

**“Photochemical Aging of Polycyclic Aromatic Hydrocarbons on Asian Particulate Matter  
During Trans-Pacific Atmospheric Transport to the U.S.”**

**NSF  
Atmospheric Science – Atmospheric Chemistry**

**Intellectual Merit:** China is currently the largest coal consumer in the world, surpassing the U.S., the European Union, and Japan combined at 1660 million tons per year as of 2003. China is also very likely the largest emitter of particulate matter (PM)-bound polycyclic aromatic hydrocarbons (PAHs) in the world. While U.S. emissions of seven of the most carcinogenic PM-bound PAHs decreased from 2000 tons in 1990 to 1400 tons in 1996, Chinese emissions of these same PAHs were estimated at 3460 tons in 2003. Unsubstituted PAHs have been shown to undergo trans-Pacific atmospheric transport to the U.S. West Coast. While incomplete combustion results in the formation of unsubstituted PAHs, substituted PAHs (both nitro-PAHs (NPAHs) and oxy-PAHs (OPAHs)) result from both direct emission during incomplete combustion and reactions of unsubstituted PAHs with photochemical reactants during the daytime (OH, O<sub>3</sub>, and NO<sub>2</sub>) and reactions with NO<sub>3</sub> radicals at night. Ozone, peroxyacetyl nitrate (PAN) and NO<sub>x</sub> have been shown to undergo trans-Pacific atmospheric transport to the U.S. West Coast and it is likely that PAHs react with O<sub>3</sub>, OH, and NO<sub>x</sub> during trans-Pacific transport to form NPAH and OPAH. Because many NPAH and OPAH have a greater mutagenic potential than the parent PAH, Asian PM intercepted on the U.S. West Coast may have a greater mutagenic potential than regional U.S. PM.

The primary objective of the research is to understand the effect of photochemical aging on the PAH composition of Asian PM during trans-Pacific atmospheric transport to the U.S. West Coast in both the field and laboratory. We hypothesize that NPAH and OPAHs are formed on Asian PM during trans-Pacific atmospheric transport. The specific goals of this research include 1) measurement of the PAH, NPAH, AND OPAH composition of size fractionated PM collected from Asia and the Pacific Northwestern U.S. and 2) use of aerosol reactors to study the photochemical aging of size-fractionated Asian PM in the laboratory.

Size fractionated PM will be collected concurrently from Hedo Station Observatory (HSO) on Okinawa, Japan and Mt. Bachelor Observatory (MBO) in Oregon from March-May 2009. The air masses sampled at HSO are representative of outflow from Asia, while the air masses sampled at MBO are representative of trans-Pacific and regional Western U.S. air masses. The PAH, NPAH, and OPAH composition of the PM will be determined and linked back to source regions using air mass trajectory calculations and satellite images. A portion of the filters, containing Asian PM, will undergo testing in aerosol reactors with OH, NO<sub>2</sub>, O<sub>3</sub>, and NO<sub>3</sub>. The PAH, NPAH, and OPAH composition of the PM will be compared before and after reactor aging to understand PAH aging in transit to the U.S. West Coast under controlled laboratory conditions. Laboratory results will be compared to the field measurements of PAH aging prior to (Okinawa) and post (Mt. Bachelor) trans-Pacific atmospheric transport to the U.S. to determine the relative importance of various oxidants on the aging of PAH on Asian PM.

**Broader Impacts:** The proposed activity includes training a post-doctoral fellow and continued inclusion of a faculty member, and her undergraduate students, from Central Oregon Community College (COCC) in the research conducted at MBO. COCC undergraduate students enrolled in chemistry courses will use the datasets, population density maps, satellite images, air mass back trajectories, and atmospheric half-lives of the various PAH to draw conclusions about U.S. source regions to MBO and central Oregon. The students will also learn to conduct statistical manipulations of a large research dataset, as well as understand the process of identifying and quantifying PAHs using mass spectrometry. Finally, the results of the research have significant global environmental policy implications with regard to combustion emission controls in Asia.

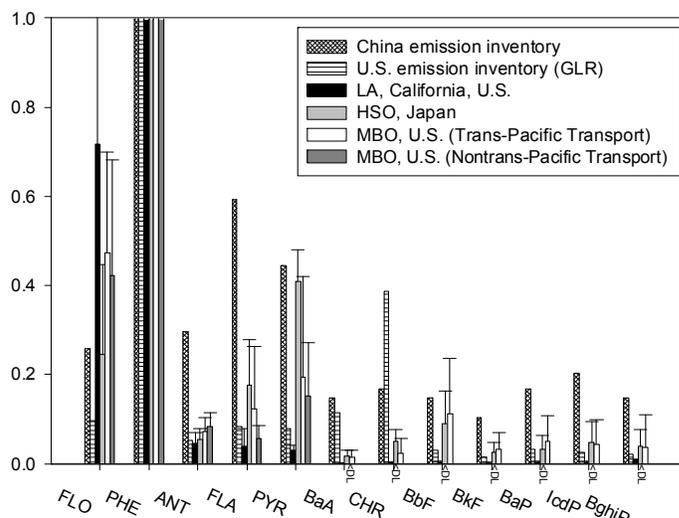
## INTRODUCTION

Asian dust events, transported across the Pacific Ocean to the Western U.S. in as little as 5-6 days, have been shown to increase PM<sub>10</sub> concentrations as far as the U.S. East Coast [1]. Many air pollutants, including mercury and semi-volatile organic compounds (SOCs) such as polycyclic aromatic hydrocarbons (PAHs) and pesticides, undergo trans-Pacific atmospheric transport to the U.S. West Coast [1-6].

China is currently the largest coal consumer in the world, surpassing the U.S., the European Union, and Japan combined at 1660 million tons per year as of 2003 [7]. China is also very likely the largest emitter of mutagenic, particulate matter (PM)-bound PAHs in the world. Combustion of coal makes up 70% of China's energy and more than 80% of the coal in China is burned without any pollution controls for residential heating in the winter months [8]. China is also among the largest petroleum users in the world, at 287 million tons as of 2003 [7], and is currently the second largest automobile market in the world. In 2003, two million cars were sold in China, an 80% increase over 2002. In addition, biomass burning is commonly practiced for agriculture [9]. These combustion emissions have resulted in PM-bound total PAH concentrations in Chinese cities that are 1-3 orders of magnitude higher than those in Los Angeles, particularly in the winter months [8]. A sediment core collected in 2003 from the East China Sea (400 km downwind of mainland China) and dated back to 1800, suggests that the outflow of PM-bound PAHs from China has increased exponentially since 1978 [10].

Emission of PAHs from major sources in China, including biofuel burning, domestic and industrial coal combustion, petroleum used in transportation and non-transportation sectors, coking and aluminum industries, and wildfires of forest and grassland, was estimated at 25,300 tons in 2003 [7,11]. The Chinese emission inventory showed a high proportion of high molecular weight PM-bound PAHs due to large contributions from domestic coal and the coking industry as compared to the U.S. emission inventory [7] (**Figure 1**). While U.S. emissions of seven of the most carcinogenic, PM-bound PAHs (benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, and dibenz[a,h]anthracene) decreased from 2000 tons in 1990 to 1400 tons in 1996, Chinese emissions of these same PAHs were estimated at 3460 tons as of 2003 [7]. In addition, 68-85% of the PM-bound PAHs measured in Beijing had an aerodynamic diameter  $\leq 2.0$   $\mu\text{m}$ , making them respirable [12].

The outflow of PAHs from Guangdong, China, a major region of PAH emission in China, was recently studied [13]. Forward air mass trajectories, using NOAA's HYSPLIT trajectory model, and a detailed PAH emission inventory for Guangdong were used to simulate the emission and outflow of PAHs from Guangdong (**Figure 2**) [13].



**Figure 1.** PAH profile (normalized to PHE) from the Chinese emission inventory, U.S. emission inventory [11], measured in Los Angeles, CA, measured in Okinawa, Japan (HSO) in air masses from China [14], and measured at Mt. Bachelor Observatory (MBO) in trans-Pacific air masses and regional air masses [5]. PAHs are listed by decreasing vapor pressure and increasing partitioning to particulate matter (left to right on the x-axis); where FLO is fluorene, PHE is phenanthrene, ANT is anthracene, FLA is fluoranthene, PYR is pyrene, RET is retene, BaA is benz[a]anthracene, CHR is chrysene, BbF is benzo[b]fluoranthene, BkF is benzo[k]fluoranthene, BaP is benzo[a]pyrene, IcdP is indeno[1,2,3-cd]pyrene, and BghiP is benzo[ghi]perylene.

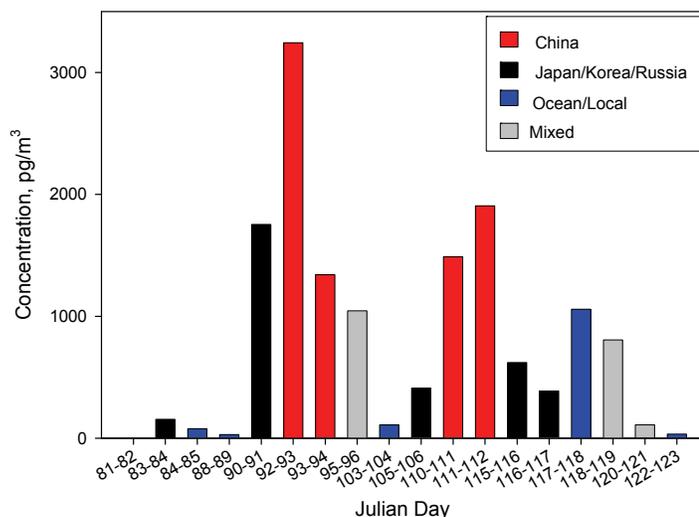
Although the major areas under influence of PAHs from Guangdong were Southeast and South Asia, a portion of the PAHs undergo long-range atmospheric transport under the influence of Westerly winds [13]. For example, on January 22 and 23, 2001, it was observed that a major atmospheric pathway of PAHs from Guangdong traveled as a narrow plume, at a height of several thousand meters in the atmosphere, and reached the middle of the Pacific Ocean (the boundary of the model) (**Figure 2**) [13]. These results suggest that the significant PM-bound PAH emissions from China result in considerable outflow to other Asian countries, including Japan and Korea.



**Figure 2.** Atmospheric transport of pyrene on January 22 (left) and 23 (right), 2001, indicating long-range transport from Guangdong, China to the middle of the Pacific Ocean [13].

In spring 2004, Dr. AAAA's laboratory participated in a sampling campaign on the island of Okinawa, Japan at Hedo Station Observatory (HSO) in order to study the outflow of PAHs from East Asia [14]. Elevated concentrations of PM-bound PAHs were measured in air masses from China as compared to air masses from Japan, Korea, Russia, and the Pacific Ocean (**Figure 3**) [14]. Recently, other researchers have confirmed the strong outflow of PAHs from China [10,15-22].

In addition, PM-bound PAH concentrations measured on Okinawa were significantly correlated ( $p < 0.05$ ) with other incomplete combustion byproduct concentrations, including elemental mercury, black carbon (BC), submicron aerosol, carbon monoxide (CO), nitrogen oxides, and sulfur dioxide concentrations. The significant positive correlation between PM-bound PAHs and elemental mercury, black carbon, and  $SO_2$  concentrations suggests that coal combustion in China is a major source of PM-bound PAHs [14].

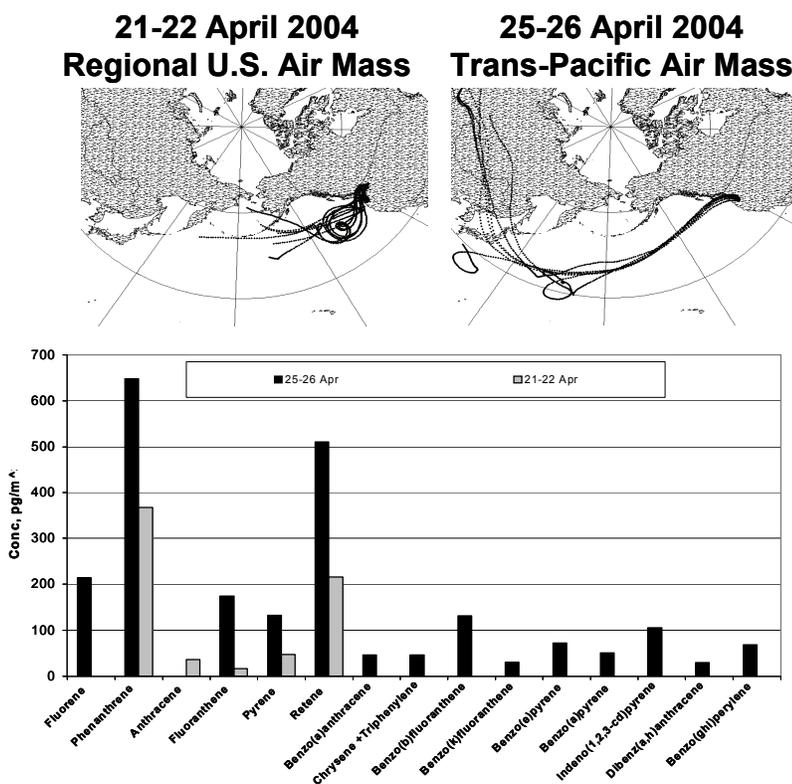


**Figure 3.** PM-bound total PAH concentrations measured on Okinawa, Japan in spring 2004 when the source region of the sampled air mass was identified as China, Japan/Korea/Russia, Ocean/Local and Mixed [14].

PAH, CO, and BC measurements on Okinawa were used to estimate the Chinese emission of six carcinogenic PM-bound PAHs (benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, and indeno[1,2,3-cd]pyrene) at 778-1728 metric tons/year [14]. This PAH emission estimate is likely significantly underestimated because the PM samples were collected in spring and do not reflect winter periods of high PAH emissions.

Enhanced concentrations of unsubstituted PAHs in trans-Pacific (Asian) air masses, as compared to regional U.S. air masses exist, arriving to the U.S. West Coast [2]. These first observations were made in the spring of 2002 as part of the ITCT 2K2 campaign at Cheeka Peak Observatory (CPO) on the Olympic Peninsula of Washington [2]. Trans-Pacific air masses resulted in up to a 400% increase in PAH concentrations at the site as compared to regional air masses [2].

In a recently published study on trans-Pacific atmospheric transport to Mt. Bachelor Observatory (MBO), in Oregon's Cascade range from 2004-2006 (including the INTEX-B campaign), several laboratories identified enhanced concentrations of PM-bound unsubstituted PAHs in trans-Pacific air masses as compared to regional U.S. air masses (**Figures 1 and 4**) [5]. Regional U.S. air masses intercepted at MBO typically have PM-bound PAH concentrations that are below the analytical detection limit (**Figures 1 and 4**) [5]. Others have also shown that concentrations of PM-bound unsubstituted PAHs at MBO increase with the percentage of air mass time in Asia, providing strong evidence that PM-bound PAHs are emitted in Asia and undergo trans-Pacific atmospheric transport to the U.S. [5]. The total PAH concentration measured by the PI's laboratory in spring 2004 at MBO during trans-Pacific atmospheric transport events ( $1.5 \text{ ng/m}^3$ ) [5] was only slightly less than the total PAH concentration measured during this same time period on Okinawa, Japan ( $5.9 \text{ ng/m}^3$ ) [14]. The total PAH concentrations measured at MBO and HSO are comparable to those measured in major U.S. cities, but with a higher proportion of PM-bound PAHs (**Figure 1**).



**Figure 4.** Ten day air mass back trajectories for the 24 hour ambient air samples collected at Mt. Bachelor, Oregon on 21-22 April 2004 and 25-26 April 2004 and the corresponding PAH concentrations measured in these air samples. The back trajectories were calculated using HYSPLIT and imported into ARC/GIS. The PM-bound PAH concentrations were below the analytical detection limit for 21-22 April 2004 (the regional U.S. air mass) [5].

In a manuscript recently submitted for publication in the journal *Environmental Science and Technology*, increased PAH concentrations in trans-Pacific air masses in the summer of 2003 at CPO and Marys Peak Observatory (MPO), located in Oregon's

Coast Range were identified, as a result of significant forest fire emissions in Siberia. These results indicate that large scale forest fires in Asia and Siberia, expected to increase in frequency and size with global warming, also result in the trans-Pacific atmospheric transport of high PAH concentrations to the U.S. Given the likelihood of increased forest fires and increased combustion of fossil fuels in Asia in the future, we expect the trans-Pacific atmospheric transport of PAHs to the U.S. to increase over time.

While incomplete combustion results in the formation of PM-bound unsubstituted PAHs, substituted PAHs (both nitro-PAHs (NPAHs) and oxy-PAHs (OPAHs)) result from both direct emission during incomplete combustion and reactions of unsubstituted PAHs with photochemical reactants during the daytime (OH, O<sub>3</sub>, and NO<sub>2</sub>) and reactions with NO<sub>3</sub> radicals at night [23-37]. For example, 1-nitropyrene and 3-nitrofluoranthene are the most abundant NPAHs measured in diesel exhaust, while 2-nitropyrene and 2-nitrofluoranthene are a result of gas-phase reactions of the unsubstituted PAHs with OH, NO<sub>2</sub>, and NO<sub>3</sub> [23,38,39]. Measurement of these different NPAH isomers gives an indication of whether the NPAHs were formed at the combustion source or by atmospheric reactions in transit to the receptor site. Ozone, peroxyacetyl nitrate (PAN) and NO<sub>x</sub> have been shown to undergo trans-Pacific atmospheric transport to the U.S. West Coast, and it is likely that unsubstituted PAHs react with O<sub>3</sub>, OH, and NO<sub>x</sub> during trans-Pacific transport to form NPAH and OPAH [4,40-46]. In addition direct emissions of NPAHs have been measured in diesel exhaust and in PM from residential coal stoves in Shenyang, China [47].

Unsubstituted PAHs become carcinogenic when they are metabolized and bind to DNA. NPAHs are more mutagenic than the corresponding parent PAH because the nitro groups have a profoundly increased DNA binding ability compared to the parent PAHs [48]. As a result, there is overwhelming evidence that NPAH are probable human carcinogens [49]. In addition, certain NPAH show relatively high direct-acting mutagenicity contributing to a significant portion of the direct-acting mutagenic response found in PM extracts [47,50,51]. OPAHs undergo potent cellular enzymatic and nonenzymatic redox cycling, producing oxidative damage to various biomolecules, including DNA [52] and are a major fraction of the PAHs present in PM [53]. PAH, NPAH and OPAH exist primarily in the 2.5 μm or smaller diameter fraction [53,54]. This small PM size allows PM-bound PAHs to penetrate into the lower respiratory tract efficiently, placing them into the gas-exchanging alveoli [55]. PAH, NPAH and OPAH on fine PM have been responsible for the mutagenic activity in bacterial assays [56] and DNA damage to cultured human cells [57]. **As a result of photochemical aging of PAH to NPAH and OPAH during trans-Pacific transport, Asian PM intercepted on the U.S. West Coast may have a greater mutagenic potential than regional U.S. PM.**

Because OPAH and NPAH have lower vapor pressures than the analogous unsubstituted PAHs, they exist primarily in the atmosphere on PM. While gas-phase PAHs have atmospheric lifetimes on the order of hours due to rapid reaction with OH radicals, the degradation of PM-bound PAHs and NPAHs is highly dependent on the

nature of the PM they are bound to. Organic rich PM acts to increase atmospheric lifetimes of PM-bound PAH and NPAH [24,29]. In addition, PM-bound PAHs and NPAHs have been measured in the most remote regions of the world, far from combustion sources, indicating that these PAHs and NPAHs have atmospheric lifetimes long enough to undergo atmospheric long-range transport, including trans-Pacific transport [51,58-61].

Finally, a large dataset has been generated from the research conducted at MBO [5,6,62]. Dr. BBBB and undergraduate students attending the local Central Oregon Community College (COCC) previously assisted in the sample collection at MBO [5,6,62]. This existing MBO dataset, and the new data generated under the proposed research, will be used by Dr. BBBB and her Department of Chemistry colleagues at COCC in a variety of science courses; including General Chemistry, Organic Chemistry, and Physical Sciences (see Dr. BBBB letter of collaboration). The COCC undergraduate students enrolled in these courses will use population density maps, air mass back trajectories, and atmospheric half-lives of the various PAH listed in the MBO dataset to draw conclusions about probable U.S. source regions to MBO and central Oregon. The COCC undergraduate students will also learn to conduct statistical manipulations of a large research dataset, as well as understand the process of identifying and quantifying PAHs using mass spectrometry.

### **OBJECTIVES AND GOALS**

The primary objective of the research is to understand the effect of photochemical aging on the PAH composition of Asian PM during trans-Pacific atmospheric transport to the U.S. West Coast in both the field and laboratory. Our hypothesis is that nitro and oxy-PAHs are formed on Asian PM during trans-Pacific atmospheric transport. The specific goals of this research include 1) measurement of the PAH, NPAH, and OPAH composition of size fractionated PM collected from Asia and the Pacific Northwestern U.S. and 2) use of aerosol reactors to study the photochemical aging of size-fractionated Asian PM in the laboratory.

### **INTELLECTUAL MERIT, BROADER IMPACTS, AND SIGNIFICANCE**

The proposed research is significant, and of intellectual merit, in that it will result in an understanding of PAH atmospheric chemistry during trans-Pacific transport to the U.S. In addition, the proposed research is focused on a class of incomplete combustion byproducts (PAHs), and their photochemical transformation products (NPAH and OPAH), that have significant relevance for human health. In addition, Asian emissions of PAHs are expected to continue to increase.

The broader impacts of the proposed research include the continued participation of Dr. BBBB and undergraduate students at the local community college (COCC) in the research conducted at MBO in addition to the use of the existing and new MBO datasets by COCC undergraduate students enrolled in chemistry courses. Use of a real-world research dataset by undergraduate students attending a community college, generated at a local research station, and our continued collaboration with Dr. BBBB and her undergraduate students in the proposed research, represents a unique

opportunity for furthering the PI's outreach and broader impact efforts beyond her initial CAREER award.

The proposed research continues to link the PI's laboratory and Oregon State University to the global atmospheric chemistry community studying trans-Pacific transport, including atmospheric scientists in Japan, France, and the University of Washington. The proposed research represents the next phase in the long-term goals of the PI's laboratory by expanding her laboratory's capabilities in the field of atmospheric chemistry and continuing to develop international collaborations in the field of atmospheric chemistry. Finally, the results of the research have significant global environmental policy implications with regard to combustion emission controls in Asia.

## **RESEARCH PLAN**

**Research Sites and PM Sampling Methodology.** Hedo Station Observatory (HSO) on Okinawa, Japan will be used as a research site for the collection of size fractionated Asian PM because it is a remote site that is downwind of Asian sources [3,14,16,63-65]. Thus, the air masses sampled at HSO are representative of outflow from Asia [3,14,16,63-65]. Previous research at the site in Spring 2004 showed increased PM-bound PAH concentrations when the air mass source region was identified as China (**Figure 3**) [14]. The location of HSO (~800 km east of the coast of China with an air mass transport time from China, the Koreas, and Japan to the site of ~24-48 hours), the ability to identify different Asian source regions for specific air masses sampled at the site [14], and the PI's previous collaboration with the Japanese scientists that operate this site make HSO an excellent location to study the outflow of PAH, NPAH and OPAH from East Asia. Sampling of size fractionated PM in Asian air masses at HSO will be conducted by the PI's laboratory from March through May xxxx in conjunction with other atmospheric measurements conducted by our Japanese collaborators (see Dr. CCCC letter of collaboration). In our previous research at HSO, the use of additional concurrent atmospheric measurements aided in the interpretation of the PAH data [14].

Mt. Bachelor Observatory (MBO), which is located in the free troposphere in Oregon's Cascade Range at 2700 m, will be used as a research site for the collection of size fractionated PM that has undergone trans-Pacific atmospheric transport and size fractionated PM in regional U.S. air masses. MBO has been used by laboratory and Prof. DDDD's laboratory since xxxx and the air masses sampled at MBO appear to be representative of trans-Pacific and regional Western U.S. air masses [4,5,40,62,66,67]. The PI's laboratory has measured enhanced PM-bound unsubstituted PAH concentrations in trans-Pacific air masses compared to regional air masses at this site [5]. In concurrent sampling, the DDDD research group has measured enhanced total gaseous mercury, carbon monoxide, and ozone concentrations in trans-Pacific air masses at MBO [4]. Both research groups utilize meteorological data, air mass back trajectories, satellite images, along with chemical measurements, to identify trans-Pacific air masses at MBO. Sampling of size fractionated PM in trans-Pacific and regional U.S. air masses will be conducted by the PI's laboratory at MBO from March through May xxxx, overlapping in time with the collection of PM at HSO. Satellite

images will be used to identify time periods of strong trans-Pacific transport of PM and the temporal resolution of the sample collection will be increased during these time periods (12 to 24 hour sampling periods). The PI's sampling at MBO will be done in conjunction with atmospheric measurements by the DDDD research group, including CO, O<sub>3</sub>, PAN, aerosol scattering, and speciated Hg measurements (see Dr. DDDD letter of collaboration). Our data interpretation at MBO has been significantly strengthened by the use of additional concurrent atmospheric measurements [5,6].

Size fractionated PM will be collected at HSO and MBO in Year 1 (March-May xxxx) using high volume air samplers (Tisch Environmental) retrofitted with a High Volume Cascade Impactor (HVCI) TE-230 (Tisch Environmental) at both HSO and MBO. This impactor has been specifically designed for collection of large amounts of PM which results in improved detection limits and has been previously used for the collection of PAH, NPAH and OPAH sorbed to PM [23,38,60,61,68-73]. The HVCI contains a series of slotted impactors for sharp PM size fractionation and collection of PM of the following size fractions: 10-4 µm, 4-2 µm, 2-1 µm and an ultra fine fraction of less than 1 µm. The PM aerodynamic size dictates the PM collection by size, shape, and mass density of the particles, which is similar to the process of particle respiration in the human lung. The collection media for the PM fractions consists of a series of quartz fiber filters located below each impactor stage. The methods for cleaning filters prior to use have been established [5,6,14]. All PM samples will be protected from sunlight and stored frozen (-30° C) until analysis or testing in the photochemical reactor.

**Selection and Measurement of PAH, NPAH, AND OPAH.** A wide array of PAHs, NPAHs, and OPAHs will be measured in the size fractionated PM samples in Years 1-3 (**Table 1**). The Cascade Impactor filters, containing Asian PM collected from HSO and MBO, will be cut in half, with one half undergoing chemical analysis and the other half undergoing testing in the photochemical reactor. PAHs, NPAHs and OPAHs, will be extracted from the filters using pressurized liquid extraction (PLE) with hexane, acetone, and dichloromethane [5,6,14,62,74-76]. The filters will be spiked with deuterium-labeled PAH and NPAH surrogates prior to extraction and will be used for recovery and quantitation in the instrumental method. The extract will be further fractionated using an aminopropyl solid phase extraction cartridge and normal-phase LC using a semi-preparative amino/cyano column or alumina and silica solid phase extraction columns to isolate the PAH, NPAH, and OPAH fractions [39,71,74]. Extract fractionation is a necessary step in order to reduce matrix interferences [39,74]. The resulting extract fractions will be concentrated using a Zymark Turbovap with N<sub>2</sub> gas prior to analysis. Gas chromatography with high resolution mass spectrometry (GC/HRMS), using the PI's JEOL GC Mate II high resolution mass spectrometer equipped with a magnetic sector mass detector and both negative chemical ionization and electron impact ionization modes, will be used to measure PAH, NPAH, and OPAH [2,5,14,39,60,61,69,71,74]. Parent PAHs (**Table 1**) will be separated using a 5% phenyl-substituted methylpolysiloxane (DB-5) J&W Scientific GC column (0.25 i.d. x 60m) [2,14]. Structural isomer pairs of 20 NPAH and 10 OPAH (**Table 1**) will be analyzed using a 50% phenyl-substituted methylpolysiloxane J&W Scientific GC column (0.25 i.d. x 30m) or a DB-5 J&W Scientific GC column (0.25 i.d. x 60m) [39,71]. If needed, a

large volume temperature programmed vaporization injector will be used to improve instrument sensitivity [71]. We will use stable isotope PAH, NPAH, and OPAH analogs for quantitation. The chemical structures of unknown peaks in the chromatograms will be identified using high resolution mass spectrometry and the structures of possible NPAH and OPAH confirmed using standards. Method validation will take place during Year 1.

**Table 1.** PAH, NPAH, and OPAH to be studied.

PAHs	NPAHs	OPAHs
Fluorene	Nitronaphthalenes	fluorenone
Anthracene	Nitrobiphenyls	phenalenone
Phenanthrene	Nitroacenaphthenes	4H-cyclopenta[def] phenanthren-4-one
Fluoranthene	Nitrofluorenes	11H-benzo[a]fluoren-11-one
Pyrene	Nitroanthracenes	7Hbenzo[c]fluoren-7-one
Retene	Nitrophenanthrenes	11H-benzo[b]fluoren-11-one
Benz(a)anthracene	Nitrofluoranthenes	7H-benz[de]anthracen-7-one
Chrysene/Triphenylene	Nitropyrenes	Cyclopenta[cd]pyren-3(4H)-one
Benzo(b)flouranthene	Nitrobenz[a]anthracenes	6H-benzo[cd]pyren-6-one
Benzo(k)flouranthene	Nitrochrysenes	7H-dibez[dej] anthracen-7-one
Benzo(e)pyrene	Nitrobenzo[e]pyrenes	anthracenequinone
Benzo(a)pyrene	Nitrobenzo[a]pyrenes	phenanthrenequinone
Indeno(1,2,3-cd)pyrene		7,12-benz[a]anthracene quinone
Dibenz(a,h)anthracene		5,12-naphthracene quinone
Benzo(ghi)perylene		1,4-chrysenequinone
Benzo(c)phenanthrene		

**Field Data Analysis and Interpretation.** NOAA's ARL hybrid single-particle Lagrangian integrated trajectory (HYSPLIT) 4.0 model will be used to calculate four-day forward and back trajectories for air masses sampled at HSO on Okinawa [14] and ten-day forward and back trajectories will be calculated for air masses sampled at MBO [5,6,62]. Using the HSO and MBO trajectories, Source Region Impact Factors (SRIFs) will be calculated to determine the percentage of the time the sampled air mass spent over different source regions and, in the case of MBO, above and below the boundary layer [5,6,14]. Finally, ARC-GIS will be used to graphically display the calculated trajectories and layer the trajectories over maps and satellite images showing population density, fire starts, and aerosol optical depth to aid in data analysis and interpretation. Meteorological data and the concentrations of CO, O<sub>3</sub>, PAN, aerosol scattering, and speciated Hg, measured simultaneously at HSO and MBO, will be used to aid in the interpretation of the PAH, NPAH, and OPAH data with respect to sources [5,14].

**Laboratory Photochemical Aging of PAHs on Asian PM.** Dr. FFFF's aerosol reactors at Universite de Bordeaux will be used in Years 2 and 3 to study the photochemical aging of PAHs bound to Asian PM collected at HSO in Year 1 (see Dr. FFFF's letter of collaboration). The reactor designs have been previously used to study the reactions of PAHs (including phenanthrene, anthracene, fluoranthene, pyrene,

chrysene, benz[a]anthracene, benzo[k]fluoranthene, benzo[e]pyrene, benzo[a]pyrene, perylene, and benzo[ghi]perylene) bound to graphite and silica particles, as well as diesel particulate exhaust (NIST SRM 1650a), with NO<sub>2</sub>, NO, O<sub>3</sub> and OH [24-26,29]. The PI has experience studying the gas-phase reactions of PAHs and other semi-volatile organic compounds in laboratory reactors. However, to date, she does not have experience studying the photochemical reactions of PAHs on particles and her laboratory does not yet have this capability. By collaborating with Dr. FFFF at Universite de Bordeaux on the use of the aerosol reactors to study the photochemical aging of PAHs on Asian PM she will develop this expertise and bring the capability back to her laboratory at Oregon State University. The PI and post-doctoral fellow will travel to Dr. FFFF's laboratory for month-long experiments several times during Years 2 and 3. Dr. FFFF will travel to the PI's laboratory at Oregon State University for a month-long visit during Year 2.

There are two different aerosol reactors at the Universite de Bordeaux. The first one consists in a quasi-static reactor used for ozonation reactions; experiments may be performed at room temperature and atmospheric pressure. The photolysis cell consists in a 60 cm long quartz tube exposed to a low-pressure mercury lamp irradiation, causing oxygen photolysis and hence formation of ozone. The reaction cell is a 10 cm long glass tube where particles deposited on a filter are introduced.

The second experimental set-up consists of a movable injector (1 cm inside diameter x 60 cm long quartz tube) sliding in a main reactor (3 cm inner diameter x 48 cm long quartz tube) [24-26,28,29,78,79]. Experiments may be conducted at room temperature ( $295 \pm 1^\circ$  K) and low pressure ( $2.4 \pm 0.3$  mbar). Various oxidant species (such as OH and NO<sub>2</sub>) will be introduced in the main reactor through the movable injector, using He as the carrier gas. Experiments will also be conducted in the absence of all oxidant species in order to evaluate the loss of PAHs by desorption from the particles. A microwave discharge will be used to generate H atoms that will react with NO<sub>2</sub> to form OH and NO.

The Cascade Impactor filters, containing Asian PM, will be cut in half, with one half undergoing chemical analysis and the other half being placed inside the reactors and exposed to the carrier gas containing the oxidizing species. Triplicate experiments will be conducted under He flow only to evaluate desorption of PAHs from the PM under the experimental conditions. Triplicate experiments will also be conducted using He/NO<sub>2</sub> to study the NO<sub>2</sub>-PAH reactions on PM. Finally, triplicate experiments will be conducted under He/NO/NO<sub>2</sub>/OH flow conditions to study the kinetics and products of the OH-PAH reactions on PM [24,29,78].

The filters will be placed inside the aerosol reactor and exposed to the He containing oxidizing species. Reaction times will be on the order of 120 to 1800 s, depending on the observed reaction rates [24,29,78]. At the end of the reaction, the glass fiber filter will be removed, extracted, and fractionated for PAH, NPAH, and OPAH analysis, including derivatization and analysis by GC/MS and/or LC/MS/MS [25]. The filter will be weighed before and after reaction to ensure that PM mass was not lost during the

experiment. All PM samples will be protected from sunlight and stored at -30° C until testing.

The Asian PM PAH, NPAH, and OPAH composition will be compared before and after reactor aging in order to understand photochemical aging in transit to the U.S. West Coast under controlled laboratory conditions. These laboratory results will be compared to the field measurements of PM-bound PAH aging prior to (Okinawa) and post (Mt. Bachelor) trans-Pacific atmospheric transport to the U.S. The field and laboratory studies, along with the associated reaction kinetics determined in the laboratory studies, will be used to determine the relative importance of various oxidants on the aging of PAH on Asian PM. Together with satellite images, these data will be used to understand the importance of photochemical aging of Asian PM in transit to the U.S. under different meteorological conditions. These *in situ* and laboratory experiments will test the hypothesis that NPAH and OPAH are formed on Asian PM in transit to the U.S. West Coast due to photochemical aging. Finally, the change in PAH, NPAH, and OPAH composition of the Asian PM will be used to estimate the relative change in PM mutagenicity.

**Personnel.** In addition to the PI, the proposed research will be used to train a post-doctoral fellow in the PI's laboratory over the 3 year period, as well as continued inclusion of Dr. BBBB and several of her undergraduate students at COCC in the research at MBO. Because the PI is currently mentoring five graduate students who already have assigned research topics and the proposed research requires significant periods of international travel starting in spring 2009 to Okinawa, Japan (in Year 1) and France in 2010 and 2011 (in Years 2 and 3), a post-doctoral fellow is more appropriate for the proposed research than a new graduate student engaged in significant coursework.

**Communication of Results.** A number of publications and presentations will result from this research over a period of three years, some of these include:

- Outflow of PAH, NPAH, and OPAH from Asia
- Trans-Pacific Atmospheric Transport of PAH, NPAH, and OPAH to the U.S. West Coast
- Efficiency of Trans-Pacific Atmospheric Transport of PAH, NPAH, and OPAH on Size Fractionated Particulate Matter
- Evidence of Photochemical Aging of PAH During Trans-Pacific Transport
- Laboratory Studies of the Photochemical Aging of PAHs on Asian Particulate Matter

Publications are likely to be submitted to *Environmental Science and Technology*, *Geophysical Research Letters*, *Journal of Geophysical Research*, *Atmospheric Environment*, and/or *Analytical Chemistry*. Presentations will be made at national and international conferences and may include American Geophysical Union, American Chemical Society, and Society for Environmental Toxicology and Chemistry.

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