

## POLYCYCLIC AROMATIC HYDROCARBONS AND POLYCHLORINATED DIBENZO-P-DIOXINS AND DIBENZOFURANS IN SEDIMENT FROM A SUB-ARCTIC LAKE IN ALASKA

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### ABSTRACT

A sediment core was collected from Wonder Lake in the sub-Arctic region of Alaska. The core was analyzed for two classes of ubiquitous organic pollutants, polycyclic aromatic hydrocarbons (PAHs) and polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) at different core depths. Two kinds of PAHs were found: parental PAHs produced from combustion and biogenic PAHs derived from natural precursors. The latter are overwhelmingly higher in concentrations than the former. The tetra to octa PCDD/Fs were found to be present at  $< 8 \text{ pg g}^{-1}$  in all the sectioned sediments with two exceptions. The concentrations of 1,2,3,4,6,7,8-HpCDD and OCDF in one section of the cored sediment deposited in the period from ~1590 through 1790 were found to be  $13 \text{ pg g}^{-1}$  and  $15 \text{ pg g}^{-1}$ , respectively. The combustion produce parental PAHs are also higher in levels in sediment accumulated in this period than the earlier and latter deposited sediments. These higher concentrations may have resulted from some natural cause such as forest fires during that period. These results also support the DE NOVA synthesis of PCDD/Fs.

### INTRODUCTION

This study was conducted in collaboration with scientists participating in the U.S. Environmental Protection Agency-sponsored Arctic Contaminant Research Program. The overall purpose of the research is to identify the possible contamination of a remote sub-Arctic regions by long distance transported pollutants. In order to determine the magnitude of contamination as well as historical inputs of contaminants to the region, sediment cores were collected from Wonder Lake, a sub-Arctic lake located in Denali National Park in the Alaska Range in April 1991. One sediment core was sectioned and dated, followed by analyses for PAHs and PCDD/Fs. These two classes of ubiquitous organic pollutants are degradation resistant in the environment and may be atmospherically transported from lower latitude sources and deposited on the sub-Arctic environment during Arctic haze conditions. They are of particular interest to the U.S. Department of

Energy because of their combustion related origins and the carcinogenic activities of some of their isomers<sup>1</sup>.

## METHODS

The sediment core was collected at the deepest basin, about 65 m, of Wonder Lake with a K-B coring device. The core itself was about 30 cm long and was sectioned in the field into 0.5-2.0 cm intervals. The sectioned sediments were freeze dried then packed and sealed in 2-mL vials for gamma radionuclide analyses using a high resolution germanium well detector. A sedimentation rate of  $\sim 0.05 \text{ cm y}^{-1}$  was estimated based on the <sup>210</sup>Pb and <sup>137</sup>Cs profiles in the sediment core. The profiles were not ideal; there was apparent mixing in the top 3 cm of the core. Because of the low sedimentation rate and small amount of sediment samples available, the 0.5-2.0 cm intervals were combined into three 10-cm sections for chemical analyses.

The freeze-dried sediment sections were spiked with three- to six-ring deuterated PAHs and <sup>13</sup>C labeled tetra to octa PCDD/Fs, besides OCDF, consisting of one isomer for each congener group, prior to Soxhlet extractions. The detailed procedures in sample preparation were described previously<sup>1</sup>. The prepared PAH fractions were analyzed by a Hewlett-Packard 5890 GC with a flame ionization detector and a HP 5988 GC/MS system, and the PCDD/F fractions by a HP 5890 Series II GC coupled to a Kratos CONCEPT 1S HRMS. Positive electron impact ionization and 30 m x 0.25 mm i.d. DB-5 fused silica capillary GC columns were used in both instruments. Parental PAHs and PCDD/Fs were identified by their GC retention times and specific ions, and biogenic PAHs by their GC retention times and mass spectra. Quantifications were carried out by selected ion monitoring of native analytes and spiked labeled standards. Because of the lack of deuterated standards, response factors of neighboring PAHs in the GC chromatograms were used for quantifications of the biogenic PAHs.

## RESULTS AND DISCUSSION

Each of the combined 10-cm sediment sections represents an estimated time period of about 200 years and the entire core dates back about 600 years. The concentrations of PAHs and PCDD/Fs found in sediments accumulated at three different time periods are listed in Table 1. Only 9-methylphenanthrene is assumed to be present in the GC peak where 9- and 4-methylphenanthrene coelute, because 4-methylphenanthrene does not seem to occur in nature<sup>2</sup> and none of this isomer has been found in petroleum. The listed data are averaged results from duplicate analyses with  $\pm 15\%$  mean deviation for PAHs and  $\pm 30\%$  for PCDD/Fs. The recoveries of spikes are around 50%.

All the highly concentrated PAHs can be traced to natural origins. The most abundant PAH, perylene, often found increasing in concentration with depth in sediments, is attributed to the diagenetic reduction, in a reducing environment, of pigments from aquatic or terrestrial organisms<sup>3-5</sup>. This phenomenon has been observed in this study.

Processes of consecutive aromatization of steranes and terpenoids during diagenesis of sedimentary organic matter contribute to the formation of certain PAHs<sup>4,5</sup>. The highly

concentrated tetra and octa hydrogenated and alkylated chrysene found in the Wonder Lake sediments are most likely derived from pentacyclic triterpenoids in higher plants, and the alkylated phenanthrene, retene, from diterpenoid abietic acid in pine resin.

Another interesting observation of the PAH compositions is the relatively high levels of phenanthrene and methylphenanthrenes compared to the other combustion-produced parental PAHs. A mechanism of dehydrogenation of steroids was proposed as the sources of these phenanthrene homologs<sup>5</sup>. The formation of 1- and 2-methylphenanthrenes may be attributed to the partial dealkylation of the biogenic retene. This dealkylation could also have led to the much lower concentration of retene compared to those of alkylated and partially hydrogenated chrysenes. Possible origins of 3- and 9-methylphenanthrene in the sediments include rearrangement of 1-methylphenanthrene<sup>6</sup> and/or methylation of phenanthrene<sup>7</sup>, respectively.

The compositions of parental PAH, besides biogenic perylene, found in the sediments resemble those observed in other environmental samples<sup>4,9</sup>, except for the pair of benzo(a)pyrene and benzo(e)pyrene. This pair is usually found at about the same level in the environment. We have no explanation for the absence here of benzo(e)pyrene.

PCDD/F levels are very low in Wonder Lake sediments. Only 1,2,3,4,6,7,8-HpCDF and OCDF were detected at 13 and 15 pg g<sup>-1</sup>, respectively, in the sediment accumulated from ~1590 through 1790. In this sediment, the combustion-produced parental PAHs are also higher than the earlier and later deposited sediments. Since HpCDD and OCDF are recognized as primarily combustion-produced PCDD/Fs, these data suggest that some natural pyrolysis process, such as forest fires, may have occurred in that period. This speculation can not be confirmed because of the lack of any historical record. However, since this period is prior to the Industrial Revolution, our results support the hypothesis of DE NOVO synthesis<sup>9</sup> which suggests that PCDD/Fs can be formed from a variety of chemically unrelated precursors, not necessarily man-made chlorinated aromatic compounds, but also natural precursors, together with a chlorine donor.

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TABLE 1. PAHs and PCDD/Fs in Wonder Lake Sediments (ng g<sup>-1</sup>).

| Compounds  | Dates     |           |           |
|--|-----------|-----------|-----------|
|  | 1390-1590 | 1590-1790 | 1790-1990 |
| Phenanthrene   | 3.8       | 6.8       | 3.7       |
| Anthracene   | 0.2       | 0.1       | 0.1       |
| 3-Methylphenanthrene   | 1.3       | 2.2       | 1.0       |
| 2-Methylphenanthrene   | 1.9       | 4.2       | 1.5       |
| 9-Methylphenanthrene   | 0.9       | 1.7       | 0.9       |
| 1-Methylphenanthrene   | 1.2       | 2.1       | 1.0       |
| Fluoranthene   | 0.7       | 2.6       | 0.9       |
| Pyrene   | 0.6       | 1.5       | 0.7       |
| Retene   | 0.8       | 1.5       | 0.6       |
| 1-Methylpyrene   | 0.1       | 0.3       | 0.1       |
| Benzo (g, h, i) fluoranthene   | 0.2       | 0.2       | 0.1       |
| Benzo (a) anthracene   | 0.3       | 0.5       | 0.4       |
| Chrysene/Triphenylene  | 0.6       | 1.3       | 0.9       |
| Tetramethyl-1,2,3,4,4a,<br>11,12,12a-octahydro-<br>chrysene          | 76        | 48        | 12        |
| 3,3,7,12a-Tetramethyl-1,<br>2,3,4,4a,11,12,12a-<br>octahydrochrysene | 1.5E2     | 1.6E2     | 33        |
| 3,4,7-Trimethyl-1,2,3,4-<br>terahydrochrysene                        | 7.4       | 5.7       | 2.5       |
| 3,3,7-Trimethyl-1,2,3,4-<br>tetrahydrochrysene                       | 62        | 79        | 31        |
| Benzo (b/j/k) fluoranthene   | 0.5       | 0.3       | 0.3       |
| Benzo (e) pyrene   | <0.1      | <0.1      | <0.1      |
| Benzo (a) pyrene   | 0.6       | 0.4       | 0.5       |
| Perylene   | 2.0E3     | 1.1E3     | 6.2E2     |
| Indeno (1,2,3-cd) pyrene   | 0.3       | 0.3       | 0.4       |
| Benzo (g, h, i) perylene   | 0.5       | 0.6       | 0.6       |
| 1,2,3,4,6,7,8-HpCDF  | <8E-3     | 1.3E-2    | <8E-3     |
| OCDF   | <8E-3     | 1.5E-3    | <8E-3     |