# Microprobe Laser Mass Spectrometry Studies of Polycyclic Aromatic Hydrocarbon Distributions on Harbor Sediments and Coals

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**Abstract.** Microprobe two-step laser mass spectrometry (μL$^2$MS) was used to assess the distribution and origin of polycyclic aromatic hydrocarbons (PAHs) on sediment particles dredged from the harbor of Milwaukee, Wisconsin. PAH concentrations are largely associated with coal-derived particles and other carbonaceous environments. PAH distributions on these coal-derived particles and carbonaceous environments, which are thought to have separate origins, were found to be quite similar. μL$^2$MS data of coal and thermally-processed coal showed profound differences from μL$^2$MS data obtained from the coal-derived particles in the sediment. The results of these experiments indicate that the coal-derived particles are not the source of PAHs in the sediment but are scavengers of PAH contaminants in the Milwaukee Harbor sediments.

## INTRODUCTION

In previous research,[1] complementary mass spectrometric and spectroscopic techniques were employed to provide direct microscale information on where polycyclic aromatic hydrocarbon (PAH) contaminants reside in Milwaukee Harbor sediment particles. Microprobe two-step laser desorption/laser ionization mass spectrometry (μL$^2$MS) was used for PAH measurements, Fourier transform infrared (FT-IR) microspectroscopy was used for organic carbon measurement, and scanning electron microscopy with wavelength dispersive X-ray spectroscopy (SEM/WDX) was used for elemental analysis. With respect to PAH contaminants, Milwaukee Harbor sediment can be divided into two principal classes of particles: a lighter density coal and wood-derived fraction that contributes 5% of the sediment weight and 62% of total PAHs; and a heavier density sand, silt, and clay fraction that contributes 95% of the sediment weight and 38% of total PAHs. The coal-derived particles were identified through coal petrography analysis. It was found through μL$^2$MS analysis that PAH concentrations on coal-derived particles were several orders of magnitude higher than on silica particles. Bare silica surfaces had PAH concentrations just slightly above detectable limits. The only significant PAH concentrations associated with silica particles came from PAHs sequestered in organic matter that had adhered to the silica particles.

Although the PAHs found in these sediments are thought to originate primarily from historic coal and wood combustion,[2,3] it is not clear if the PAH-rich coal-derived particles identified in the sediments carried the PAHs into the sediment or acted as a historic sink for PAHs coming from different sources into the sediment. A clearer understanding of the role of coal-derived particles in PAH accumulation in the sediment is important. Such information will allow the assessment of: (1) long-term effects of continued future atmospheric or aqueous inputs of PAHs into the sediment; (2) effects of further inputs of coal-derived particles into the sediment from ongoing harbor industrial and transportation activities; and (3) possible reasons behind the significantly slower desorption kinetics of PAHs from the coal-derived particles compared to sediment silt and clay particles, as reported by Ghosh et al.[1]

Coal originates predominately from the geological processing of organisms of the plant kingdom by bacterial action, burial, compaction, and geothermal heating.[4] Chemical changes that occur in the coalification of plant

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*Author to whom correspondence should be addressed. E-mail: zare@stanford.edu material include condensation, polymerization, aromatization, and the loss of functional groups containing nitrogen, sulfur, and oxygen. These processes lead to the formation of the relatively stable PAH molecule. When PAHs are formed at lower temperatures, such as in coalification, they tend to be more alkylated than PAHs formed at higher temperatures, which are generally associated with anthropogenic sources.[5] The Milwaukee Harbor is a major shipping lane used to transport mined coal. These coal-shipping and coal-handling operations may have resulted in the introduction of coal particles into the harbor.

In addition to coal-shipping operations, historic coal-coking and gasification units located near the Milwaukee Harbor are thought to be sources of coal in the sediment at this site.[6] The coal-to-coke transformation takes place by heating the coal in brick ovens.[7] From 375 °C to 475 °C, the coal decomposes to form plastic layers near each wall. At about 475 °C to 600 °C, tar and aromatic hydrocarbon compounds are evolved, followed by resolidification of the plastic mass into semi-coke. From 600 °C to 1100 °C, the coke stabilization phase begins. This phase is characterized by contraction of coke mass, structural development of coke, and hydrogen evolution.[7] The coke mass is then removed from the oven and wet or dry quenched.

In the work described in this paper, PAH distributions and concentrations on coal-derived particles, on organic matter attached to silica, and on silt and clay are compared to investigate whether these different sediment environments have PAHs originating from the same sources. Additionally, to investigate the nature of PAHs formed during coal processing, a coal sample is thermally processed to mimic typical coking processes. PAH analysis data from the sediment coal-derived particles are compared to data from both unprocessed coal and thermally-processed coal to investigate any similarity in the PAH profiles.

## EXPERIMENTAL

The sediment used in this study was obtained from the confined disposal facility at Jones Island, Milwaukee, WI, operated by the Milwaukee Harbor Port Authority and serving the Milwaukee Harbor. The confined disposal facility serves as a storage area for sediments that have been dredged from the Milwaukee Harbor to maintain navigability of the waterways. Average PAH concentrations in the confined disposal facility range from about 50 to 275 mg/kg, depending on depth.[8] The sediment sample used in this study was air-dried for seven days and then sieved.

To simulate the coal-coking process in the laboratory, samples of a bituminous coal (Illinois No. 6 coal, obtained from Illinois Basin Coal Sample Program) were sealed in aluminum foil and placed in a furnace for heating. Individual coal samples were heated to temperatures ranging from 350 °C to 1050 °C in 50 °C increments and baked at that temperature for 30 min. When the melting point of the aluminum foil was surpassed, the coal was sealed in a small steel container that was purged with nitrogen. After the coal was baked for 30 min, it was removed from the furnace and quenched.

$\mu L^2MS$, as described in Gillette et al.,[9] was used to identify and characterize the trace distribution of PAHs on sediment particles. The first step in the $\mu L^2MS$ analysis desorbs constituent molecules on a particle with a pulsed infrared (IR) laser beam focused to a 40-μm spot using a reflecting microscope objective. The power of the IR laser is adjusted so that only neutral molecules are removed from the surface. In the second step, the desorbed molecules are selectively ionized with a pulsed ultraviolet (UV) laser (266 nm), and the resulting ions are extracted into a reflectron time-of-flight mass spectrometer. The power of the UV laser is sufficient to ionize the PAHs but small enough so that a spectrum consisting primarily of parent ions is obtained.

When quantitative comparisons were made, multiple laser shots were taken from a single spot until all PAHs were depleted and the signal was summed. This procedure was used to account for possible differences in the desorbing matrices. The PAH detection limit of the $\mu L^2MS$ instrument was estimated to be in the sub-attomole range. Sampling depth was assessed to be approximately 0.5–1.0 μm using PAHs embedded in thin resin sections.

## RESULTS

Figure 1 presents reflected light images of a silica particle containing attached organic matter and a coal-derived particle. The coal-derived particle and the attached organic matter appear different under a microscope. The organic matter on the silica particle is more amorphous than the crystalline-like coal particle. Surface elemental analysis of the coal particles using SEM/WDX revealed a predominance of carbon and small quantities of oxygen and other elements. The organic matter spots on silica particles and the clay/silt particles showed similar surface elemental composition, with silicon, oxygen, aluminum, carbon, and magnesium as the primary constituents. FT-IR microspectroscopy indicated that the attached organic matter on silica particles and clay/silt particles have a more aliphatic character than the coal-derived particles. FT-IR spectra of the attached organic matter also contain an absorbance feature from 3200–3500 $cm^{-1}$ that is not present in the spectra of the coal-derived particle, indicating the presence of hydrogen bonding. These analyses provide evidence that the two separate carbon environments containing PAHs in the Milwaukee Harbor sediment were vastly different and possibly originated from different sources.

Figure 2 presents a comparison between $\mu L^2MS$

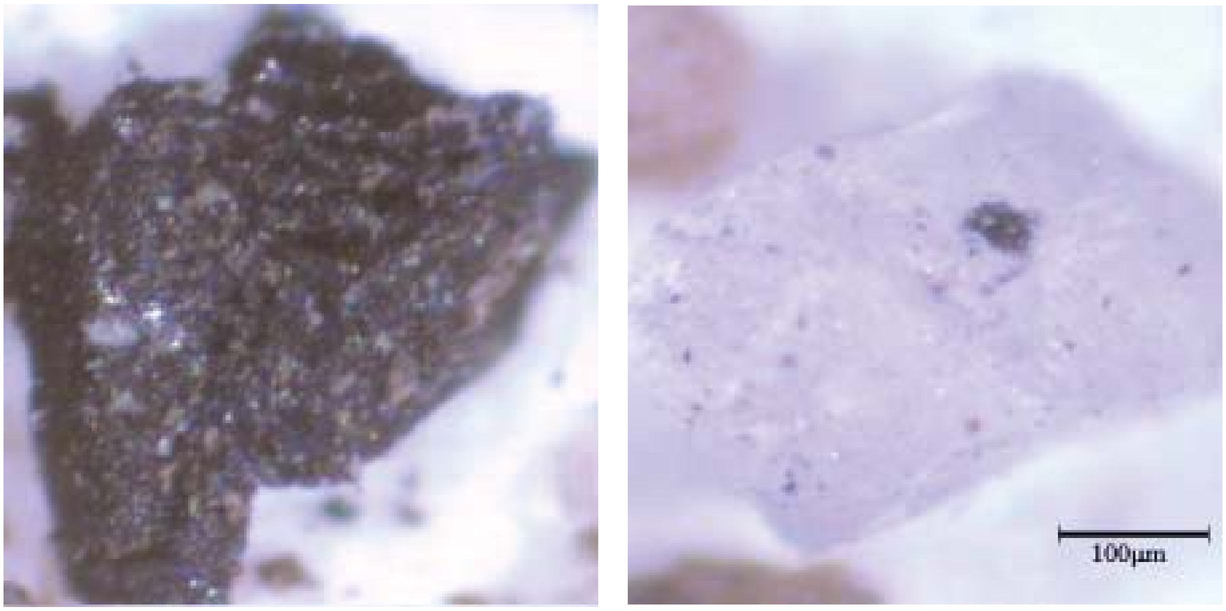

Fig. 1. Images of a coal-derived particle (*left*) and a silica particle containing attached organic matter (*right*).

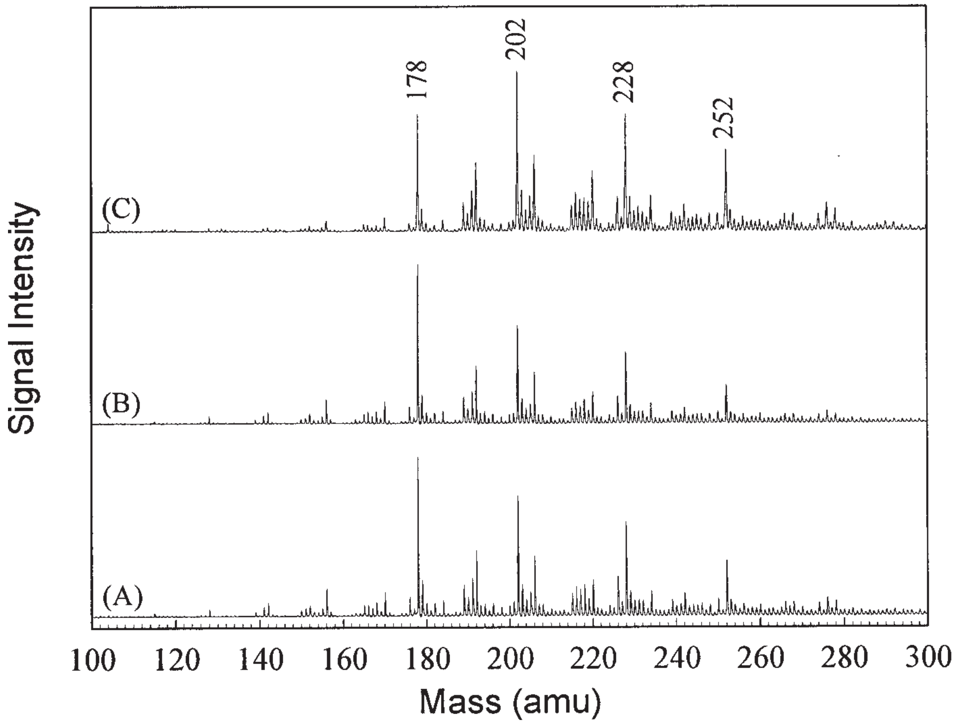

Fig. 2. µL$^2$MS spectra comparing the PAH distributions of three separate components of Milwaukee Harbor sediment. Spectrum A results from the analysis of a coal-derived particle approximately 500 µm in diameter. Spectrum B results from the analysis of PAHs associated with organic material that has attached to a silica particle approximately 500 µm in diameter. Spectrum C results from the analysis of clay/silt and fine particles that are smaller than 63 µm.

spectra obtained from a coal-derived particle (Fig. 2A), organic material attached to a silica particle (Fig. 2B), and clay/silt particles that were isolated from the sediment (Fig. 2C). These spectra were obtained by averaging the signal intensity from multiple spots across the sample surface. Quantitative comparisons involving numerous particles indicated that the coal-derived particles contain at least an order of magnitude greater PAH concentrations than the organic matter on silica particles. However, as spectra in Figs. 2A and 2B illustrate, the PAH distribution seen on each of the particles is remarkably similar. The largest peaks seen in each of the spectra result from the detection of the parent PAH compounds anthracene/phenanthrene (178 amu), fluoranthene/pyrene (202 amu), benzo(a)anthracene/chrysene (228 amu), and benzo(b)fluoranthene/benzo(k)fluoranthene/benzo(a)pyrene (252 amu). The spectrum shown in Fig. 2C results from the μL$^2$MS analysis of silt and clay contained in the Milwaukee Harbor sediment. This clay/silt fraction contains about 38% of the total PAH concentration in the sediment. The major peaks seen in spectra of the coal-derived particle and the organic matter attached to silica are also the major peaks seen in the spectrum of the clay/silt particles. The similarity of the PAH distributions seen in these three separate particle environments indicates that the PAHs were sorbed on these different particle types through a similar process, possibly the historic contamination of Milwaukee Harbor.

The possibility exists that the attached organic matter on silica particles had trapped tiny pieces of coal-derived particles that were not apparent when visualized under a microscope. This possibility necessitated further investigation into the PAH distributions of coal and coal-derived particles. Figure 3 compares a μL$^2$MS spectrum obtained from the analysis of coal removed from a mine in Illinois (No. 6 coal) with a μL$^2$MS spectrum obtained from the analysis of a coal-derived particle from the Milwaukee Harbor sediment. These spectra were recorded by taking one laser shot and moving to a fresh site. When site-to-site concentrations on the Illinois No. 6 coal and the coal-derived sediment particles are compared, the coal-derived sediment particles contain at least two orders of magnitude greater PAH concentration. These relative PAH concentrations were obtained by summing the PAH signal intensity from a number of laser shots from an individual site on the coal and coal-derived particles. During analysis, it

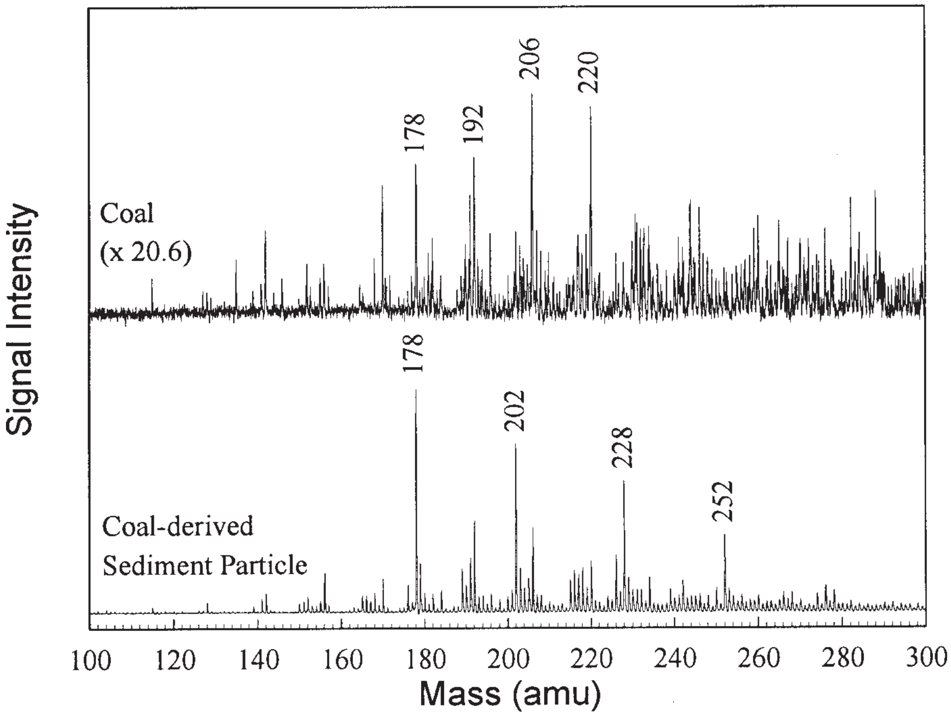

Fig. 3. μL$^2$MS spectra comparing the distribution and concentration of a coal-derived particle from the Milwaukee Harbor and a particle of Illinois No. 6 coal. The signal intensity of the coal particle spectrum has been magnified 20.6 times for ease of comparison.

was noted that most of the PAHs on one spot are removed from the Illinois No. 6 coal within one or two shots, whereas the sediment coal-derived particle can take as many as fifteen shots.

The PAH distributions are quite different in the two spectra shown in Fig. 3. The major peaks in the coal spectrum are at 178, 192, 206, and 220 amu. These peaks correspond to anthracene/phenanthrene (178 amu) and its alkylated derivatives: methylanthracene/phenanthrene (192 amu), dimethylanthracene/phenanthrene (206 amu), and trimethylanthracene/phenanthrene (220 amu). This result is consistent with the formation of PAHs at low temperatures, as discussed in Blumer.[5] In contrast, the major peaks in the sediment occur at 178, 202, 228, and 252 amu, which arise from the parent PAH compounds listed previously. Peak areas from the parent PAHs weighing 178, 202, 228, and 252 amu and from the alkylated PAHs weighing 192, 206, 220, and 234 amu were integrated and summed. The ratio of parent to alkylated PAH peaks is 2.4 for the sediment coal-derived particle and 0.53 for the coal particle. Integrating peaks from the spectra of other coal and coal-derived sediment particles gave similar results. Using the Illinois No. 6 coal as a representative of coals used and transported in the region, the spectra presented in Fig. 3 indicate that the PAHs on the coal-derived particles are not from the original coal matrix, but were either formed or deposited on the particles at a later time.

As discussed earlier, coal-coking and coal-processing operations create PAHs through pyrolysis.[7] These PAHs may be lost in escaping gases or liquid waste streams from the industry, or may remain as residual PAHs on the processed coal particles. Figure 4 presents μL$^2$MS spectra taken of coals that were heated and baked at temperatures increasing from 350 °C to 1050 °C. Each of the spectra shown is normalized to the largest peak. All of the spectra presented in Fig. 4 result from taking one laser shot of the surface and moving to a fresh site on an individual particle. Quantitative comparisons showed that the thermally-processed coals contain more PAHs than an unbaked coal, but still about an order of magnitude less than what is seen in the coal-derived sediment particles. Numerous particles were examined, and their spectra varied only slightly from particle to particle. It is seen that the alkylated peaks are less abundant after baking and the dominant peaks occur at 178 and 202 amu. The amount of PAHs weighing

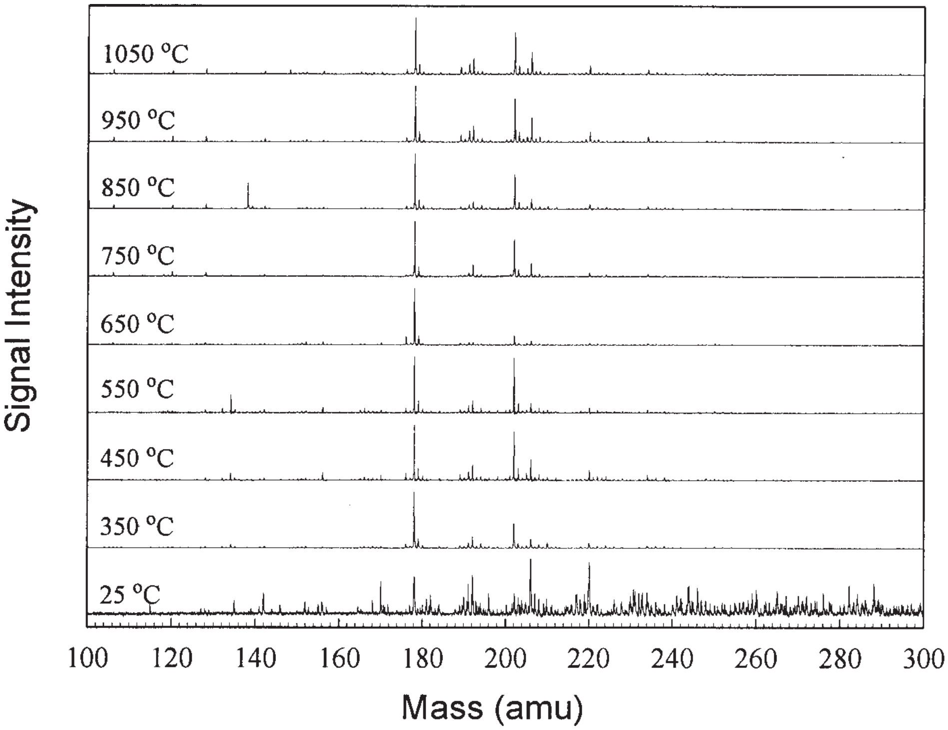

Fig. 4. μL$^2$MS spectra of unprocessed Illinois No. 6 coal and Illinois No. 6 coal that has been thermally processed. The thermal processing covers temperatures ranging from 350 °C to 1050 °C.

178 amu and 202 amu increases, but the number of species detected decreases. It appears that the PAHs are losing side chains and converting to more stable parent PAH skeletons. Blackening of the foil was seen in the samples that were baked in the 350 °C to 500 °C ranges. The discoloration may result from the adsorption of products emitted during the coal combustion process. The discolored foil was analyzed using $\mu L^2MS$, but no PAHs were detected. At temperatures above 700 °C, the resulting processed coal became increasingly shiny, having an appearance similar to graphite. Comparing the spectra presented in Fig. 4 with spectra of coal-derived sediment particles, it appears that thermally-processed coal particles are not responsible for introducing the PAHs seen in the Milwaukee Harbor sediment.

## DISCUSSION AND CONCLUSIONS

Based on the comparison of PAH distributions on coal-derived and other particles in the sediment and from assessment of PAH distributions on thermally-processed and unprocessed coal, it is evident that coal-derived particles were not the major source of PAHs seen in the Milwaukee Harbor sediment. The coal-derived particles probably arrived in the sediment with a few PAHs and accumulated the rest through a process of adsorption from the aqueous medium. Prior work involving cross sectional measurement of PAH concentrations on coal-derived sediment particles revealed a near-surface abundance of PAHs[1] that is consistent with a sorption process. PAHs formed on a coal-derived particle through pyrolysis would probably be more uniformly distributed across the particle interior.

Previous work has also suggested the importance of atmospheric loading of PAHs in the Lake Michigan sediments. Simick et al.[10] suggested that the higher molecular weight PAHs are deposited onto the lake through atmospheric aerosols and are incorporated into sediments. The lower molecular weight PAHs reach the sediment from the gas phase through air–water exchange and then partition into the organic carbon of the sediment. Once the PAHs are in the sediment they can be strongly bound to the highly sorbent coal-derived particles. In a parallel study,[11] we have demonstrated that PAHs sorbed on coal-derived particles are associated with a much higher desorption activation energy compared to the PAHs sorbed on clay and silica particles. Thus, the PAHs associated with coal-derived particles in these sediments may be strongly bound and less available for release. In an earlier study, the effect of PAH association with different types of sediment particles was assessed by sediment bioslurry treatments and earthworm bioaccumulation tests.[12] It was found that PAHs associated with the clay/silt fraction are more easily degraded than PAHs associated with coal-derived particles. The strongly bound PAHs on the coal-derived particles are relatively unavailable for biological treatment. Although bioslurry treatment achieved only a modest overall reduction in total PAHs from the sediment, there was nearly a 75% reduction in PAH uptake by earthworms, owing to the degradation of the available PAHs from the clay/silt fraction. Therefore, concern for PAH toxicity in these sediments should focus on the clay/silt/sand-associated available PAHs. The coal-derived particles appear to have a beneficial effect on the sediments by acting as a strongly sorbing sink of available PAHs.

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