

# FATE OF PAHS AND THE OCEANIC MODULATION IN THE CHANGING ARCTIC

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## Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a class of semivolatile organic compounds of great concern due to their toxicity and carcinogenic effects on humans and ecosystems<sup>1,2</sup>. They have ongoing emissions from pyrogenic or petrogenic sources, and could arrive in polar regions through long-range transport through the air or ocean currents<sup>3,4</sup>. Although global emissions have been reduced, two decades of measurements of PAH in the Arctic did not show a significant decreasing trend, and future climate changes may contribute to a re-volatilization of environmental persistent organic pollutants (POPs) to increase their storage in the Arctic<sup>5,6</sup>.

Oceans are important reservoirs and sinks for most POPs, and several interface processes, such as air-sea exchange, phase partitioning and particle sinking, are especially taking place at their upper layer<sup>7,8</sup>. Oceanic processes could lead to pollutants transporting in different spatial and dimensional scales, and pose direct and indirect impacts on their source-sink patterns in the marine environments<sup>9,10</sup>. Therefore, it is still unclear about the fate of PAHs in the Arctic Ocean and their responses to the changing environments.

After entering the surface seawater by air-sea exchange, dry/wet deposition, or riverine input, PAHs are prone to be absorbed by organisms or adsorbed onto particles, mainly onto the organic matter<sup>11,12</sup>. PAHs accumulated on these particles could be subsequently transported to the deep ocean via vertical sinking, partly serving as the biological pump to remove particulate pollutants, deplete dissolved concentrations, and enhance their flux from air to water<sup>13,14</sup>. These biogeochemical processes are receiving increasing concern because of their role in modulating atmospheric transport and the fate of POPs in the Arctic<sup>15</sup>.

The objectives of this study are: (1) to get knowledge on the air-sea exchange and fate of PAHs during their poleward long-range transport; (2) to identify and quantify the contribution of Arctic marginal sources and other processes on PAHs' spatial variations; (3) to quantify the export flux of particulate PAHs and evaluate the Shelf Sink Effect on PAHs during their transport from the Bering Sea to the fast-changing Arctic; and (4) to tease out the transport routes of different PAHs and understand how future climate change and anthropogenic activities may affect the deposition of PAHs in this important Arctic ecosystem.

## Materials and methods

Sampling was conducted in the Western Pacific, Bering Sea, Chukchi Sea, and Canada Basin during the 4th-6th Chinese National Arctic Research Expeditions in 2010-2014, onboard *RV XUELONG*. 20 L of seawater were collected and filtered through a glass fiber filter (GF/F) (0.7  $\mu\text{m}$  pore size) for analyzing particulate PAHs. We used C<sub>18</sub> SPE cartridges to extract PAHs for each filtered seawater sample (4L). Low-density polyethylenes (LDPEs) are used in passive sampling to obtain the freely-dissolved PAHs in the atmosphere. After solvent extract and evaporation with a nitrogen stream, PAHs were analyzed by gas chromatography coupled with GC-MS-MS.

## Results and discussion

### *Net volatilization of PAHs from the North Pacific to the Arctic Ocean*

The gaseous concentrations of  $\Sigma_9\text{PAH}$  ranged from 0.67 to 13  $\text{ng m}^{-3}$  and displayed a significant decreasing trend with latitude, which was dominated by long-range transport and photochemical-degradation of PAHs. Different distributions were explained by air mass back trajectories, coupled with the influence of air-sea exchange and dry/wet deposition processes. The concentrations of total freely dissolved  $\Sigma_{11}\text{PAH}$  ranged from 1.8 to 16  $\text{ng L}^{-1}$  with a higher abundance of high molecular weight PAHs relative to air. The changes in PAH profiles can likely be attributed to their relative propensity to undergo biodegradation and dry/wet deposition. Molecular ratios of the PAHs in atmosphere and surface seawater indicated combustion sources, and the source indication might provide some evidence for LRAT of high-latitude marine environmental PAHs. Overall, the air-sea fluxes of PAHs presented mostly net volatilizations with special regional and monthly changes, controlled by seawater concentrations (Figure 1). The air-sea exchange process showed only a relatively minor importance of air concentrations, instead the fluxes and dry/wet depositions from atmosphere to seawater might were more important especially in the Arctic.

### *Remobilization of PAHs from the margins to the central basins*

The content of dissolved PAHs in 2010 was significantly higher in the Chukchi Sea marginal ice zone than that in the continental shelf area, and the PAHs concentration in adjacent sections of the basin area differed by nearly an order of magnitude. Based on the above results, this study proposes that continental margin inputs, such as river

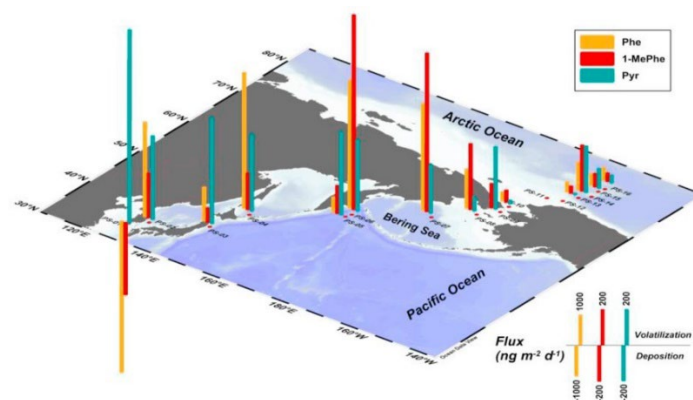
runoff and seasonal sea ice melt, are important input routes of PAHs in the western Arctic Ocean at present. At the same time, different PAHs marginal inputs in Eurasia and North America were driven to the Canada Basin by Transpolar Drift and Beaufort Gyre, respectively. The results of the mass balance model show that the sources of PAHs in the upper arctic are mainly river input and sea ice melting (76%), and there is still an input flux from an unknown source (about 1251 tons/year).

#### *Settling Export of Particulate PAHs in the Euphotic Layer*

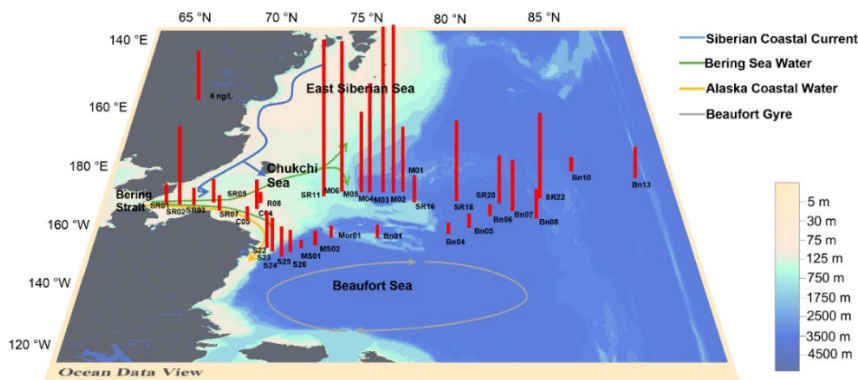
According to the  $^{210}\text{Po}/^{210}\text{Pb}$  deficit on the Bering Shelf, the export fluxes of particulate PAHs ranged from  $1201\pm 276$  to  $3650\pm 1570$   $\text{ng m}^{-2} \text{d}^{-1}$ , and their residence time ranged from  $55\pm 23$  to  $133\pm 31$  days. From the Bering Shelf to the Chukchi Sea, the decreased inventories of dissolved PAHs were positively related to their vertical particulate export fluxes ( $R^2=0.62$ ), suggesting the “Shelf Sink Effect” on PAHs (Figure 3). Settling export of particulate organic pollutants is a crucial mechanism in the oceanic uptake of atmospheric pollutants, and is a precondition for their storage in bottom sediment. We suggested the removal of particulate PAHs from the upper water column via marine particle settling supports the theory that the deep-ocean and sediments are the major global sinks of PAHs.

#### *Natural generation as inner source of PAHs in the Arctic*

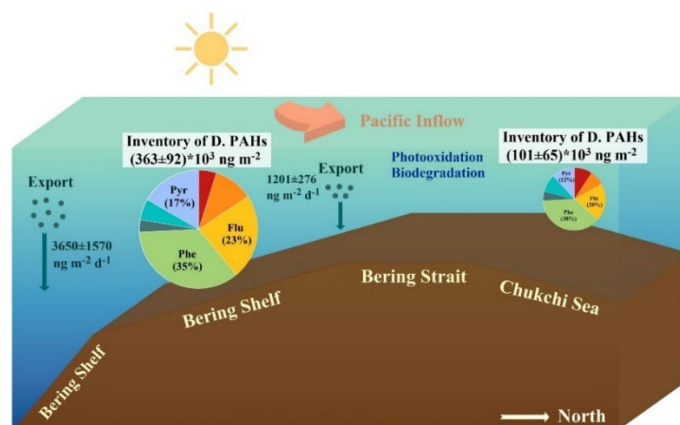
The total PAH concentrations ( $50.4$  to  $896.0$   $\text{ng/g dw}$ ) exhibited a “hilly” shape with the increase of latitude, showing the highest level of PAHs in the northeast Chukchi Sea. Most PAHs showed positive correlations with silt content, total organic carbon, stable carbon isotopes and black carbon ( $p < 0.01$  or  $0.05$ ). Generally, source apportionment methods revealed an increasing petrogenic source of PAHs with latitudes. The PMF model further differentiated two petrogenic (36.7%), two pyrogenic (softwood and fossil fuel combustion, 35.5%) and one in-situ biogenic source (Perylene, 27.8%). An extremely high petrogenic signal was captured in the Canada Basin margin, possibly originating from the Mackenzie River via ice drifting with Beaufort Gyre, while another petrogenic source may come from coal deposit erosion by deglaciation. Softwood combustion (characterized by Retene) exhibited exclusively higher contribution in the northeast Chukchi Sea and might result from the increasing wildfire in Alaska due to climate change, whereas fossil fuel combustion exhibited similar contributions across different latitudes. Our results revealed natural PAHs as important “inside sources” in the Arctic, which are highly sensitive to global warming and deserves more attention.



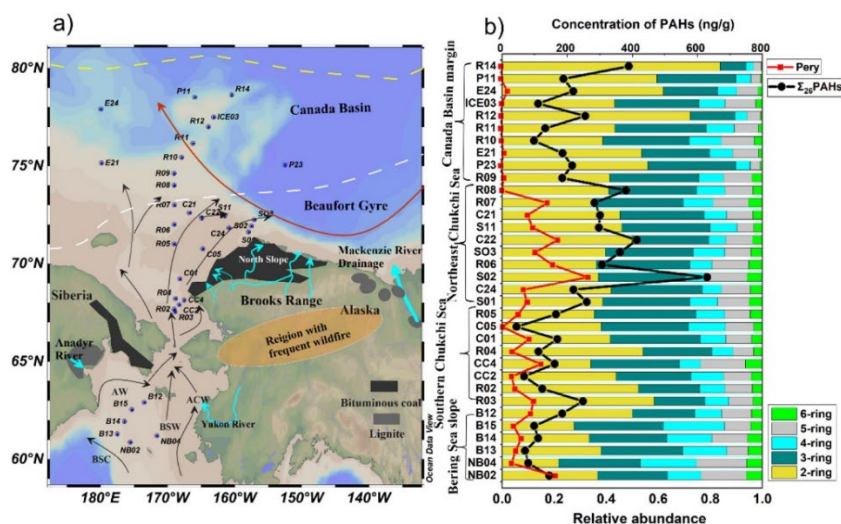
**Figure 1.** The distribution of PAH air-sea exchange fluxes from the North Pacific to the Arctic Ocean<sup>8</sup>.



**Figure 2.** Spatial distribution of dissolved concentrations (ng/L) of  $\Sigma_7$ PAH and main ocean currents in the Chukchi Sea and Canadian Basin.



**Figure 3.** Schematic diagram of particulate PAHs export during their lateral transport from the Bering Sea to the Chukchi Sea. Pie charts indicate inventories of dissolved PAHs in the water column (0-30 m).



**Figure 4.** (a) Factors that may affect the deposition of PAHs at the Northern Bering-Chukchi margin. (b) Latitudinal variations of PAHs concentrations and compositions<sup>4</sup>.

### Acknowledgements

We thank all the members of the 4th, 5th and 6th Chinese National Arctic Research Expedition. This study was supported by National Natural Science Foundation of China (NSFC) (U2005207, 41976216, 41576180 and 41776088), the Natural Science Foundation of Fujian Province, China (2014J06014). We thank Peng Huang and Hengxiang Deng for their sampling works. We thank Rainer Lohmann, Min Chen, and Ruibo Lei for their help in data analysis.

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