher in 2010 than in 2011, at Cabbage Hill ($p <$

232   0.05) (by ~2.5 x for PAHs and OPAHs and ~ 4 x for NPAHs). .

233   The measured PAH, OPAH, and NPAH concentrations at MBO and CTUIR (Cabbage

234   Hill site) were directly compared using only overlapping sampling periods (March to May in

235   2010 and 2011). In 2010, the mean $\sum PAH_{32}$, $\sum OPAH_{10}$, and $\sum NPAH_{27}$ concentrations at

236   CTUIR were significantly different ($p < 0.05$) and were ~1.3x, ~20x, and ~6x, times higher,

237   respectively, than at MBO. However, in 2011, the mean $\sum PAH_{32}$, $\sum OPAH_{10}$, and $\sum NPAH_{27}$

238   concentrations at CTUIR were not statistically different from the concentrations at MBO.

239   Figure S6 shows the 24 hr $PM_{2.5}$ concentration at the Mission site, the 24 hr $PM_{2.5}$

240   concentration at the ODEQ site, and the organic carbon concentration on $PM_{2.5}$ at Cabbage Hill.

10

241   Over the entire sampling period, the 24 hr $PM_{2.5}$ concentration at the Mission and ODEQ sites

242   were significantly positively correlated ($p < 0.05$) with each other. Over the same time period,

243   the mean 24 hr $PM_{2.5}$ concentration at the Mission site was 5.78 ± 2.6 μg/m^3 and was statistically

244   significantly higher than the mean 24 hr $PM_{2.5}$ concentration of 4.69 ± 3.0 μg/m^3 measured at the

245   ODEQ site ($p < 0.05$). This is likely because the Mission site is impacted more by local $PM_{2.5}$

246   sources (including wood smoke), than the ODEQ site.

247   ***Source Regions Impact Factors and Meteorological Conditions at CTUIR***

248   The source regions to CTUIR are shown in Figure 1A and were used to assess the path

249   the air masses traveled prior to being sampled at CTUIR. The SRIFs for CTUIR are shown in

250   Figure S4. The majority of the air masses sampled at CTUIR had spent a large percentage of

251   time locally, passing over Washington (WA), British Columbia (BC), or California (CA) in late

252   spring/summer, and Asia and Siberia in early spring (and periodically throughout the year).

253   Table S4 shows that few individual PAH and PAH derivative concentrations or sums of PAH

254   and PAH derivative concentrations at CTUIR were correlated with SRIFs, except for 2,6-

255   DMNAP, 1-MPYR, ACY, DBT, FLA, PYR, BcFLO, DacA, 3-NBP, 3-NBF, 1-NP, 6-NCH,

256   2NTP, 9,10-ANQ,Ben(c)-1,4, BcdPYRO which were correlated with local source regions,

257   including BC, WA, and CA. In general, the mean Asia% SRIF for MBO was greater than for

258   CTUIR (14% and 8%, respectively).

259   To understand the effect of meteorological conditions on the air quality at the Cabbage

260   Hill, Mission and ODEQ sampling sites, the measured PAH, NPAH, OPAH, OC, $PM_{2.5}$

261   concentrations   were   compared   to   metrological   conditions   around   the   sampling   sites.

262   Precipitation data recorded at Eastern Oregon Airport was used to assess the impact of

263   precipitation scavenging on the measured PAH, NPAH, OPAH, $PM_{2.5}$ and OC concentrations but

264   no statistically significant correlations were observed. Wind data (direction and speed) from the

265   Eastern Oregon Airport was used to generate wind rose plots for the 2010 and 2011 sampling

266   periods at CTUIR (Figure S5). The predominant wind direction was westerly, occurring over

267   ~50% of the sampling time, in both 2010 and 2011. Table S3 shows the statistically significant

268   correlations between the PAH, NPAH, and OPAH concentrations at CTUIR and HYSPLIT

269   model output ($\sum$precipitation during the trajectory (ppt (mm/hr)) and the amount of time the

270   trajectories spent above or below the boundary layer (% above and % below, respectively)[41]),

271   weather conditions (water vapor (WV) (g/kg), relative humidity (RH) and ambient pressure

272   (mbar) and 1000/Temperature (K^{-1})), and atmospheric pollutant concentrations (O_3 (ppbv) and

273   CO (ppbv)).

274   ***Influence of the Boardman Plant Emissions on Measured $PM_{2.5}$ and PAH concentrations at***

275   ***CTUIR***

276   The PAH isomer diagnostic ratios, BaA/ (BaA+CHR) and IcdP/ (IcdP+BghiP), have been

277   used in numerous studies[43-45] to aid the identification of the combustion source types. The

278   thresholds, determined by Yunker et al.,[46] were used to help identify PAH sources to Cabbage

279   Hill and the data is shown in Figure 4. Figure 4A shows that in 2010, CTUIR was influenced

280   primarily by a wood, grass, or coal combustion sources, while in 2011, CTUIR was influenced

281   primarily by mixed sources/petroleum sources. This suggested that a shift occurred in PAH

282   source types at the CTUIR Cabbage Hill site between 2010 and 2011.

283   This prompted us to investigate the significant difference in mean $\sum PAH_{32}$, $\sum OPAH_{10}$,

284     $\sum NPAH_{27}$, and OC concentrations at Cabbage Hill in 2010 and 2011 (Figure 3 and S6), as well

285   as the difference in PAH diagnostic ratios in 2010 and 2011 (Figure 4). The Cabbage Hill site

286   lies ~2 km from I-84, the likely source of mixed source/petroleum source, as well as 80 km east

12

287   of Portland General Electric's 585 MW coal fired power plant in Boardman, OR (Figure 1B).

288   The Boardman Plant has been previously shown to be a source of $PM_{2.5}$ in the CRG National

289   Scenic Area.[47, 48] According to data from the EPA AirData website, the Boardman Plant was also

290   the largest point source of SO_2 and NOx in the State of Oregon for 2010 and 2011..[49] Using the

291   IMPROVE Wishram site (~102 km west of Boardman in the CRG), in 2010, Jaffe et al.[47] found

292   that the Boardman Plant had a significant impact on the $PM_{2.5}$ concentration in the CRG,

293   increasing background $PM_{2.5}$ concentrations by 14% over the entire year and by 56% during the

294   month of November.

295   To see if the air masses sampled at CTUIR passed over the Boardman Plant, source region boxes

296   "West" and "East" of CTUIR were added (Figure 1B) and the SRIFs for these boxes were

297   calculated for each sampling day. Only statistically significant negative correlations ($p < 0.05$)

298   were found for PYR, 6-NBaP, and 9-FLU concentrations with the west box SRIF, indicating that

299   days not influenced from the west may have been enhanced in these PAH concentrations and

300   could be associated with other sources, such as diesel emissions from I-84. Because there was

301   minimal correlation between PAH and PAH derivative concentrations at Cabbage Hill and the

302   West and East SRIFs, in addition to no differences in PAH concentration on sampling days

303   defined as "west" or "east" based on predominant wind direction, the atmosphere of the

304   Columbia Plateau and at the Cabbage Hill sampling site appeared to be well mixed during the

305   sampling periods. This may be due to the relatively high wind speeds in the CRG and on the

306   plateau.

307   The operational NOx, SO_2, and CO_2 emissions data from the Boardman Plant was

308   compared to the PAH, PAH derivative, OC and $PM_{2.5}$ concentrations measured at CTUIR, during

309   normal plant operation and during temporary plant closures, to directly assess the impact of the

310   Boardman Plant on air quality at CTUIR. The NOx, SO_2, and CO_2 emissions from the Boardman

311   Plant were obtained from the U.S. Environmental Protection Agency's Air Markets Program

312   Data Acid Rain program archive[49] for the entire sampling period at CTUIR. In the spring of

313   2011, after the annual shutdown of the power plant from April to June, two new emission

314   controls were added to the Boardman Plant: 1.) low-NOx burners and modified airports and 2.)

315   an activated carbon injection system to allow for the capture and removal of mercury.[50]

316   Figure 3 shows the three distinct operational timeframes of the Boardman Plant, when the

317   plant was on (before the upgrade), when the plant was on (after the upgrade), and when the plant

318   was off, as well as the temporal variation and mean $\sum PAH_{32}$, $\sum OPAH_{10}$, $\sum NPAH_{27}$

319   concentrations measured during these operational time frames. The mean PAH, OPAH and

320   NPAH concentrations when the plant was on (before the upgrade) were statistically different ($p <$

321   0.05), and ~3x, ~2x and ~12x higher, respectively, than when the plant was off. PAH and OPAH

322   concentrations measured when the plant was off and when it was on (after the upgrade) were not

323   found to be statistically significantly different, while NPAH concentrations were still

324   significantly ($p < 0.05$) different and ~6x higher when the plant was on.

325   Figure S6 shows the temporal variation of the mean OC concentration at Cabbage Hill

326   and $PM_{2.5}$ concentrations at the Mission and ODEQ sites. When the plant was off, the $PM_{2.5}$

327   concentrations at Mission were statistically significant higher by ~1.5x than at the ODEQ site (p

328   < 0.05). When the plant was on (after the upgrade), the $PM_{2.5}$ and OC concentration were

329   significantly increased, by ~1.3x and 2x respectively, as compared to when the plant was off at

330   both sites. In addition, the $PM_{2.5}$ concentration at both sites and OC concentrations measured at

331   Cabbage Hill when the plant was on (after the upgrade) were not statistically different from

332   concentrations measured when the plant was on (before upgrade). Together, these data suggest

333 that the emission controls installed to the Boardman Plant in the spring of 2011 reduced PAH

334 and OPAH concentrations, but not $PM_{2.5}$, OC, NPAH concentrations at CTUIR.

335 The PAH isomer diagnostic ratio cross plot in Figure 4B shows that, when the Boardman

336 Plant was off, the PAH source type at the Cabbage Hill site was primarily mixed sources, while

337 when the Boardman Plant was on (before upgrade) the PAH source type was primarily coal,

338 grass, or wood combustion. When the plant was on (after upgrade) the PAH source type at the

339 Cabbage Hill site was primarily mixed sources. This data also suggests that the Boardman Plant

340 had a greater impact on PAH concentrations at the Cabbage Hill site before the 2011 upgrade, as

341 compared to after the upgrade.

342 The hourly SO_2, NOx and CO_2 (kg/hr) emission rates from the Boardman Plant were

343 used to calculate the total SO_2, NOx and CO_2 (kg) emissions for each sampling day at CTUIR.[49]

344 Figures S7, S8, and S9 show the correlation of the NOx, SO_2 and CO_2 emissions from the

345 Boardman Plant with the $\sum PAH_{32}$, $\sum OPAH_{10}$, $\sum NPAH_{27}$, and OC concentrations measured at

346 Cabbage Hill, as well as the $PM_{2.5}$ concentrations measured at the Mission and ODEQ sites. The

347 $\sum PAH_{32}$, $\sum OPAH_{10}$, $\sum NPAH_{27}$, OC, and $PM_{2.5}$ concentrations at CTUIR were significantly

348 positively correlated with the NOx, SO_2 and CO_2 emissions from the Boardman Plant ($p < 0.05$).

349 Many individual PAH, NPAH and OPAH isomers, as well as the $\sum PAH_{16\text{-US priority}}$, were also

350 significantly positively correlated ($p < 0.05$) with the SO_2, NOx and CO_2 emissions from the

351 Boardman Plant. These statistically significant positive correlations strongly suggest that the air

352 quality at the CTUIR sampling sites was impacted by emissions from the Boardman Plant.

353 The Boardman Plant emissions were also significantly correlated ($p < 0.05$) with

354 $\sum PAH_{32}$, $\sum OPAH_{10}$, $\sum NPAH_{27}$, OC, and $PM_{2.5}$ concentrations (at Mission and ODEQ) when

355 separated into the different plant operational timeframes. However, during the operational

15

356   timeframe when the plant was on (after upgrade), only statistical positive correlations were found

357   between Boardman Plant CO_2 emissions and $\sum NPAH_{27}$, OC, and $PM_{2.5}$ concentrations (at

358   Mission and ODEQ).   This indicates that the Boardman Plant emissions could still have

359   influenced the NPAH, $PM_{2.5}$ and OC concentrations at CTUIR even after the upgrade.

360   ***Boardman's Impact on Columbia River Gorge and Columbia Plateau Air Quality***

361   To quantify the effect of the Boardman Plant emissions on the PAH and PAH derivative

362   concentrations at Cabbage Hill, the PAH concentrations measured when the plant was off were

363   compared to when the plant was on. Table S5 compares the PAH, OC, and $PM_{2.5}$ concentrations

364   at CTUIR when the Boardman Plant was on (before the upgrade) to when the plant was off.

365   Significantly increased ($p < 0.05$) concentrations (in pg/m^3) of: individual PAHs (0.30-2.51),

366    $\sum PAH_{3ring}$ (1.48), $\sum PAH_{4ring}$ (7.76), $\sum PAH_{56ring}$ (3.64), $\sum PAH_{16\text{-US priority}}$ (9.10), $\sum PAH_{32}$ (6.48),

367   individual NPAHs (0.04-.18), $\sum NPAH_{27}$ (1.16), individual OPAHs (0.12-9.95), $\sum OPAH_{10}$

368   (18.35), OC (0.62 $\mu g/m^3$), and $PM_{2.5}$ (2.19 $\mu g/m^3$),   (at ODEQ) were measured when the

369   Boardman Plant was on (before upgrade) as compared to when the plant was off. This indicates

370   that, when the Boardman Plant was on (before upgrade), it was a significant source of PAHs,

371   NPAHs, OPAHs, OC, and $PM_{2.5}$ to CTUIR and the CRG.

372   Table S6 compares the PAH, OC, and $PM_{2.5}$ concentrations at Cabbage Hill when the

373   Boardman Plant was on (after upgrade) to when the Boardman Plant was off.   Significantly

374   increased ($p < 0.05$) concentrations of (in pg/m^3) of: 6-NBaP (0.58), $\sum NPAH_{27}$ (0.60), OC (1.21

375    $\mu g/m^3$), EC (0.06 $\mu g/m3$) and $PM_{2.5}$ (2.20 and 1.08 $\mu g/m^3$) (for Mission and ODEQ,

376   respectively), as well as significantly reduced ($p < 0.05$) concentrations of (in pg/m^3) of: 2,6-

377   DMNAP(-0.20), 1,3-DMNAP (-0.30), BaA (-0.16), IcdP (-0.29) and $\sum PAH_{2ring}$ (-0.74), and

378    $\sum PAH_{56ring}$ (-1.67) were measured when the plant was on. These results indicate the Boardman

16

379 Plant had a more significant negative impact on CTUIR air quality before the upgrade than after

380 the upgrade. The upgrades installed to the Boardman Plant significantly reduced the PAH and

381 OPAH concentrations at CTUIR so that the PAH concentrations at the site were comparable to

382 when the plant was off. The NPAH, OC and $PM_{2.5}$ concentrations at CTUIR were not

383 significantly reduced by the Boardman Plant upgrades.

384 Table S7 compares the PAH, OC, and $PM_{2.5}$ concentrations when the Boardman Plant

385 was on (before the upgrade) to when the Boardman Plant was on (after the upgrade).

386 Significantly reduced (p < 0.05) concentrations (in pg/m^3) of: individual PAHs (-0.14 to -1.62),

387 $\sum PAH_{2ring}$ (-1.32), $\sum PAH_{3ring}$ (-1.20), $\sum PAH_{4ring}$ (-7.05), $\sum PAH_{56ring}$ (-5.00), $\sum PAH_{16\text{-US priority}}$ (-

388 10.98), $\sum PAH_{32}$ (-14.64), individual NPAHs (-0.01 to -0.54), individual OPAHs (-0.12 to -9.94),

389 and $\sum OPAH_{10}$ (-13.43) were measured when the plant was on (after upgrade). There was no

390 statistically significant difference in the $\sum NPAH_{27}$, OC and $PM_{2.5}$ concentrations between the

391 two timeframes and there was a significant increase (p < 0.05) in 6-NBaP concentration (0.54

392 pg/m^3) after the upgrade. This further indicates that the Boardman Plant upgrades significantly

393 reduced the PAH and OPAH concentrations at CTUIR, but not the $\sum NPAH_{27}$, OC and $PM_{2.5}$

394 concentrations.

395 The installation of low-NOx burners and modified airports at the Boardman Plant

396 potentially resulted in more incomplete combustion, which would result in an increase in PAH

397 emissions.[51] However, the activated carbon injection system also installed at the Boardman Plan

398 captures and removes mercury by injecting activated carbon into the flue gas before the

399 electrostatic precipitator and has been shown to reduce PAH emissions in coal fired plants >

400 90%[37] and, in simulated waste incineration facilities, by >80%.[52] Therefore, the activated carbon

401 injection system may have led to reduced PAH emissions from the Boardman Plant, and in turn,

402   reduced PAH concentrations at CTUIR and the CRG. It is unclear why the NPAH emissions

403   were not reduced and may indicate that I-84 traffic is the major source of NPAHs to the Cabbage

404   Hill site.

405   *Ames Assay Results at CTUIR*

406   Figure S10 shows there was low direct acting mutagenicity in the CTUIR samples,

407   especially in 2011. There were 16 days in 2010 (3/15/10, 3/19/10, 3/26/10, 4/13/10, 4/19/10,

408   4/23/10, 4/26/10, 5/14/10, 5/19/10, 5/21/10, 8/12/10, 8/18/10, 8/24/10, 9/17/10, and 9/23/10) and

409   only 1 day in 2011 (4/9/11), when the Boardman Plant was on and before the upgrade, with

410   significant direct acting mutagenicity (-S9 rat liver enzyme) statistically different ($p < 0.05$) from

411   the negative control. Of these 16 days in 2010, 3 occurred on days when the Boardman Plant was

412   off (5/14/10, 5/19/10, and 5/21/10) and 13 occurred on days when the Boardman Plant was on

413   (before the upgrade). No correlations were found between OPAH and NPAH concentrations and

414   revertants/plate·m^3. There were no days at CTUIR in which the indirect acting mutagenicity

415   (+S9 rat liver enzyme) was statistically different from the negative control. These data further

416   show that the Boardman Plant had a significant impact on CTUIR (and CRG) air quality prior to

417   the installation of the upgrades in the spring of 2011.

418   No trans-Pacific transport events, with high PAH transport, were readily identifiable at

419   CTUIR during the 2010 and 2011 sampling periods, likely because the Boardman Plant was a

420   major regional source of PAHs. Now that the Boardman Plant is no longer a major source of

421   PAHs to the CRG Plateau, trans-Pacific atmospheric transport of PAHs may be more evident to

422   this region of the Pacific Northwest.

423   **Acknowledgements**

Supporting Information Available

431   This information is available free of charge via the Internet at http://pubs.acs.org.

References

433 1. Finlayson-Pitts, B. J.; Pitts, J. N., Tropospheric Air Pollution: Ozone, Airborne Toxics,
434   Polycyclic Aromatic Hydrocarbons, and Particles. *Science* **1997,** *276*, (5315), 1045-1051.
435 2. Wang, W.; Jariyasopit, N.; Schrlau, J.; Jia, Y.; Tao, S.; Yu, T.-W.; Dashwood, R. H.; Zhang,
436   W.; Wang, X.; Simonich, S. L. M., Concentration and Photochemistry of PAHs, NPAHs, and
437   OPAHs and Toxicity of PM2.5 during the Beijing Olympic Games. *Environmental Science*
438   *& Technology* **2011,** *45*, (16), 6887-6895.
439 3. Chen, Y.; Sheng, G.; Bi, X.; Feng, Y.; Mai, B.; Fu, J., Emission Factors for Carbonaceous
440   Particles and Polycyclic Aromatic Hydrocarbons from Residential Coal Combustion in
441   China. *Environmental Science & Technology* **2005,** *39*, (6), 1861-1867.
442 4. Xu, S.; Liu, W.; Tao, S., Emission of Polycyclic Aromatic Hydrocarbons in China.
443   *Environmental Science & Technology* **2006,** *40*, (3), 702-708.
444 5. Marr, L. C.; Kirchstetter, T. W.; Harley, R. A.; Miguel, A. H.; Hering, S. V.; Hammond, S.
445   K., Characterization of Polycyclic Aromatic Hydrocarbons in Motor Vehicle Fuels and
446   Exhaust Emissions. *Environmental Science & Technology* **1999,** *33*, (18), 3091-3099.
447 6. Genualdi, S. A.; Killin, R. K.; Woods, J.; Wilson, G.; Schmedding, D.; Simonich, S. L. M.,
448   Trans-Pacific and Regional Atmospheric Transport of Polycyclic Aromatic Hydrocarbons
449   and Pesticides in Biomass Burning Emissions to Western North America. *Environmental*
450   *Science & Technology* **2009,** *43*, (4), 1061-1066.
451 7. Stracquadanio, M.; Dinelli, E.; Trombini, C., Role of volcanic dust in the atmospheric
452   transport and deposition of polycyclic aromatic hydrocarbons and mercury. *Journal of*
453   *Environmental Monitoring* **2003,** *5*, (6), 984-988.
454 8. Zhang, Y.; Tao, S.; Shen, H.; Ma, J., Inhalation exposure to ambient polycyclic aromatic
455   hydrocarbons and lung cancer risk of Chinese population. *Proceedings of the National*
456   *Academy of Sciences* **2009,** *106*, (50), 21063-21067.
457 9. Motorykin, O.; Matzke, M. M.; Waters, K. M.; Massey Simonich, S. L., Association of
458   Carcinogenic Polycyclic Aromatic Hydrocarbon Emissions and Smoking with Lung Cancer
459   Mortality Rates on a Global Scale. *Environmental Science & Technology* **2013,** *47*, (7),
460   3410-3416.

461   10. Primbs, T.; Simonich, S.; Schmedding, D.; Wilson, G.; Jaffe, D.; Takami, A.; Kato, S.;
462   Hatakeyama, S.; Kajii, Y., Atmospheric Outflow of Anthropogenic Semivolatile Organic
463   Compounds from East Asia in Spring 2004. *Environmental Science & Technology* **2007**, *41*,
464   (10), 3551-3558.
465   11. Hsu, N. C.; Li, C.; Krotkov, N. A.; Liang, Q.; Yang, K.; Tsay, S.-C., Rapid transpacific
466   transport in autumn observed by the A-train satellites. *Journal of Geophysical Research:*
467   *Atmospheres* **2012**, *117*, (D6), D06312.
468   12. Jaffe, D.; Prestbo, E.; Swartzendruber, P.; Weiss-Penzias, P.; Kato, S.; Takami, A.;
469   Hatakeyama, S.; Kajii, Y., Export of atmospheric mercury from Asia. *Atmospheric*
470   *Environment* **2005**, *39*, (17), 3029-3038.
471   13. Fischer, E. V.; Jaffe, D. A.; Weatherhead, E. C., Free tropospheric peroxyacetyl nitrate
472   (PAN) and ozone at Mount Bachelor: causes of variability and timescale for trend detection.
473   *Atmos. Chem. Phys. Discuss.* **2011**, *11*, (2), 4105-4139.
474   14. Timonen, H.; Wigder, N.; Jaffe, D., Influence of background particulate matter (PM) on
475   urban air quality in the Pacific Northwest. *Journal of Environmental Management* **2013**, *129*,
476   (0), 333-340.
477   15. Primbs, T.; Piekarz, A.; Wilson, G.; Schmedding, D.; Higginbotham, C.; Field, J.; Simonich,
478   S. M., Influence of Asian and Western United States Urban Areas and Fires on the
479   Atmospheric Transport of Polycyclic Aromatic Hydrocarbons, Polychlorinated Biphenyls,
480   and Fluorotelomer Alcohols in the Western United States. *Environmental Science &*
481   *Technology* **2008**, *42*, (17), 6385-6391.
482   16. Killin, R. K.; Simonich, S. L.; Jaffe, D. A.; DeForest, C. L.; Wilson, G. R., Transpacific and
483   regional atmospheric transport of anthropogenic semivolatile organic compounds to Cheeka
484   Peak Observatory during the spring of 2002. *Journal of Geophysical Research: Atmospheres*
485   **2004**, *109*, (D23), D23S15.
486   17. Zelenyuk, A.; Imre, D.; Beránek, J.; Abramson, E.; Wilson, J.; Shrivastava, M., Synergy
487   between Secondary Organic Aerosols and Long-Range Transport of Polycyclic Aromatic
488   Hydrocarbons. *Environmental Science & Technology* **2012**, *46*, (22), 12459-12466.
489   18. Jariyasopit, N.; McIntosh, M.; Zimmermann, K.; Arey, J.; Atkinson, R.; Cheong, P. H.-Y.;
490   Carter, R. G.; Yu, T.-W.; Dashwood, R. H.; Massey Simonich, S. L., Novel Nitro-PAH
491   Formation from Heterogeneous Reactions of PAHs with NO2, NO3/N2O5, and OH
492   Radicals: Prediction, Laboratory Studies, and Mutagenicity. *Environmental Science &*
493   *Technology* **2014**, *48*, (1), 412-419.
494   19. Jariyasopit, N.; Zimmermann, K.; Schrlau, J.; Arey, J.; Atkinson, R.; Yu, T.-W.; Dashwood,
495   R. H.; Tao, S.; Simonich, S. L. M., Heterogeneous Reactions of Particulate Matter-Bound
496   PAHs and NPAHs with NO3/N2O5, OH Radicals, and O3 under Simulated Long-Range
497   Atmospheric Transport Conditions: Reactivity and Mutagenicity. *Environmental Science &*
498   *Technology* **2014**, *48*, (17), 10155-10164.
499   20. Albinet, A.; Leoz-Garziandia, E.; Budzinski, H.; Villenave, E.; Jaffrezo, J. L., Nitrated and
500   oxygenated derivatives of polycyclic aromatic hydrocarbons in the ambient air of two French
501   alpine valleys: Part 1: Concentrations, sources and gas/particle partitioning. *Atmospheric*
502   *Environment* **2008**, *42*, (1), 43-54.
503   21. Reisen, F.; Arey, J., Atmospheric Reactions Influence Seasonal PAH and Nitro-PAH
504   Concentrations in the Los Angeles Basin. *Environmental Science & Technology* **2004**, *39*,
505   (1), 64-73.

22. Simonich, S. L. M.; Motorykin, O.; Jariyasopit, N., PAH intermediates: Links between the atmosphere and biological systems. *Chemico-Biological Interactions* **2011,** *192*, (1–2), 26-29.

23. Vaughan, J. K.; Claiborn, C.; Finn, D., April 1998 Asian dust event over the Columbia Plateau. *Journal of Geophysical Research: Atmospheres* **2001,** *106*, (D16), 18381-18402.

24. U.S. Census Bureau Pendleton, Oregon. http://quickfacts.census.gov/qfd/states/41/4157150.html (Acessed Nov 1, 2014)

25. AAroads Interstate Guide Interstate 84 Oregon Annual Average Daily Traffic. http://www.interstate-guide.com/i-084_aadt.html (Acessed Nov 1, 2014)

26. Wang, W.; Primbs, T.; Tao, S.; Simonich, S. L. M., Atmospheric Particulate Matter Pollution during the 2008 Beijing Olympics. *Environmental Science & Technology* **2009,** *43*, (14), 5314-5320.

27. Cadle, S. H.; Groblicki, P. J.; Mulawa, P. A., Problems in the sampling and analysis of carbon particulate. *Atmospheric Environment (1967)* **1983,** *17*, (3), 593-600.

28. Galasyn, J. F.; Hornig, J. F.; Soderberg, R. H., The loss of PAH from quartz fiber high volume filters. *Journal of the Air Pollution Control Association* **1984,** *34*, (1), 57-59.

29. Schwartz, G. P.; Daisey, J. M.; Lioy, P. J., Effect of sampling duration on the concentration of particulate organics collected on glass fiber filters. *American Industrial Hygiene Association Journal* **1981,** *42*, (4), 258-263.

30. Van Vaeck, L.; Van Cauwenberghe, K.; Janssens, J., The gas-particle distribution of organic aerosol constituents: Measurement of the volatilisation artefact in Hi-Vol cascade impactor sampling. *Atmospheric Environment (1967)* **1984,** *18*, (2), 417-430.

31. Usenko, S.; Hageman, K. J.; Schmedding, D. W.; Wilson, G. R.; Simonich, S. L., Trace Analysis of Semivolatile Organic Compounds in Large Volume Samples of Snow, Lake Water, and Groundwater. *Environmental Science & Technology* **2005,** *39*, (16), 6006-6015.

32. Birch, M. E.; Cary, R. A., Elemental Carbon-Based Method for Monitoring Occupational Exposures to Particulate Diesel Exhaust. *Aerosol Science and Technology* **1996,** *25*, (3), 221-241.

33. Draxler, R. R. HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory) Model access via NOAA ARL READY website. http://ready.arl.noaa.gov/hypub-bin/trajasrc.pl (Acessed Dec 12, 2013)

34. Maron, D. M.; Ames, B. N., Revised methods for the Salmonella mutagenicity test. *Mutation Research/Environmental Mutagenesis and Related Subjects* **1983,** *113*, (3–4), 173-215.

35. Fischer, E. V.; Jaffe, D. A.; Marley, N. A.; Gaffney, J. S.; Marchany-Rivera, A., Optical properties of aged Asian aerosols observed over the U.S. Pacific Northwest. *Journal of Geophysical Research: Atmospheres* **2010,** *115*, (D20), D20209.

36. Fischer, E. V.; Perry, K. D.; Jaffe, D. A., Optical and chemical properties of aerosols transported to Mount Bachelor during spring 2010. *Journal of Geophysical Research: Atmospheres* **2011,** *116*, (D18), D18202.

37. Cudahy, J. J.; Helsel, R. W., Removal of products of incomplete combustion with carbon. *Waste Management* **2000,** *20*, (5–6), 339-345.

38. Giugliano, M.; Lonati, G.; Butelli, P.; Romele, L.; Tardivo, R.; Grosso, M., Fine particulate (PM2.5–PM1) at urban sites with different traffic exposure. *Atmospheric Environment* **2005,** *39*, (13), 2421-2431.

39. Saarnio, K.; Aurela, M.; Timonen, H.; Saarikoski, S.; Teinilä, K.; Mäkelä, T.; Sofiev, M.; Koskinen, J.; Aalto, P. P.; Kulmala, M.; Kukkonen, J.; Hillamo, R., Chemical composition of

552 fine particles in fresh smoke plumes from boreal wild-land fires in Europe. *Science of The*
553 *Total Environment* **2010**, *408*, (12), 2527-2542.
554 40. Vecchi, R.; Marcazzan, G.; Valli, G.; Ceriani, M.; Antoniazzi, C., The role of atmospheric
555 dispersion in the seasonal variation of PM1 and PM2.5 concentration and composition in the
556 urban area of Milan (Italy). *Atmospheric Environment* **2004**, *38*, (27), 4437-4446.
557 41. Genualdi, S. A.; Simonich, S. L. M.; Primbs, T. K.; Bidleman, T. F.; Jantunen, L. M.; Ryoo,
558 K.-S.; Zhu, T., Enantiomeric Signatures of Organochlorine Pesticides in Asian, Trans-
559 Pacific, and Western U.S. Air Masses. *Environmental Science & Technology* **2009**, *43*, (8),
560 2806-2811.
561 42. Weiss-Penzias, P.; Jaffe, D. A.; Swartzendruber, P.; Dennison, J. B.; Chand, D.; Hafner, W.;
562 Prestbo, E., Observations of Asian air pollution in the free troposphere at Mount Bachelor
563 Observatory during the spring of 2004. *Journal of Geophysical Research: Atmospheres* **2006**,
564 *111*, (D10), D10304.
565 43. Simoneit, B. R. T.; Bi, X.; Oros, D. R.; Medeiros, P. M.; Sheng, G.; Fu, J., Phenols and
566 Hydroxy-PAHs (Arylphenols) as Tracers for Coal Smoke Particulate Matter: Source Tests
567 and Ambient Aerosol Assessments. *Environmental Science & Technology* **2007**, *41*, (21),
568 7294-7302.
569 44. Zhang, X. L.; Tao, S.; Liu, W. X.; Yang, Y.; Zuo, Q.; Liu, S. Z., Source Diagnostics of
570 Polycyclic Aromatic Hydrocarbons Based on Species Ratios: A Multimedia Approach.
571 *Environmental Science & Technology* **2005**, *39*, (23), 9109-9114.
572 45. Alam, M. S.; Delgado-Saborit, J. M.; Stark, C.; Harrison, R. M., Using atmospheric
573 measurements of PAH and quinone compounds at roadside and urban background sites to
574 assess sources and reactivity. *Atmospheric Environment* **2013**, *77*, (0), 24-35.
575 46. Yunker, M. B.; Macdonald, R. W.; Vingarzan, R.; Mitchell, R. H.; Goyette, D.; Sylvestre, S.,
576 PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH
577 source and composition. *Organic Geochemistry* **2002**, *33*, (4), 489-515.
578 47. Jaffe, D. A.; Reidmiller, D. R., Now you see it, now you don't: impact of temporary closures
579 of a coal-fired power plant on air quality in the Columbia River Gorge National Scenic Area.
580 *Atmos. Chem. Phys. Discuss.* **2009**, *9*, (3), 14235-14261.
581 48. Pitchford, M. L., Green, M. C., Morris, R., Emery, C., Sakata, R., Swab, C., and Mairose, P.
582 T Columbia River Gorge Air Quality Study, Final Science Summary Report.
583 http://www.swcleanair.org/gorgereports.htm (Acessed Nov 13, 2014)
584 49. U.S. Enviromental Protection Agency Air Markets Program Data. http://ampd.epa.gov/ampd/
585 (Acessed Sept, 2014)
586 50. Portland General Electric Boardman Plant Air Emissions.
587 https://www.portlandgeneral.com/community_environment/initiatives/boardman_plant_air_e
588 missions.aspx (Acessed Jun 1, 2014)
589 51. Zevenhoven, R.; Kilpinen, P., Control of Pollutants in Flue Gases and Fuel Gases. In *Cross-*
590 *interacting effects of control methods*, 2005.
591 52. Zhou, H.-C.; Zhong, Z.-P.; Jin, B.-S.; Huang, Y.-J.; Xiao, R., Experimental study on the
592 removal of PAHs using in-duct activated carbon injection. *Chemosphere* **2005**, *59*, (6), 861-
593 869.
594
595

596
597 **Figure 1.** A.) Representative 10 day air mass backtrajectories from MBO for April 23, 2010 and
598 the source region boxes used for both CTUIR and MBO (Oregon, OR; Washington, WA;
599 Alaska; California, CA; British Columbia, BC, Siberia and Asia). B.) Location of air sampling
600 sites in the Pacfic Northwest at MBO and CTUIR, as well as the locations of regional air quality
601 sites near Pendleton, OR: ODEQ and CTUIR Mission Site. The location of the coal fired power
602 plant in Boardman, OR is also indicated.
603
604 **Figure 2.** Temporal variation of mean $\sum PAH_{32}$, $\sum OPAH_{10}$, and $\sum NPAH_{27}$ concentrations at
605 MBO during the sampling periods.
606
607 **Figure 3.** Three operational timeframes of the Boardman Plant (plant on (before upgrade), plant
608 on (after upgrade) and plant off) and $\sum PAH_{32}$, $\sum OPAH_{10}$ and $\sum NPAH_{27}$ concentrations at
609 Cabbage Hill during the sampling periods.
610
611 **Figure 4.** A.) PAH diagnostic ratio cross plot BaA/(BaA+CHR) vs IcdP/(IcdP+BghiP) using
612 thresholds from Yunker et al.[46] at CTUIR in 2010 and 2011 and B) the three operational
613 timeframes of Boardman Plant (plant on (before upgrade), plant off and plant on (after
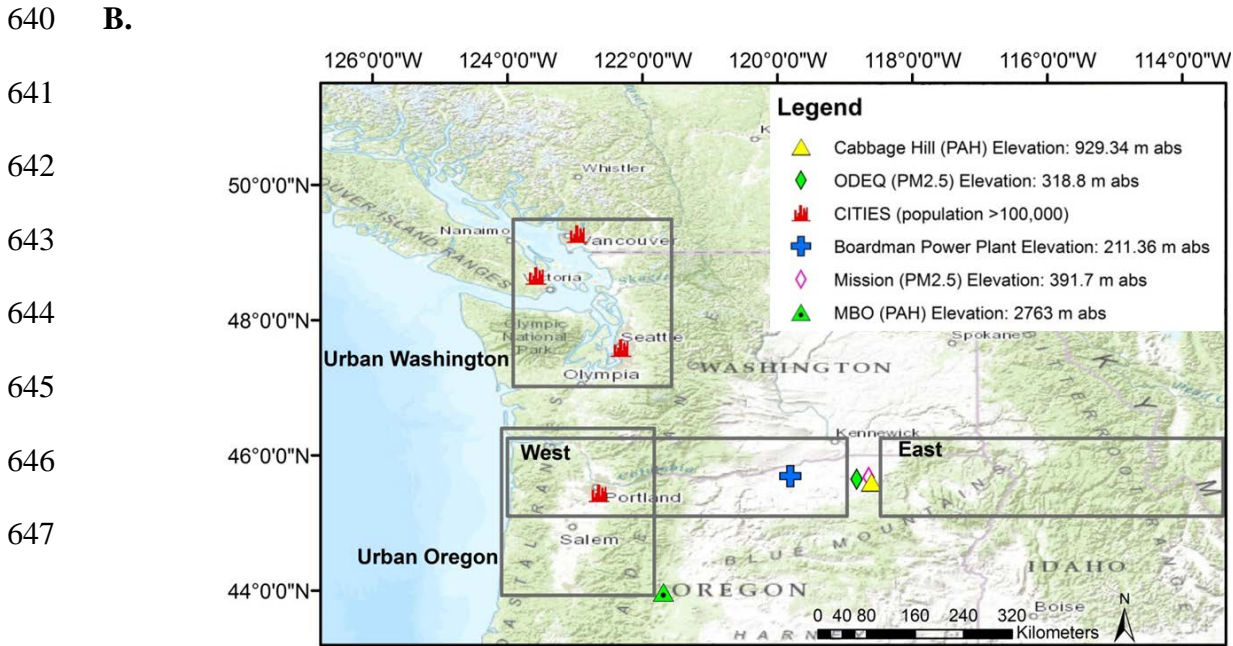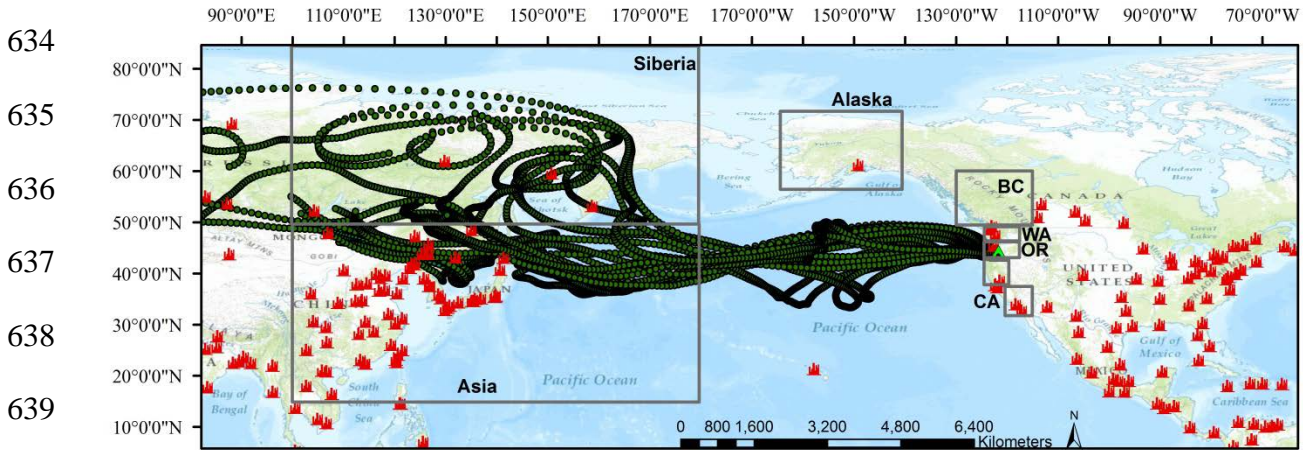614 upgrades).
615
616
617
618
619
620
621
622
623
624

Table 1. List of the PAHs, NPAHs and OPAHs measured in this study and their abbreviations.

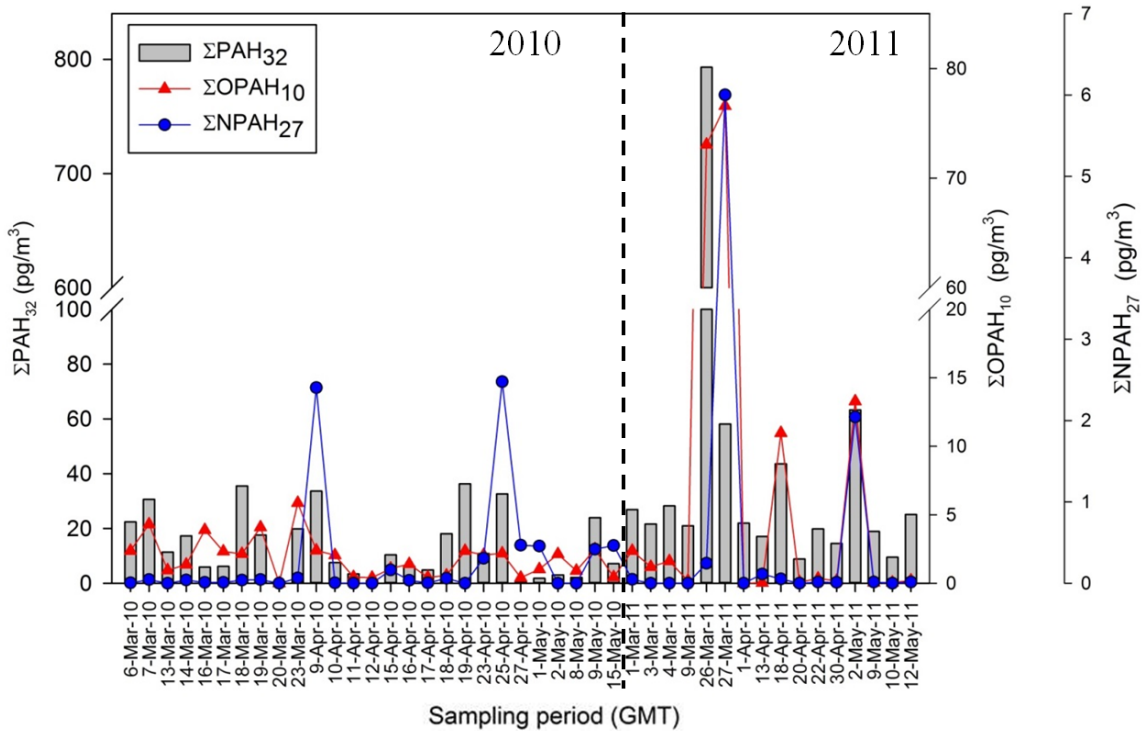| PAHs	Abv.	NPAHs	Abv.	OPAHs	Abv.
2-Methylnaphthalene	2-MNAP	1-nitronaphthalene	1-NN	9-fluorenone	9-FLU
1-Methylnaphthalene	1-MNAP	2-nitronaphthalene	2-NN	phenanthrene-1,4-dione	PHEN-1,4
2,6-Dimethylnaphthalene	2,6-DMNAP	2-nitrobiphenyl	2-NBP	9,10-anthraquinone	9,10-ANQ
1,3-Dimethylnaphthalene	1,3-DMNAP	3-nitrobiphenyl	3-NBP	2-methyl-9.10-anthraquinone	2-MANQ
2-Methylphenanthrene	2-MPHE	4-nitrobiphenyl	4-NBP	Benzo(a)fluorenone	BaFLO
2-Methylanthracene	2-MANT	3-nitrodibenzofuran	3-NBF	benzanthrone	BenzANT
1-Methylphenanthrene	1-MPHE	5-nitroacenaphthene	5-NAC	Aceanthrenequinone	AceANQ
3,6-Dimethylphenanthrene	3,6-DMPHE	2-nitrofluorene	2-NFL	benz[a]anthracene-7,12-dione	Ba-7,12-AD
1-Methylpyrene	1-MPYR	9-nitroanthracene	9-NAN	benzo[c]phenanthrene-1,4 quinone	Benz[c]-1,4
6-Methylchrysene	6-MCHR	9-nitrophenanthrene	9-NPH	Benzo[cd]pyreone	BcdPYRO
Naphthalene	NAP	2-nitrodibenzothiophene	2-NDB	SUM OF ALL 10 INDIVIDUAL OPAH	$\sum OPAH_{10}$
Acenaphthylene	ACY	3-nitrophenanthrene	3-NPH		
Acenaphthene	ACE	2-nitroanthracene	2-NAN		
Fluorene	FLO	(2+3)-nitrofluoranthene	(2+3)NF		
Dibenzothiophene	DBT	1-nitropyrene	1-NP		
Phenanthrene	PHE	2-nitropyrene	2-NP		
Anthracene	ANT	2,8-dinitrodibenzothiophene	2,8-DNDB		
Fluoranthene	FLA	7-nitrobenz[a]anthracene	7-NBaA		
Pyrene	PYR	1-nitrotriphenylene	1-NTP		
Retene	RET	6-nitrochrysene	6-NCH		
Benz[c]fluorene	BcFLO	3-nitrobenzanthrone	3-NBENZ		
Benzo(a)anthracene	BaA	2-nitrotriphenylene	2-NTP		
Chrysene + Triphenylene	CHR+TRI	1,3-dinitropyrene	1,3-DNP		
Benzo(b)fluoranthene	BbF	1,6-dinitropyrene	1,6-DNP		
Benzo(k)fluoranthene	BkF	1,8-dinitropyrene	1,8-DNP		
Benz(e)pyrene	BeP	6-nitrobenzo[a]pyrene	6-NBaP		
Benzo(a)pyrene	BaP	SUM OF ALL 27 INDIVIDUAL NPAH	$\sum NPAH_{27}$		
Dibenz(a,h)anthracene	DahA				
Indeno(1,2,3-cd)pyrene	IcdP				
Dibenzo[a,c]anthracene	DacA				
Benzo(ghi)perylene	BghiP				
NAP + 2-MNAP + 1-MNAP +2,6-DMNAP + 1,3-DMNAP + ACY + FLO + DBT	$\sum PAH_{2ring}$				
PHE + ANT + 2-MPHE + 2-MANT + 1-MPHE + 3,6-DMPHE	$\sum PAH_{3ring}$				
FLA + PYR + RET + 1-MPYR + BaA + (CHR+TRI) + 6-MCHR	$\sum PAH_{4ring}$				
BbF + BkF + BeP + BaP + DahA + IcdP + DacA + BghiP	$\sum PAH_{56ring}$				
NAP + ACY + FLO + PHE + ANT + FLA + PYR + BaA + (CHR+TRI) + BbF + BkF + BaP + IcdP + DahA + BghiP	$\sum PAH_{USpri}$				
SUM OF ALL 32 INDIVIDUAL PAH	$\sum PAH_{32}$				

626
627
628
629
630
631
632

633
634
635
636
637
638
639
640
641
642
643
644
645
646
647

Figure 1. A.) Representative 10 day air mass backtrajectories from MBO for April 23, 2010 and the source region boxes used for both CTUIR and MBO (Oregon, OR; Washington, WA; Alaska; California, CA; British Columbia, BC, Siberia and Asia). B.) Location of air sampling sites in the Pacfic Northwest at MBO and CTUIR, as well as the locations of regional air quality sites near Pendleton, OR: ODEQ and CTUIR Mission Site. The location of the coal fired power plant in Boardman, OR is also indicated.

A.

B.

Figure 2. Temporal variation of mean $\sum PAH_{32}$, $\sum OPAH_{10}$, and $\sum NPAH_{27}$ concentrations at
MBO during the sampling periods.

Figure 3. Three operational timeframes of the Boardman Plant (plant on (before upgrade), plant on (after upgrade) and plant off) and $\sum PAH_{32}$, $\sum OPAH_{10}$ and $\sum NPAH_{27}$ concentrations at CTUIR (Cabbage Hill) during the sampling periods.
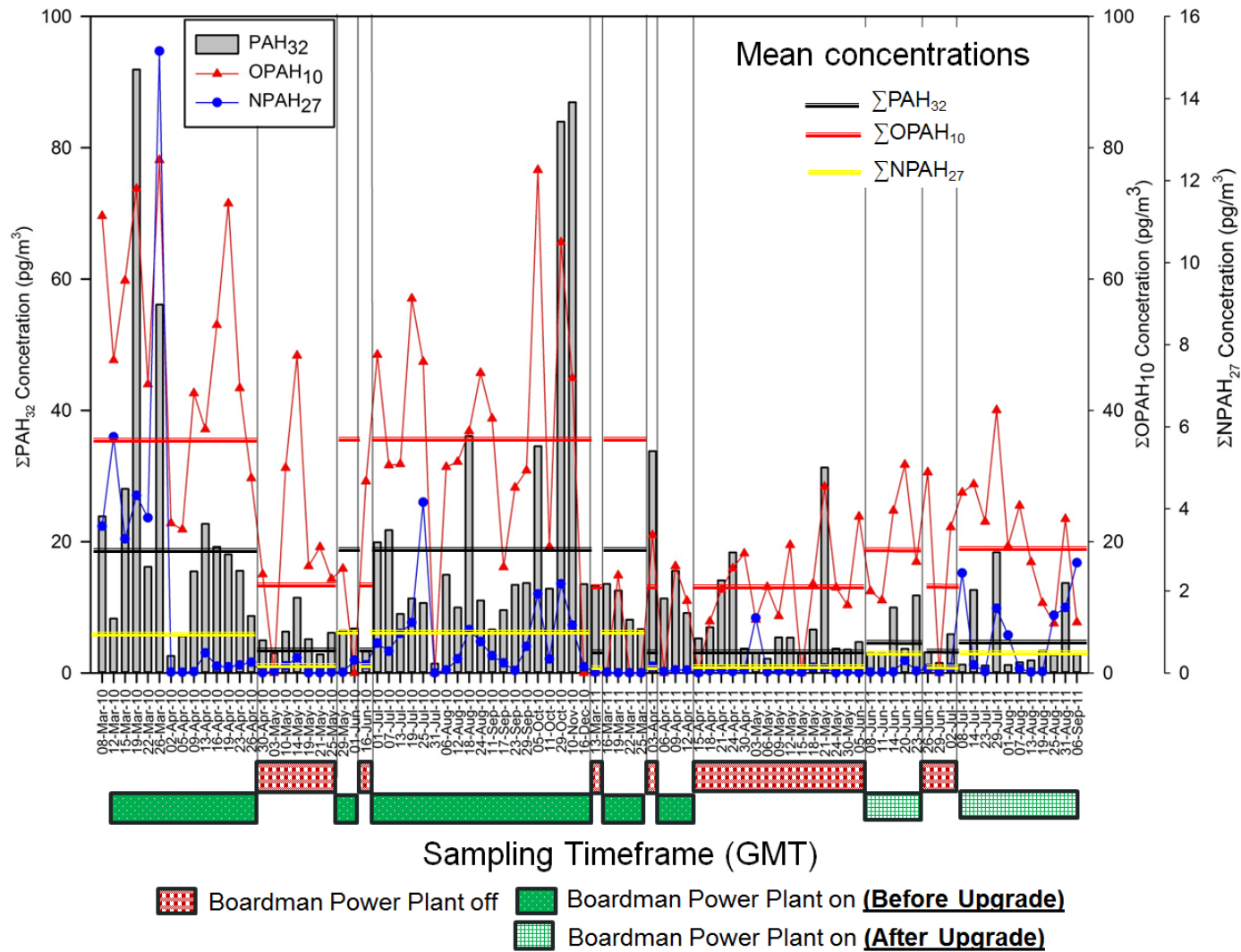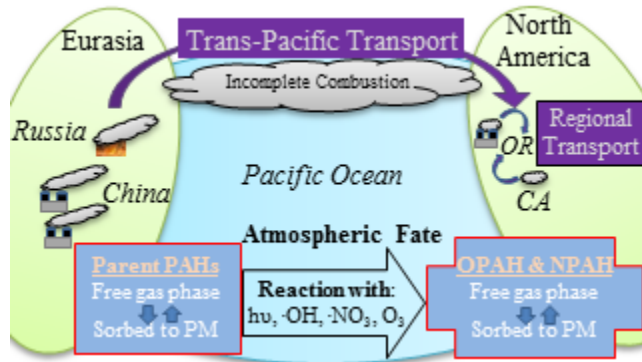
718 **Figure 4.** A.) PAH diagnostic ratio cross plot BaA/(BaA+CHR) vs IcdP/(IcdP+BghiP)
719 using thresholds from Yunker et al.[46] at CTUIR in 2010 and 2011 and B) the three
720 operational timeframes of Boardman Plant (plant on (before upgrade), plant off and plant
721 on (after upgrades).
722
723
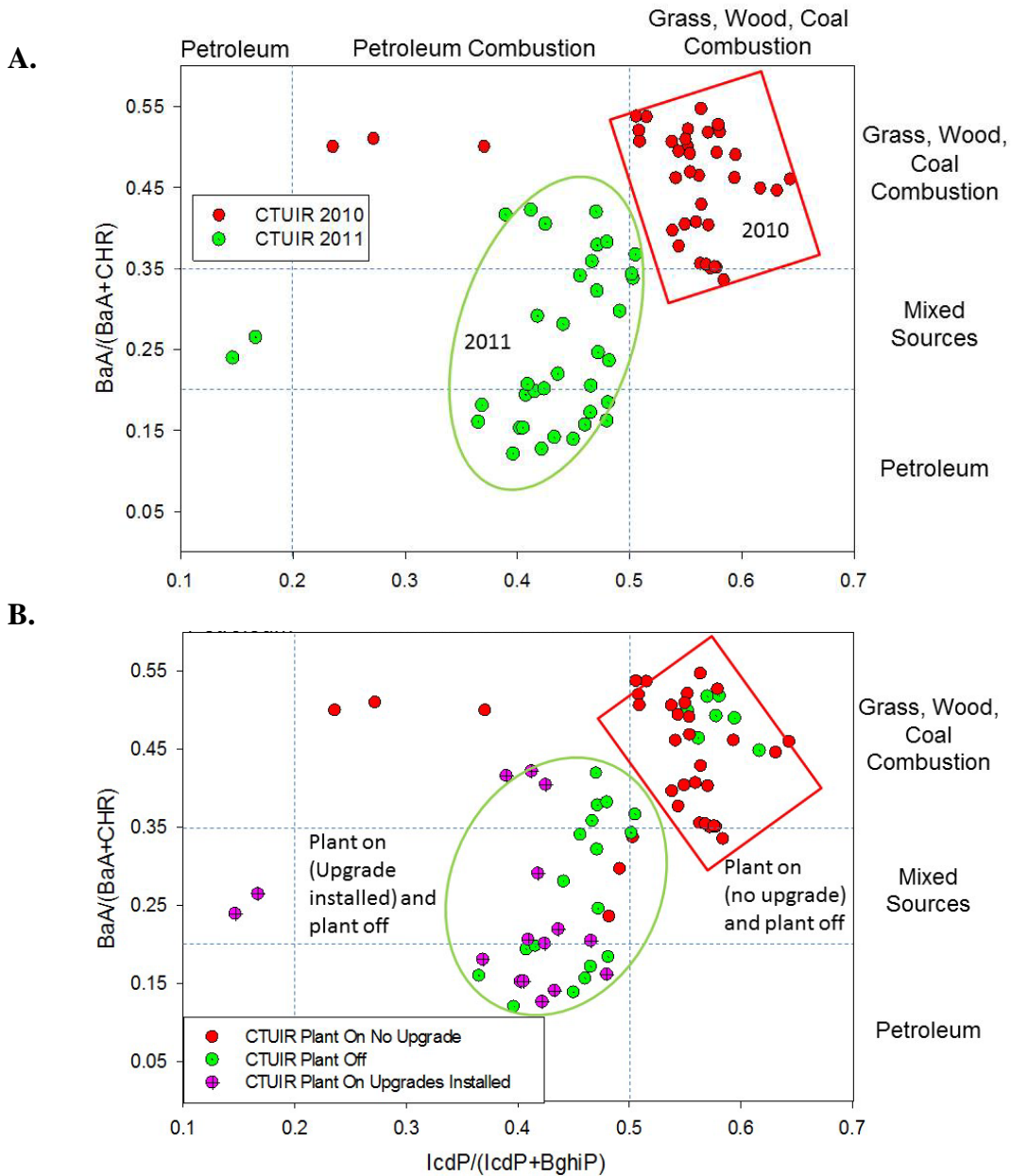
745 **TOC Art:**
746

747
748
749
750
751