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PAH Intermediates: Links between the Atmosphere and Biological Systems

STACI L. MASSEY SIMONICH^{1,2,*}, OLEKSII MOTORYKIN², and NARUMOL JARIYASOPIT^{2,*}

¹Environmental and Molecular Toxicology, Oregon State University, Corvallis, Oregon, USA, 97331

²Department of Chemistry, Oregon State University, Corvallis, Oregon USA 97331

Abstract

China is now the world's largest emitter of polycyclic aromatic hydrocarbons (PAHs). In addition, PAHs, and their reactive intermediates, undergo trans-Pacific atmospheric transport to the Western U.S. The objectives of our research are to predict, identify and quantify novel PAH intermediates in the atmosphere and biological systems, using computational methods, as well as laboratory and field experiments. Gaussian is used to predict the thermodynamic properties of parent structure PAHs, as well as the associated nitro-, oxy-, and hydroxy- PAH intermediates. Based on these predictions, state-of-the-art analytical chemistry techniques are used to identify and quantify these potential intermediates on Asian particulate matter before and after reaction in a continuous flow photochemical reactor. These same techniques are used to identify the relative proportion of PAH intermediates in PAH source regions (such as Beijing, China) and during long-range atmospheric transport to the Western U.S. PAH personal exposure studies in China and the Confederated Tribes of the Umatilla Indian Reservation in Oregon will be used to assess the similarities and differences in the PAH intermediates in biological systems relative to the atmosphere.

Keywords

PAH; photochemical transformation; metabolic transformation; intermediate

1. Introduction

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 in 2003 [1], and very likely the largest emitter of mutagenic, particulate matter (PM) bound polycyclic aromatic hydrocarbons (PAHs) in the world. Combustion of coal makes up 70% of China's energy. More than 80% of the coal in China is burned with minimal pollution controls for residential heating in the winter months [2]. China is also among the largest petroleum users in the world, at 287 million tons in 2003 [1] 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 [3]. These combustion emissions have resulted in PM-bound total PAH concentrations in Chinese cities that are 1-3

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

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orders of magnitude higher than those in Los Angeles, particularly in the winter months [2]. 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 [4].

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 PM₁₀ concentrations as far as the U.S. East Coast [5]. Parent PAHs, and their reactive intermediates, have also been observed to undergo trans-Pacific atmospheric transport to the U.S. West Coast [6-8].

Incomplete combustion of any organic fuel (coal, diesel, gasoline, and biomass) can result in the formation of PM-bound parent PAHs such as benzo[a]pyrene (BaP). However, reactive intermediates, including nitro- (NPAH), oxy- (OPAH), and hydroxy- PAH (OH PAH), can result from both direct emission during incomplete combustion and atmospheric gas-phase reactions of parent PAHs with reactants during the daytime (OH radical, O₃, and NO₂) and reactions with NO₃ radicals at night [9]. OPAH and NPAH have lower vapor pressures than the analogous parent PAHs and primarily exist in the atmosphere on PM.

The objectives of our current study are to predict, identify and quantify novel PAH intermediates in the atmosphere and biological systems, using computational methods, as well as laboratory and field experiments.

2. Materials and Methods

2.1 Computational Methods

The thermodynamic properties of parent PAH, NPAH, OPAH, and OH PAH in the ideal gas phase are being calculated using Gaussian 03 on the B3LYP/6-31G(d)//B3LYP/6-31G(d) level using methods we previously developed for polybrominated diphenyl ethers [10].

2.2 Laboratory Experiments

An aerosol flow reactor that consists of a movable injector (1 cm inside diameter × 60 cm long quartz tube) sliding in a main reactor (3 cm inner diameter × 48 cm long quartz tube) is being used to study the intermediates formed in the photochemistry of PM-bound PAHs [11-14]. Experiments are conducted at room temperature ($293 \pm 5^\circ \text{K}$) and atmospheric pressure ($1013 \pm 0.3 \text{ mbar}$). Various oxidant species (such as OH radical, NO₂, O₃, and NO₃) are introduced in the main reactor through the movable injector, using He as the carrier gas. Experiments are also conducted in the absence of all oxidant species in order to evaluate the loss of PAHs by sorption to the reactor walls.

2.3 Personal Exposure Studies

The PM bound PAH composition and exposure to non-smoking Chinese and American Indian men and women is being measured. Chinese study participants, nonsmoking men, women, and children (ages 18-21) living in Tianjin, have been recruited. Three categories of non-smoking indoor environments in the Beijing-Tianjin metropolitan area are being studied, including 1) apartments with natural gas for cooking and centralized heating in urban districts, 2) traditional residences using a coal stove for cooking and heating in the suburban areas, and 3) farm houses using coal and biofuel for cooking and heating. The personal exposure of American Indian men and women to PAHs is also being studied during traditional food smoking activities using similar personal exposure methods.

2.4 Field Studies

A series of monitoring sites from Beijing, China to Okinawa, Japan to the Confederated Tribes of the Umatilla Indian Reservations (CTUIR) and Mt. Bachelor, Oregon is being used to track the atmospheric aging of PAH from Asia to the U.S. (Figure 1) using methods we have previously developed for ambient air monitoring [6-8,15].

3.0 Results and Discussion

Figure 2 shows the potential sources of some PAH reactive intermediates, including direct combustion, photochemistry, and diet. Direct sources to the atmosphere include combustion of fossil fuels, while direct sources to humans include inhalation of combustion emissions and consumption in the diet. There is significant overlap in the types of PAH reactive intermediates produced from these sources. Ultimately, hydroxylated PAHs can result from both the photochemistry and metabolic transformation of these reactive intermediates.

Conceptually, the photochemical and metabolic pathways that result in the formation of PAH reactive intermediates are shown in Figure 3. In the atmosphere and biological systems, the parent PAH and PAH reactive intermediates circulate and partition into aqueous or solid phases based on their physico-chemical properties and route of entry [16]. Photochemical transformation in the atmosphere and metabolic transformation in biological systems result in the formation of some of the same PAH reactive intermediates, along with their associated health effects [17].

A specific example of the links between the atmosphere and biological systems is shown in Figure 4 for pyrene. 1-nitropyrene (1NP) is formed as a result of direct combustion, while 2-nitropyrene (2NP) is formed photochemically by reaction with hydroxyl radical and NO₂. These reactive intermediates result in hydroxynitropyrene when metabolized. Hydroxypyrenes can result from direct combustion, photochemical reaction with hydroxyl radical and metabolic transformation.

Ultimately, a better understanding of the photochemical and metabolic transformation of PAH reactive intermediates, through better prediction of stable structures, the development of analytical methods, and confirmation of their presence in the atmosphere and in biological systems, will aid in the identification of novel markers of PAH exposure. In turn, this will result in a better understanding of the metabolism and toxicology effects of PAHs.

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References

1. Xu S, Liu W, Tao S. Emission of Polycyclic Aromatic Hydrocarbons in China. *Environmental Science & Technology*. 2006; 40:702–708. [PubMed: 16509306]
2. Wang G, Kawamura K, Lee S, Ho K, Cao J. Molecular, Seasonal, and Spatial Distributions of Organic Aerosols from Fourteen Chinese Cities. *Environmental Science & Technology*. 2006; 40:4619–4625. [PubMed: 16913115]
3. Tao S, et al. Dispersion Modeling of Polycyclic Aromatic Hydrocarbons from Combustion of Biomass and Fossil Fuels and Production of Coke in Tianjin, China. *Environmental Science & Technology*. 2006; 40:4586–4591. [PubMed: 16913110]

4. Guo ZG, et al. High-resolution depositional records of polycyclic aromatic hydrocarbons in the central continental shelf mud of the East China Sea. *Environmental Science & Technology*. 2006; 40(17):5304–5311. [PubMed: 16999103]
5. Jaffe D, Snow J, Cooper O. The 2001 Asian dust events: Transport and Impact on surface aerosol concentrations in the U.S. EOS, Transactions, American Geophysical Union. 2003; 84:501–516.
6. Primbs T, et al. Atmospheric outflow of anthropogenic semivolatile organic compounds from East Asia in spring 2004. *Environmental Science & Technology*. 2007; 41(10):3551–3558. [PubMed: 17547177]
7. Primbs T, et al. Influence of Asian and Western United States urban areas and fires on the atmospheric transport of polycyclic aromatic hydrocarbons, polychlorinated biphenyls, and fluorotelomer alcohols in the Western United States. *Environmental Science & Technology*. 2008; 42(17):6385–6391. [PubMed: 18800505]
8. Killin RK, et al. Transpacific and regional atmospheric transport of anthropogenic semivolatile organic compounds to Cheeka Peak Observatory during the spring of 2002. *Journal of Geophysical Research-Atmospheres*. 2004; 109(D23)
9. Reisen F, Arey J. Atmospheric reactions influence seasonal PAH and Nitro-PAH concentrations in the Los Angeles Basin. *Environmental Science & Technology*. 2005; 39:64–73. [PubMed: 15667076]
10. Zeng X, et al. Development and Validation of a Congener-Specific Photodegradation Model for Polybrominated Diphenyl Ethers. *Environmental Toxicology and Chemistry*. 2008; 27(12):2427–2435. [PubMed: 18613751]
11. Esteve W, Budzinski H, Villenave E. Relative rate constants for the heterogeneous reactions of NO₂ and OH radicals with polycyclic aromatic hydrocarbons adsorbed on carbonaceous particles. Part 2: PAHs adsorbed on diesel particulate exhaust SRM 1650a. *Atmospheric Environment*. 2006; 40(2):201–211.
12. Esteve W, Budzinski H, Villenave E. Relative rate constants for the heterogeneous reactions of OH, NO₂ and NO radicals with polycyclic aromatic hydrocarbons adsorbed on carbonaceous particles. Part 1: PAHs adsorbed on 1-2 μ m calibrated graphite particles. *Atmospheric Environment*. 2004; 38(35):6063–6072.
13. Esteve W, Budzinski H, Villenave E. Heterogeneous reactivity of OH radicals with phenanthrene. *Polycyclic Aromatic Compounds*. 2003; 23(5):441–456.
14. Esteve W, Budzinski H, Villenave E. Experimental study of the reactions of OH radicals with polycyclic aromatic hydrocarbons adsorbed on graphite particles. *Abstracts of Papers of the American Chemical Society*. 2001; 221:U525–U525.
15. Primbs T, Genualdi S, Simonich SM. Solvent selection for pressurized liquid extraction of polymeric sorbents used in air sampling. *Environmental Toxicology and Chemistry*. 2008; 27(6): 1267–1272. [PubMed: 18220448]
16. Ramesh A, et al. Bioavailability and risk assessment of orally ingested polycyclic aromatic hydrocarbons. *International Journal of Toxicology*. 2004; 23(5):301–333. [PubMed: 15513831]
17. Yu HT. Environmental carcinogenic polycyclic aromatic hydrocarbons: photochemistry and phototoxicity. *Journal of Environmental Science and Health Part C-Environmental Carcinogenesis & Ecotoxicology Reviews*. 2002; 20(2):149–183.

Figure 1.
Ambient air sampling sites being used to study the formation of PAH reactive intermediates in the atmosphere.

Figure 2.
Potential sources of some PAH reactive intermediates.

Figure 3.
Links between photochemical and metabolic pathways resulting in the formation of PAH reactive intermediates. Adapted from [18].

Figure 4.
Conversion of pyrene to reactive intermediates via combustion, photochemistry, and metabolic transformation.