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Relative Influence of Trans-Pacific and Regional Atmospheric Transport of PAHs in the Pacific Northwest, U.S.

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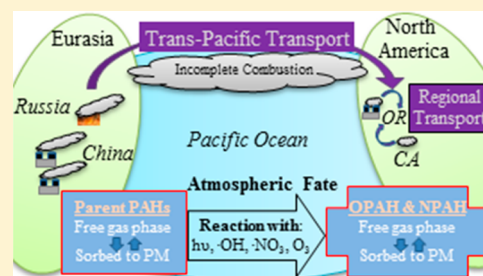
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Supporting Information

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 ($\text{PM}_{2.5}$) were investigated in the Pacific Northwest, U.S. in 2010–2011. Ambient high volume $\text{PM}_{2.5}$ 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, NO_x , 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 $\text{PM}_{2.5}$ concentrations. By comparing the Boardman Plant operational time frames when the plant was operating to when it was shut down, the plant was found to contribute a large percentage of the measured PAH (67%), NPAH (91%), OPAH (54%), $\text{PM}_{2.5}$ (39%), and OC (38%) concentrations at CTUIR and the CRG prior to Spring 2011 and likely masked trans-Pacific atmospheric transport events to the CRG. Upgrades installed to the Boardman Plant in the spring of 2011 dramatically reduced the plant's contribution to PAH and OPAH concentrations (by $\sim 72\%$ and $\sim 40\%$, respectively) at CTUIR and the CRG, but not NPAH, $\text{PM}_{2.5}$ or OC concentrations.



INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are formed during incomplete combustion and are emitted directly into the gas-phase, as well as sorbed onto particulate matter of 2.5 μm in diameter ($\text{PM}_{2.5}$), composed of black carbon (BC) and organic carbon (OC).^{1–3} Incomplete combustion sources include anthropogenic sources, such as coal combustion⁴ and vehicular emissions,⁵ as well as natural sources, such as forest fires⁶ and volcanoes.⁷ PAHs are a human health concern because some PAHs are mutagenic components of $\text{PM}_{2.5}$.^{8,9}

Previous studies have determined that there is significant outflow of particulate-phase PAHs from Asia,¹⁰ as well as the trans-Pacific atmospheric transport of polluted dust,¹¹ mercury,¹² ozone,¹³ PM_{10} and particulate phase PAHs^{6,15,16} to the western U.S. Zelenyuk et al.¹⁷ recently explained the relatively high PAH concentrations measured during trans-Pacific atmospheric transport events by rationalizing that, during particle formation, PAHs become entrapped in a semi solid secondary organic aerosol and protected from evaporation

or oxidation during transport. In addition, Timonen et al.¹⁴ estimated that, during the spring (March–May), Asian sources account for approximately 50–80% of the total $\text{PM}_{2.5}$ measured in clean background areas of the Pacific Northwest (PNW) and approximately 36%–50% in urban areas of the PNW. Given that $\text{PM}_{2.5}$ and PAHs are often coemitted from the same sources, the percentages may be similar for PAHs.

PAH derivatives (nitro-PAH (NPAH) and oxy-PAH (OPAH)) form directly during incomplete combustion processes, as well as from gas phase reaction and heterogeneous reactions of PM-bound parent PAHs with other atmospheric pollutants, such as OH radical, O_3 , NO_2 , and NO_3 radical.

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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]pyrene	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 _{5ring}				
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				

Based on the behavior of their analogous parent PAHs, NPAHs, and OPAHs may undergo trans-Pacific atmospheric transport bound to PM_{2.5}.^{18,19} Previous studies have measured PAH derivatives at remote and rural sites far from point sources,²⁰ as well as urban sites.²¹

The primary objectives of this research were to (1) measure the PAH and PAH derivative (NPAH and OPAH) concentrations on PM_{2.5} in ambient air masses in the Pacific Northwest and (2) determine the relative influence of trans-Pacific and regional transport at a remote mountain site in the Oregon Cascade Range (Mt. Bachelor Observatory) and at a regional, rural site on the Confederated Tribes of the Umatilla Indian Reservation (CTUIR) located on the Columbia Plateau and bordering the Columbia River Gorge (CRG) national

scenic area in 2010 and 2011. Understanding the relative influence of these transport pathways will help to formulate regional, national, and international air quality regulations.

EXPERIMENTAL SECTION

Chemicals. All of the PAHs, NPAHs, and OPAHs analyzed for in this study, and their abbreviations, are listed in Table 1. PAHs, NPAHs, and OPAHs were purchased from AccuStandard (New Haven, CT), Chem Service (West Chester, PA), Chiron AS (Trondheim, Norway) and Sigma-Aldrich (St. Louis, MO). Deuterium-labeled PAHs and NPAHs were purchased from CDN Isotopes (Point-Claire, Quebec, Canada) and Cambridge Isotope Laboratories (Andover, MA). These isotopically labeled standards were used as recovery surrogates

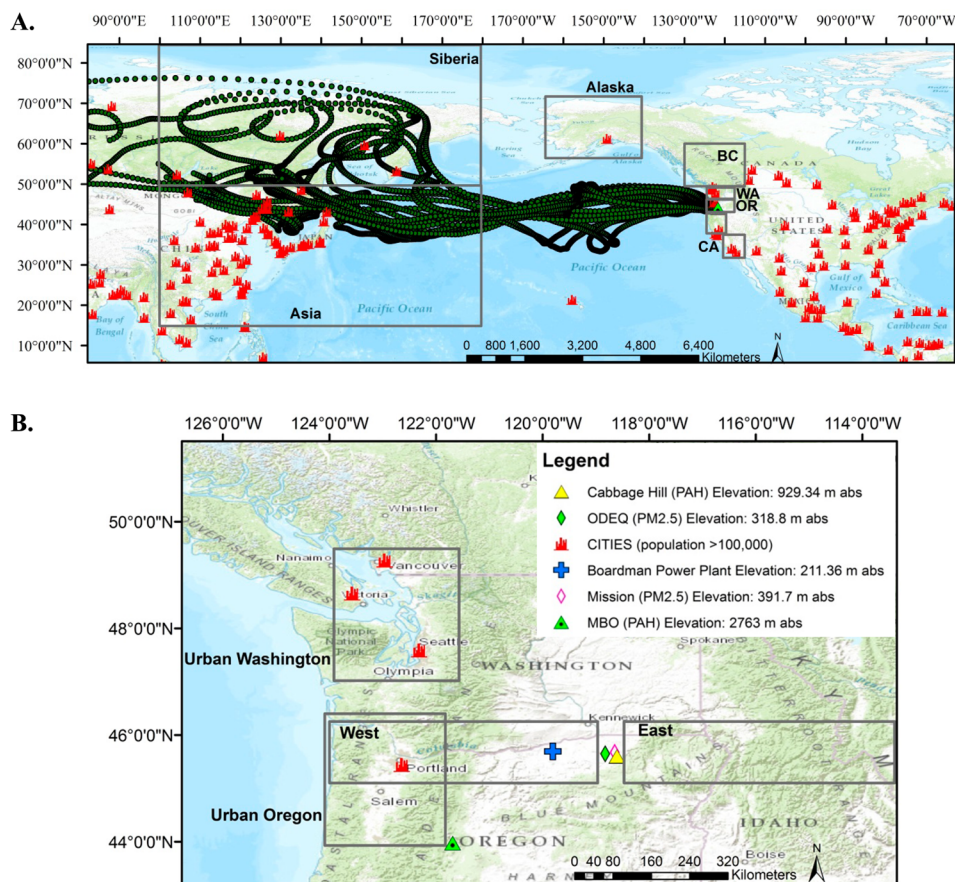


Figure 1. (A) Representative 10 day air mass backtrajectories from MBO for April 23, 2010 and the source region boxes used for both CTUIR and MBO (Oregon, OR; Washington, WA; Alaska; California, CA; British Columbia, BC, Siberia and Asia). (B) Location of air sampling sites in the Pacific Northwest at 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.

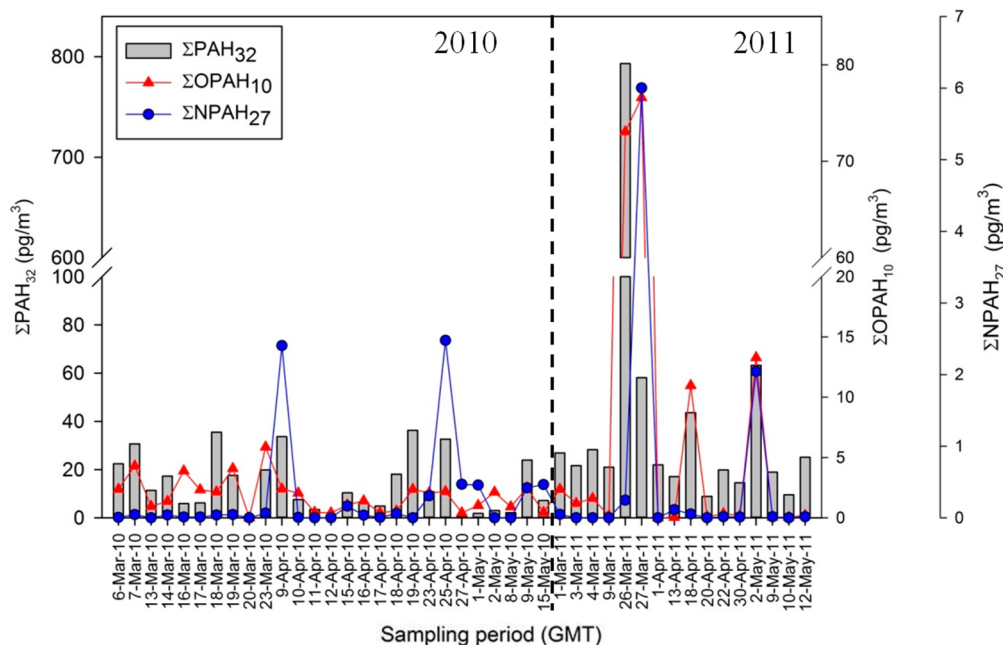


Figure 2. Temporal variation of mean ΣPAH_{32} , ΣOPAH_{10} , and ΣNPAH_{27} concentrations at MBO during the sampling periods.

and internal standards as previously described in detail by Wang et al.² Only HR-GC OmniSolv grade solvents (Reagents, Charlotte, NC) were used.

Sampling Sites and Sample Collection. Two sampling sites, in Oregon, were chosen for this study (Figure 1B). The mountain top sampling site at Mount Bachelor Observatory

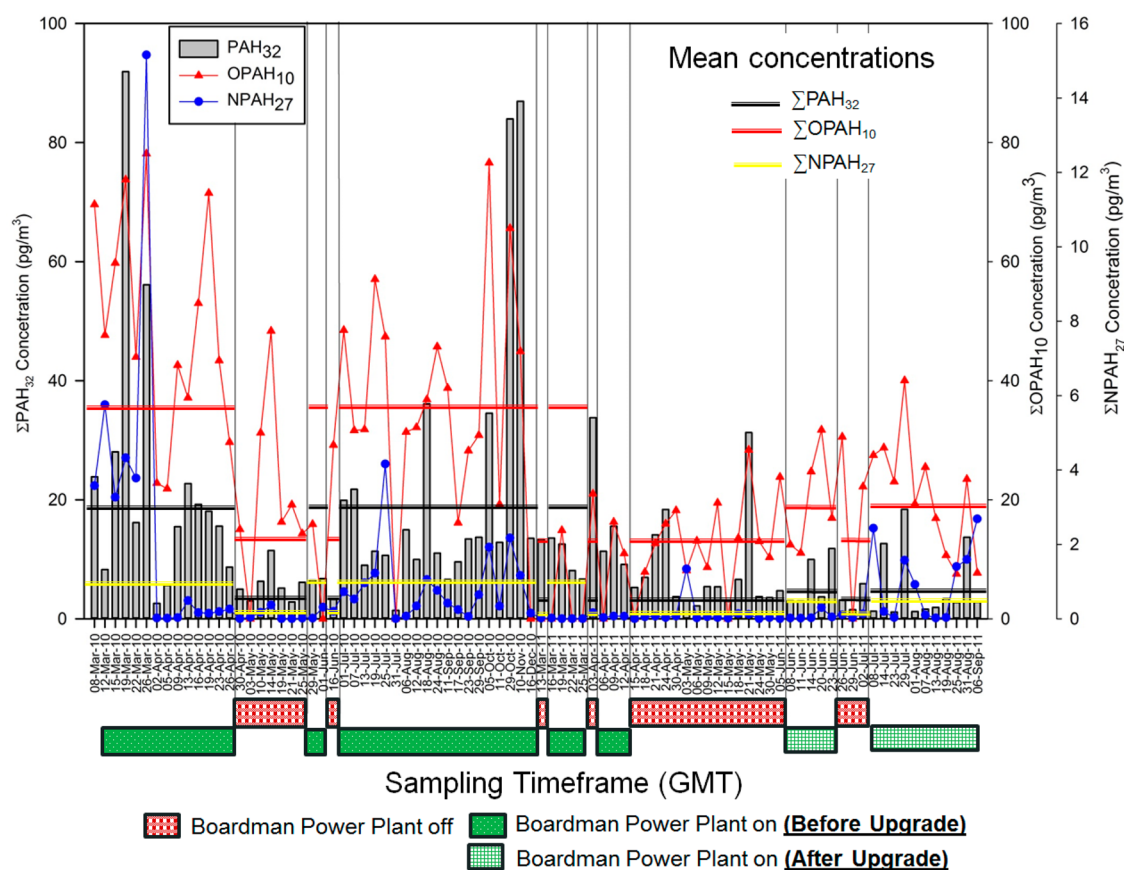


Figure 3. Three operational timeframes of the Boardman Plant (plant on (before upgrade), plant on (after upgrade) and plant off) and ΣPAH_{32} , ΣOPAH_{10} , and ΣNPAH_{27} concentrations at CTUIR (Cabbage Hill) during the sampling periods.

(MBO) (43.98°N 121.69°W , 2783 m above sea level (asl)) is located ~ 180 km east of the Pacific Ocean in Oregon's Cascade Range and was established to observe trans-Pacific atmospheric transport events.¹² Previous studies at MBO have measured the trans-Pacific and regional atmospheric transport of particulate phase PAHs¹⁵ and PM_{10} .¹⁴ Episodic trans-Pacific atmospheric transport is most likely to occur at MBO in the spring of the year, from March to May.¹⁵ $\text{PM}_{2.5}$ samples were collected at MBO from March to May 2010 (27 samples collected) and March to May 2011 (16 samples collected). The specific dates sampled at MBO are shown in Figure 2.

The other sampling site was on the CTUIR on Cabbage Hill (45.60°N 118.61°W , 929.34 m asl) (see Figure 1B) and was selected because it was a representative site for the CRG and the CRG Plateau. This sampling site lies ~ 302 km northeast of MBO and ~ 179 km from the eastern edge of the CRG National Scenic area in the rolling hills of the Columbia Plateau. PM_{10} and $\text{PM}_{2.5}$ concentrations were observed by Vaughan et al. to increase by 370% and 134% respectively, from the trans-Pacific transport of Asian dust to sites on the Columbia Plateau.²³ The Cabbage Hill sampling site lies ~ 20 km southeast of Pendleton, OR (estimated 2013 population $\sim 16,935$)²⁴ and ~ 2 km from a section of I-84, with an annual daily traffic volume of $\sim 10,000$ vehicles/day,²⁵ including diesel and personal automobiles. $\text{PM}_{2.5}$ samples were collected at the Cabbage Hill site on the CTUIR from March to December 2010 (43 samples collected) and March to September 2011 (43 samples collected). The specific dates sampled at CTUIR are shown in Figure 3. $\text{PM}_{2.5}$ samples were collected at both MBO and CTUIR from March to May in 2010 and 2011.

At both MBO and Cabbage Hill, $\text{PM}_{2.5}$ was collected a high volume cascade impactor (Series 230, Tisch Environmental, Cleves, OH) which was operated in accordance to the procedures established by the U.S. Environmental Protection Agency (CFR40, Part 50.11, Appendix B, July 1, 1975) and ASTM Specification D2009.²⁶ We cannot eliminate the potential for both positive²⁷ and negative^{28–30} sampling artifacts. However, given that both sites are relatively rural and remote, we have assumed that the measured PAH, NPAH, and OPAH concentrations at the sites are representative. Quartz fiber filters (QFFs) were used and were prebaked at 350°C prior to sample collection. Field blanks were also collected over the sampling time periods (10 field blanks at CTUIR and 4 field blanks at MBO) along with lab blanks and were analyzed for the PAH, NPAH, and OPAH listed in Table 1 following the procedure outlined in both Wang et al. and Jariyasopit et al.^{2,19}

During the sampling periods, direct mass measurements of $\text{PM}_{2.5}$ were also made at CTUIR's Mission sampling site (45.68°N 118.65°W , 391.7 m asl, ~ 10 km from Cabbage Hill site) (see Figure 1B) using a Thermo Scientific Taper Oscillating Microbalance (TEOM) monitor (Thermo Scientific, Franklin, MA). Direct $\text{PM}_{2.5}$ mass measurements were also made during the sampling periods at the Oregon Department of Environmental Quality (ODEQ) air quality monitoring station in Pendleton, OR (45.65°N 118.82°W , 318.8 m asl, ~ 18 km from the Cabbage Hill Sampling site) using a nephelometer (see Figure 1B). Additional information on sample collection is provided in the Supporting Information.

Sample Extraction and Chemical Analysis. The sample extraction and analysis procedures have been previously

validated^{2,15,19} and are described in the Supporting Information. In brief, the samples were extracted using a pressurized liquid extraction (PLE) method outlined by in Wang et al. and Jariyasopit et al.^{2,19} After extracting the filters twice with dichloromethane (DCM), the resulting extract was split in half by weight for chemical analysis using GC/MS and toxicological analysis using the Ames assay.² A signal-to-noise ratio of 10:1 was used to define the limit of quantitation. Site specific estimated detection limits (EDLs) were calculated from EPA-method 8280A,³¹ and were defined as a signal-to-noise ratio of 3:1 in the sample matrix.

Organic Carbon and Black Carbon Analysis. A Sunset EC/OC analyzer (Sunset Lab, Tigard, OR) was used to analyze for organic carbon (OC) and black carbon (BC),³² concentrations on the ambient PM_{2.5} samples collected at MBO and Cabbage Hill using a 1 × 1 in. section cut from the filters. We focus on OC here because PAHs are a component of the OC on PM.

Back Trajectory Analysis and Calculation of Source Region Impact Factors. The methods used to conduct the back trajectory analysis and calculation of source region impact factors (SRIFs) have been described in detail by Primbs et al.¹⁵ and are given in the SI. In brief, ten day air mass back-trajectories were calculated using NOAA's ARL HYSPLIT online model³³ and data from the GDAS (Global Data Assimilation System) archive and were calculated at three arrival elevations above model ground level (1300, 1500, and 1700 m for MBO and 400, 600, and 800 m for CTUIR), every 3 h, over the 24 h sampling period (including the start and stop time), for a total of 27 trajectories per sample. The 10 day back trajectories were used to determine the impact of different source regions (Oregon, Washington, California, Asia, Siberia, British Columbia, Alaska, West and East) on the air masses sampled (Figure 1A).¹⁰

Ames Assay. The method reported by Maron et al.³⁴ was used as described by Wang et al.² and the details are provided in the SI. Salmonella strain TA98 (Xenometrix, Inc., Allschwil, Switzerland) was used and the test was conducted, with and without metabolic activation, by using rat S9 mix.

RESULTS AND DISCUSSION

Pollutant Concentrations and Sources to MBO. Figure 2 shows the $\sum\text{PAH}_{32}$, $\sum\text{OPAH}_{10}$, $\sum\text{NPAH}_{27}$ concentrations on PM_{2.5} measured at MBO. Significant positive correlations ($p < 0.05$) between $\sum\text{PAH}_{32}$ and $\sum\text{OPAH}_{10}$ concentrations, as well as between $\sum\text{OPAH}_{10}$ and $\sum\text{NPAH}_{27}$, were measured. However, $\sum\text{PAH}_{32}$ and $\sum\text{NPAH}_{27}$ concentrations were not significantly correlated with each other. Overall, the individual PAH and $\sum\text{PAH}_{32}$ concentrations were relatively low (pg/m³) at MBO in 2010 and 2011 compared to other studies that identified trans-Pacific transport of PAHs,^{6,16} including at MBO.¹⁵ This suggests that the trans-Pacific transport of PAHs was not particularly strong in the spring of 2010 and 2011 and is consistent with Fischer et al.^{35,36} who found that anomalous meteorology (such as cloud scavenging of aerosols and a more persistent wind flow from the south) reduced the aerosol concentration at MBO during this time period. It is unclear why the $\sum\text{PAH}_{32}$, $\sum\text{OPAH}_{10}$, $\sum\text{NPAH}_{27}$ concentrations were significantly elevated at MBO on March 26 and 27, 2011 (Figure 2). However, the mean $\sum\text{PAH}_{32}$, $\sum\text{OPAH}_{10}$, $\sum\text{NPAH}_{27}$ concentrations at MBO were not statistically different between 2010 and 2011.

PM₁, and not PM_{2.5}, mass concentration was measured at MBO, during the sampling periods¹⁴ and is shown in Supporting Information Figure S1. The difference between PM₁ and PM_{2.5} concentrations has been shown to be ~10–40%.^{37–40} However, we assumed that the fluctuations in PM₁ concentration at MBO would be representative of fluctuations in the PM_{2.5} concentrations at MBO. No statistical difference in the mean PM₁ concentration was found between 2010 and 2011. The OC, $\sum\text{PAH}_{5,6\text{ring}}$, and individual PAH (RET, BaA, CHR+TRI, BbF BkF, BeP, BaP DcaA, IcdP and BghiP) concentrations were positively correlated with the PM₁ concentrations ($p < 0.05$) at MBO. However, there were no statistically significant correlations between $\sum\text{PAH}_{32}$, $\sum\text{OPAH}_{10}$, $\sum\text{NPAH}_{27}$, and PM₁ concentrations at MBO.

Source Region Impact Factors and Meteorological Conditions at MBO. The source regions to MBO have been previously defined¹⁵ and include regional/urban sources regions (Oregon, Washington, Urban Oregon, Urban Washington, British Columbia, Alaska, and California), as well as source regions in Asia and Siberia (Figure 1A). Supporting Information Figure S2 shows the calculated SRIFs for MBO for the sampling days. Similar to Primbs et al. in 2004–2006 at MBO,¹⁵ elevated SRIFs for California, Oregon and Washington were observed during the spring sampling periods in 2010 and 2011. There were minimal correlations between the individual PAHs and PAH derivative concentrations and SRIFs (Supporting Information Table S1). There were significant positive correlations ($p < 0.05$) with 6-NCH and OC concentrations and CA %, with BenzANT and OC concentration and Urban WA % and with 1-NP concentration and Alaska% and BC%. These correlations indicate that these compounds may be a result of regional atmospheric transport.

$\sum\text{NPAH}_{27}$ and 1,8-DNP concentrations were significantly positively correlated with the Asia SRIF% ($p < 0.05$). 1,8-DNP was found to form in chamber reaction studies under simulated atmospheric conditions with Beijing PM under exposure to NO₃/N₂O₅ and expected to lead to increased mutagenicity.¹⁹ This indicates that 1,8-DNP may be a potential marker for trans-Pacific atmospheric transport.

Supporting Information Table S2 shows the statistically significant correlations between the PAH, NPAH, and OPAH concentrations at MBO and HYSPLIT model output (\sum precipitation during the trajectory (ppt (mm/h)) and the amount of time the trajectories spent above or below the boundary layer (% above and % below, respectively)⁴¹), weather conditions (water vapor (WV) (g/kg), relative humidity (RH) and ambient pressure (mbar) and 1000/Temperature (K⁻¹)), and atmospheric pollutant concentrations (O₃ (ppbv) and CO (ppbv)).^{12,42} At MBO during the spring, increased CO and O₃ concentrations have been shown to be associated with Asian air masses.^{15,42} Significant negative correlations ($p < 0.05$) between CO concentrations and 2-MNAP, 1-MNAP, 2,6-DMNAP, 1,3-DMNAP, 2-MPHE, 1-MPHE, NAP, ACY, and ACE concentrations at MBO (Supporting Information Table S2 and S3) suggest that these PAHs may be indicators of regional transport. Primbs et al. attributed these same PAHs to regional transport from the Western U.S.¹⁵ There was a significant positive correlation ($p < 0.05$) between BghiP and CO concentrations (Supporting Information Table S2), suggesting that BghiP concentrations at MBO may be a marker for trans-Pacific air masses.

Significant negative correlations, between many PAH and PAH derivative concentrations with O₃ concentrations were

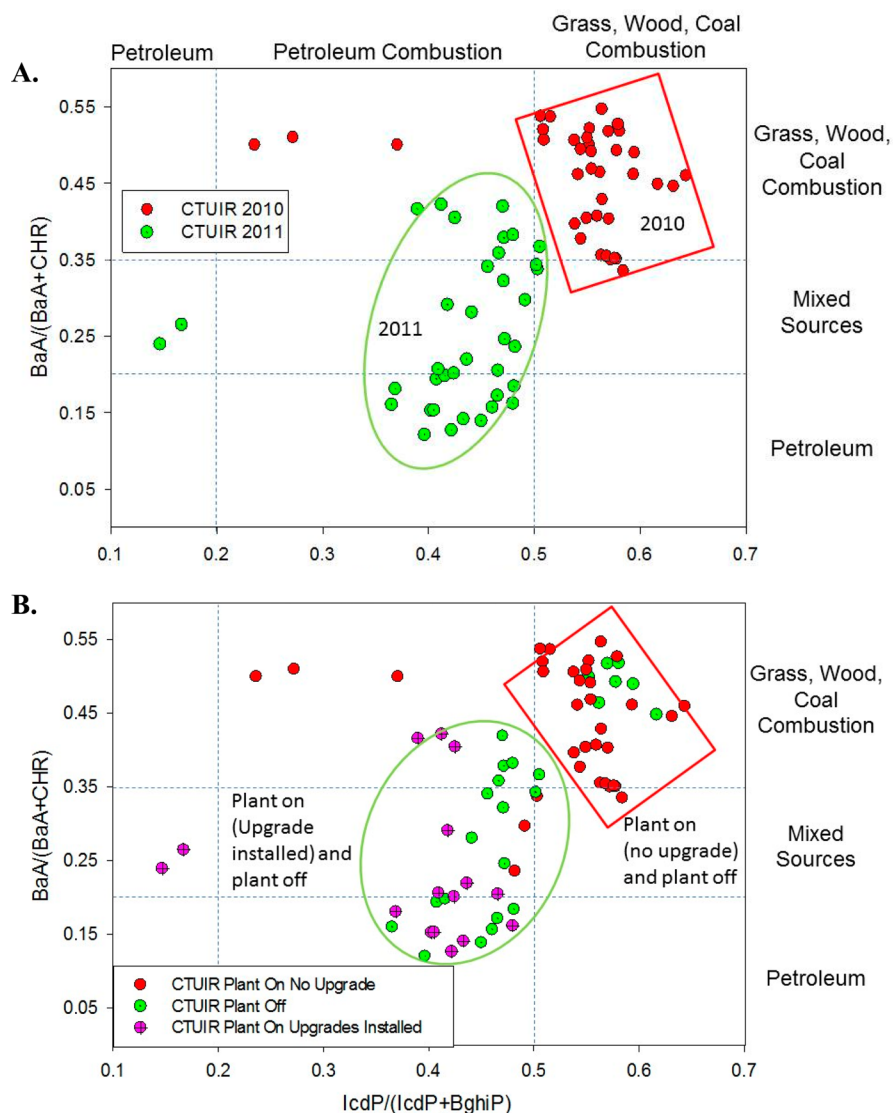


Figure 4. A) PAH diagnostic ratio cross plot $BaA/(BaA+CHR)$ vs $IcdP/(IcdP+BghiP)$ using thresholds from Yunker et al.⁴⁶ at CTUIR in 2010 and 2011 and B) the three operational timeframes of Boardman Plant (plant on (before upgrade), plant off and plant on (after upgrades)).

observed at MBO (Supporting Information Table S2). Recently, Jariyasopit et al.¹⁹ found that, under simulated trans-Pacific transport conditions, O_3 exposure resulted in significant degradation of PAHs bound to Beijing PM. This may suggest that some PAHs, including BbF, BkF, BeP, BaP, IcdP, degrade during trans-Pacific transport due to reaction with O_3 . However, we cannot eliminate the possibility that this result may be due to a sampling artifact from drawing O_3 over the PM-bound PAHs on the filter, resulting in their degradation.

Ames Assay Results at MBO. 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, 5/2/11, 5/9/11, and 5/12/11) out of 43 sampling days at MBO with direct acting mutagenicity (-S9 rat liver enzyme) statistically different ($p < 0.05$) from the negative control (Figure S3). Of these 10 days, 2 days were previously identified by Timonen et al. as trans-Pacific events at MBO (4/19/10 and 5/12/11).¹⁴ NPAHs and OPAHs have been shown to be direct acting mutagens.² However, no correlations were found between OPAH and NPAH concentrations at MBO and revertants/(plate·m³), likely because of the low OPAH and

NPAH concentrations measured. There were no sampling days at MBO in which the indirect acting mutagenicity (+S9 rat liver enzyme) was statistically different from the negative control.

Pollutant Concentrations and Sources to CTUIR. Figure 3 shows the $\sum PAH_{32}$, $\sum OPAH_{10}$, $\sum NPAH_{27}$ concentrations measured at the CTUIR Cabbage Hill site. The $\sum PAH_{32}$, $\sum OPAH_{10}$, $\sum NPAH_{27}$ concentrations were significantly positively correlated ($p < 0.05$) with each other. In addition, the mean $\sum PAH_{32}$, $\sum OPAH_{10}$, and $\sum NPAH_{27}$ concentrations were significantly higher in 2010 than in 2011, at Cabbage Hill ($p < 0.05$) (by ~ 2.5 x for PAHs and OPAHs and ~ 4 x for NPAHs).

The measured PAH, OPAH, and NPAH concentrations at MBO and CTUIR (Cabbage Hill site) were directly compared using only overlapping sampling periods (March to May in 2010 and 2011). In 2010, the mean $\sum PAH_{32}$, $\sum OPAH_{10}$, and $\sum NPAH_{27}$ concentrations at CTUIR were significantly different ($p < 0.05$) and were ~ 1.3 x, ~ 20 x, and ~ 6 x, times higher, respectively, than at MBO. However, in 2011, the mean $\sum PAH_{32}$, $\sum OPAH_{10}$, and $\sum NPAH_{27}$ concentrations at

CTUIR were not statistically different from the concentrations at MBO.

Figure S6 shows the 24 h $PM_{2.5}$ concentration at the Mission site, the 24 h $PM_{2.5}$ concentration at the ODEQ site, and the organic carbon concentration on $PM_{2.5}$ at Cabbage Hill. Over the entire sampling period, the 24 h $PM_{2.5}$ concentration at the Mission and ODEQ sites were significantly positively correlated ($p < 0.05$) with each other. Over the same time period, the mean 24 h $PM_{2.5}$ concentration at the Mission site was $5.78 \pm 2.6 \mu\text{g}/\text{m}^3$ and was statistically significantly higher than the mean 24 h $PM_{2.5}$ concentration of $4.69 \pm 3.0 \mu\text{g}/\text{m}^3$ measured at the ODEQ site ($p < 0.05$). This is likely because the Mission site is impacted more by local $PM_{2.5}$ sources (including wood smoke), than the ODEQ site.

Source Regions Impact Factors and Meteorological Conditions at CTUIR. The source regions to CTUIR are shown in Figure 1A and were used to assess the path the air masses traveled prior to being sampled at CTUIR. The SRIFs for CTUIR are shown in Figure S4. The majority of the air masses sampled at CTUIR had spent a large percentage of time locally, passing over Washington (WA), British Columbia (BC), or California (CA) in late spring/summer, and Asia and Siberia in early spring (and periodically throughout the year). Table S4 shows that few individual PAH and PAH derivative concentrations or sums of PAH and PAH derivative concentrations at CTUIR were correlated with SRIFs, except for 2,6-DMNAP, 1-MPYR, ACY, DBT, FLA, PYR, BcFLO, DacA, 3-NBP, 3-NBF, 1-NP, 6-NCH, 2NTP, 9,10-ANQ, Ben-(c)-1,4, BcdPYRO which were correlated with local source regions, including BC, WA, and CA. In general, the mean Asia% SRIF for MBO was greater than for CTUIR (14% and 8%, respectively).

To understand the effect of meteorological conditions on the air quality at the Cabbage Hill, Mission and ODEQ sampling sites, the measured PAH, NPAH, OPAH, OC, $PM_{2.5}$ concentrations were compared to meteorological conditions around the sampling sites. Precipitation data recorded at Eastern Oregon Airport was used to assess the impact of precipitation scavenging on the measured PAH, NPAH, OPAH, $PM_{2.5}$ and OC concentrations but no statistically significant correlations were observed. Wind data (direction and speed) from the Eastern Oregon Airport was used to generate wind rose plots for the 2010 and 2011 sampling periods at CTUIR (Figure S5). The predominant wind direction was westerly, occurring over ~50% of the sampling time, in both 2010 and 2011. Table S3 shows the statistically significant correlations between the PAH, NPAH, and OPAH concentrations at CTUIR and HYSPLIT model output (\sum precipitation during the trajectory (ppt (mm/h)) and the amount of time the trajectories spent above or below the boundary layer (% above and % below, respectively)⁴¹), weather conditions (water vapor (WV) (g/kg), relative humidity (RH) and ambient pressure (mbar) and 1000/Temperature (K^{-1})), and atmospheric pollutant concentrations (O_3 (ppbv) and CO (ppbv)).

Influence of the Boardman Plant Emissions on Measured $PM_{2.5}$ and PAH Concentrations at CTUIR. The PAH isomer diagnostic ratios, BaA/ (BaA+CHR) and IcdP/ (IcdP+BghiP), have been used in numerous studies^{43–45} to aid the identification of the combustion source types. The thresholds, determined by Yunker et al.,⁴⁶ were used to help identify PAH sources to Cabbage Hill and the data is shown in Figure 4. Figure 4A shows that in 2010, CTUIR was influenced primarily by a wood, grass, or coal combustion sources, while in

2011, CTUIR was influenced primarily by mixed sources/petroleum sources. This suggested that a shift occurred in PAH source types at the CTUIR Cabbage Hill site between 2010 and 2011.

This prompted us to investigate the significant difference in mean $\sum\text{PAH}_{32}$, $\sum\text{OPAH}_{10}$, $\sum\text{NPAH}_{27}$, and OC concentrations at Cabbage Hill in 2010 and 2011 (Figure 3 and Supporting Information Figure S6), as well as the difference in PAH diagnostic ratios in 2010 and 2011 (Figure 4). The Cabbage Hill site lies ~2 km from I-84, the likely source of mixed source/petroleum source, as well as 80 km east of Portland General Electric's 585 MW coal fired power plant in Boardman, OR (Figure 1B). The Boardman Plant has been previously shown to be a source of $PM_{2.5}$ in the CRG National Scenic Area.^{47,48} According to data from the EPA AirData Web site, the Boardman Plant was also the largest point source of SO_2 and NO_x in the State of Oregon for 2010 and 2011.⁴⁹ Using the IMPROVE Wishram site (~102 km west of Boardman in the CRG), in 2010, Jaffe et al.⁴⁷ found that the Boardman Plant had a significant impact on the $PM_{2.5}$ concentration in the CRG, increasing background $PM_{2.5}$ concentrations by 14% over the entire year and by 56% during the month of November.

To see if the air masses sampled at CTUIR passed over the Boardman Plant, source region boxes "West" and "East" of CTUIR were added (Figure 1B) and the SRIFs for these boxes were calculated for each sampling day. Only statistically significant negative correlations ($p < 0.05$) were found for PYR, 6-NBaP, and 9-FLU concentrations with the west box SRIF, indicating that days not influenced from the west may have been enhanced in these PAH concentrations and could be associated with other sources, such as diesel emissions from I-84. Because there was minimal correlation between PAH and PAH derivative concentrations at Cabbage Hill and the West and East SRIFs, in addition to no differences in PAH concentration on sampling days defined as "west" or "east" based on predominant wind direction, the atmosphere of the Columbia Plateau and at the Cabbage Hill sampling site appeared to be well mixed during the sampling periods. This may be due to the relatively high wind speeds in the CRG and on the plateau.

The operational NO_x , SO_2 , and CO_2 emissions data from the Boardman Plant was compared to the PAH, PAH derivative, OC, and $PM_{2.5}$ concentrations measured at CTUIR, during normal plant operation and during temporary plant closures, to directly assess the impact of the Boardman Plant on air quality at CTUIR. The NO_x , SO_2 , and CO_2 emissions from the Boardman Plant were obtained from the U.S. Environmental Protection Agency's Air Markets Program Data Acid Rain program archive⁴⁹ for the entire sampling period at CTUIR. In the spring of 2011, after the annual shutdown of the power plant from April to June, two new emission controls were added to the Boardman Plant: (1) low- NO_x burners and modified airports and (2) an activated carbon injection system to allow for the capture and removal of mercury.⁵⁰

Figure 3 shows the three distinct operational timeframes of the Boardman Plant, when the plant was on (before the upgrade), when the plant was on (after the upgrade), and when the plant was off, as well as the temporal variation and mean $\sum\text{PAH}_{32}$, $\sum\text{OPAH}_{10}$, $\sum\text{NPAH}_{27}$ concentrations measured during these operational time frames. The mean PAH, OPAH, and NPAH concentrations when the plant was on (before the upgrade) were statistically different ($p < 0.05$), and

$\sim 3\times$, $\sim 2\times$, and $\sim 12\times$ higher, respectively, than when the plant was off. PAH and OPAH concentrations measured when the plant was off and when it was on (after the upgrade) were not statistically significantly different, while NPAH concentrations were still significantly ($p < 0.05$) different and $\sim 6\times$ higher when the plant was on.

Supporting Information Figure S6 shows the temporal variation of the mean OC concentration at Cabbage Hill and $PM_{2.5}$ concentrations at the Mission and ODEQ sites. When the plant was off, the $PM_{2.5}$ concentrations at Mission were statistically significant higher by $\sim 1.5\times$ than at the ODEQ site ($p < 0.05$). When the plant was on (after the upgrade), the $PM_{2.5}$ and OC concentration were significantly increased, by $\sim 1.3\times$ and $2\times$ respectively, as compared to when the plant was off at both sites. In addition, the $PM_{2.5}$ concentration at both sites and OC concentrations measured at Cabbage Hill when the plant was on (after the upgrade) were not statistically different from concentrations measured when the plant was on (before upgrade). Together, these data suggest that the emission controls installed to the Boardman Plant in the spring of 2011 reduced PAH and OPAH concentrations, but not $PM_{2.5}$, OC, NPAH concentrations at CTUIR.

The PAH isomer diagnostic ratio cross plot in Figure 4B shows that, when the Boardman Plant was off, the PAH source type at the Cabbage Hill site was primarily mixed sources, while when the Boardman Plant was on (before upgrade) the PAH source type was primarily coal, grass, or wood combustion. When the plant was on (after upgrade) the PAH source type at the Cabbage Hill site was primarily mixed sources. This data also suggests that the Boardman Plant had a greater impact on PAH concentrations at the Cabbage Hill site before the 2011 upgrade, as compared to after the upgrade.

The hourly SO_2 , NO_x , and CO_2 (kg/h) emission rates from the Boardman Plant were used to calculate the total SO_2 , NO_x , and CO_2 (kg) emissions for each sampling day at CTUIR.⁴⁹ Supporting Information Figures S7, S8, and S9 show the correlation of the NO_x , SO_2 , and CO_2 emissions from the Boardman Plant with the $\sum PAH_{32}$, $\sum OPAH_{10}$, $\sum NPAH_{27}$, and OC concentrations measured at Cabbage Hill, as well as the $PM_{2.5}$ concentrations measured at the Mission and ODEQ sites. The $\sum PAH_{32}$, $\sum OPAH_{10}$, $\sum NPAH_{27}$, OC, and $PM_{2.5}$ concentrations at CTUIR were significantly positively correlated with the NO_x , SO_2 , and CO_2 emissions from the Boardman Plant ($p < 0.05$). Many individual PAH, NPAH, and OPAH isomer concentrations, as well as the $\sum PAH_{16-US\ priority}$ concentration, were also significantly positively correlated ($p < 0.05$) with the SO_2 , NO_x , and CO_2 emissions from the Boardman Plant. These statistically significant positive correlations strongly suggest that the air quality at the CTUIR sampling sites was impacted by emissions from the Boardman Plant.

The Boardman Plant emissions were also significantly correlated ($p < 0.05$) with $\sum PAH_{32}$, $\sum OPAH_{10}$, $\sum NPAH_{27}$, OC, and $PM_{2.5}$ concentrations (at Mission and ODEQ) when separated into the different plant operational timeframes. However, during the operational time frame when the plant was on (after upgrade), only statistical positive correlations were found between Boardman Plant CO_2 emissions and $\sum NPAH_{27}$, OC, and $PM_{2.5}$ concentrations (at Mission and ODEQ). This indicates that the Boardman Plant emissions could still have influenced the NPAH, $PM_{2.5}$ and OC concentrations at CTUIR even after the upgrade.

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

To quantify the effect of the Boardman Plant emissions on the PAH and PAH derivative concentrations at Cabbage Hill, the PAH concentrations measured when the plant was off were compared to when the plant was on. Supporting Information Table S5 compares the PAH, OC, and $PM_{2.5}$ concentrations at CTUIR when the Boardman Plant was on (before the upgrade) to when the plant was off. Significantly increased ($p < 0.05$) concentrations (in pg/m^3) of: individual PAHs (0.30–2.51), $\sum PAH_{3ring}$ (1.48), $\sum PAH_{4ring}$ (7.76), $\sum PAH_{5ring}$ (3.64), $\sum PAH_{16-US\ priority}$ (9.10), $\sum PAH_{32}$ (6.48), individual NPAHs (0.04–1.8), $\sum NPAH_{27}$ (1.16), individual OPAHs (0.12–9.95), $\sum OPAH_{10}$ (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 Boardman Plant was on (before upgrade) as compared to when the plant was off. This indicates that, when the Boardman Plant was on (before upgrade), it was a significant source of PAHs, NPAHs, OPAHs, OC, and $PM_{2.5}$ to CTUIR and the CRG.

Supporting Information Table S6 compares the PAH, OC, and $PM_{2.5}$ concentrations at Cabbage Hill when the Boardman Plant was on (after upgrade) to when the Boardman Plant was off. Significantly increased ($p < 0.05$) concentrations (in pg/m^3) of: 6-NBaP (0.58), $\sum NPAH_{27}$ (0.60), OC (1.21 $\mu g/m^3$), EC (0.06 $\mu g/m^3$) and $PM_{2.5}$ (2.20 and 1.08 $\mu g/m^3$) (for Mission and ODEQ, respectively), as well as significantly reduced ($p < 0.05$) concentrations (in pg/m^3) of: 2,6-DMNAP (−0.20), 1,3-DMNAP (−0.30), BaA (−0.16), IcdP (−0.29), and $\sum PAH_{2ring}$ (−0.74), and $\sum PAH_{5ring}$ (−1.67) were measured when the plant was on. These results indicate the Boardman Plant had a more significant negative impact on CTUIR air quality before the upgrade than after the upgrade. The upgrades installed to the Boardman Plant significantly reduced the PAH and OPAH concentrations at CTUIR so that the PAH concentrations at the site were comparable to when the plant was off. The NPAH, OC, and $PM_{2.5}$ concentrations at CTUIR were not significantly reduced by the Boardman Plant upgrades.

Supporting Information Table S7 compares the PAH, OC, and $PM_{2.5}$ concentrations when the Boardman Plant was on (before the upgrade) to when the Boardman Plant was on (after the upgrade). Significantly reduced ($p < 0.05$) concentrations (in pg/m^3) of: individual PAHs (−0.14 to −1.62), $\sum PAH_{2ring}$ (−1.32), $\sum PAH_{3ring}$ (−1.20), $\sum PAH_{4ring}$ (−7.05), $\sum PAH_{5ring}$ (−5.00), $\sum PAH_{16-US\ priority}$ (−10.98), $\sum PAH_{32}$ (−14.64), individual NPAHs (−0.01 to −0.54), individual OPAHs (−0.12 to −9.94), and $\sum OPAH_{10}$ (−13.43) were measured when the plant was on (after upgrade). There was no statistically significant difference in the $\sum NPAH_{27}$, OC and $PM_{2.5}$ concentrations between the two timeframes and there was a significant increase ($p < 0.05$) in 6-NBaP concentration (0.54 pg/m^3) after the upgrade. This further indicates that the Boardman Plant upgrades significantly reduced the PAH and OPAH concentrations at CTUIR, but not the $\sum NPAH_{27}$, OC and $PM_{2.5}$ concentrations.

The installation of low- NO_x burners and modified airports at the Boardman Plant potentially resulted in more incomplete combustion, which would result in an increase in PAH emissions.⁵¹ However, the activated carbon injection system also installed at the Boardman Plant captures and removes mercury by injecting activated carbon into the flue gas before the electrostatic precipitator and has been shown to reduce PAH emissions in coal fired plants $>90\%$ ³⁷ and, in simulated

waste incineration facilities, by >80%.⁵² Therefore, the activated carbon injection system may have led to reduced PAH emissions from the Boardman Plant, and in turn, reduced PAH concentrations at CTUIR and the CRG. It is unclear why the NPAH emissions were not reduced and may indicate that I-84 traffic is the major source of NPAHs to the Cabbage Hill site.

Ames Assay Results at CTUIR. Supporting Information Figure S10 shows there was low direct acting mutagenicity in the CTUIR samples, especially in 2011. There were 16 days in 2010 (3/15/10, 3/19/10, 3/26/10, 4/13/10, 4/19/10, 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 only 1 day in 2011 (4/9/11), when the Boardman Plant was on and before the upgrade, with significant direct acting mutagenicity (-S9 rat liver enzyme) statistically different ($p < 0.05$) from the negative control. Of these 16 days in 2010, 3 occurred on days when the Boardman Plant was off (5/14/10, 5/19/10, and 5/21/10) and 13 occurred on days when the Boardman Plant was on (before the upgrade). No correlations were found between OPAH and NPAH concentrations and revertants/plate \cdot m³. There were no days at CTUIR in which the indirect acting mutagenicity (+S9 rat liver enzyme) was statistically different from the negative control. These data further show that the Boardman Plant had a significant impact on CTUIR (and CRG) air quality prior to the installation of the upgrades in the spring of 2011.

No trans-Pacific transport events, with high PAH transport, were readily identifiable at CTUIR during the 2010 and 2011 sampling periods, likely because the Boardman Plant was a major regional source of PAHs. Now that the Boardman Plant is no longer a major source of PAHs to the CRG Plateau, trans-Pacific atmospheric transport of PAHs may be more evident to this region of the Pacific Northwest.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b00800.

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Notes

The authors declare no competing financial interest.

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