Enhanced Sorption of PAHs in Natural-Fire-Impacted Sediments from Oriole Lake, California

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Supporting Information

ABSTRACT: Surface sediment cores from Oriole Lake (CA) were analyzed for organic carbon (OC), black carbon (BC), and their δ13C isotope ratios. Sediments displayed high OC (20–25%) and increasing BC concentrations from ∼0.40% (in 1800 C.E.) to ∼0.60% dry weight (in 2000 C.E.). Petrographic analysis confirmed the presence of fire-derived carbonaceous particles/BC at ∼2% of total OC. Natural fires were the most likely cause of both elevated polycyclic aromatic hydrocarbon (PAH) concentrations and enhanced sorption in Oriole Lake sediments prior to 1850, consistent with their tree-ring-based fire history. In contrast to other PAHs, retene and perylene displayed decreasing concentrations during periods with natural fires, questioning their use as fire tracers. The occurrence of natural fires, however, did not result in elevated concentrations of black carbon or chars in the sediments. Only the 1912–2007 sediment layer contained anthropogenic particles, such as soot BC. In this layer, combining OC absorption with adsorption to soot BC (using a Freundlich coefficient n = 0.7) explained the observed sorption well. In the older layers, n needed to be 0.3 and 0.5 to explain the enhanced sorption to the sediments, indicating the importance of natural chars/inertinites in sorbing PAHs. For phenanthrene, values of n differed significantly between sorption to natural chars (0.1–0.4) and sorption to anthropogenic black carbon (>0.5), suggesting it could serve as an in situ probe of sorbents.

INTRODUCTION

The fate of hydrophobic organic compounds (HOCs), such as polycyclic aromatic hydrocarbons (PAHs), in sediments and soils depends largely on their sorption to solid phases.1,2 In urban/industrial sediments and soils, sorption is often dominated by anthropogenically derived geosorbents, such as soot, tar, pitch, coal, or nonaqueous phase liquids (NAPL).2–5 Soot black carbon (BC) is formed by the condensation of small aromatic moieties in the gas phase of high-temperature combustion processes.6

Much less attention has been paid to the effect of natural produced charcoals and chars have on the sorption of HOCs in the field. Natural fires affect huge areas and have major impacts on land cover, atmospheric chemistry, and regional and global climate.7–9 For example, in the U.S. alone, close to 4 million hectares have been subject to prescribed and wildland fires annually.10 The deposition of charred biomass and charcoal from these fires changes the geochemistry6 and physical properties of soils and sediments.11,12 Highly reflecting organic particles with porous char morphology are classified as natural char.13 They are formed under the influence of heat from fire on gelified organic matter (for example, burning of gelified organic matter in the organic horizon of a forest soil, occurring during a ground fire). Fusinite particles (charcoal), which form by burning of fresh or more or less unaltered plant tissues, differ from natural char by their typical well-preserved cellular structures and the absence of degassing pores.14

In this field study, we took sediment samples from Oriole Lake (latitude, 36.4602226 N; longitude, 118.7370406 W), a small 6.8 m
To determine the importance of soot BC in the sorption of HOCs, we employed a nondepletive, polyethylene (PE) passive sampler technique. BC reference standards were used to calibrate the PE sorbers. This approach was validated by comparing the results with those obtained using the Accelerated Solvent Extraction (ASE) method. The PE samplers were deployed at different depths in Oriole Lake sediments, and the sorption coefficients were estimated for PAHs. The results showed that PE sorbers can be used to trace past environmental conditions and assess the historical deposition of PAHs in the lake sediments.
between 20% and 25% (Figure 1). $\delta^{13}C$ values of BC were consistently heavier by 2–3% (i.e., more enriched in $^{13}C$) than $\delta^{13}C$ values of the OC fraction (Figure 1). The OC fraction displayed a significant change in $\delta^{13}C$ values from 1630 to 2007, resulting in more depleted $\delta^{13}C$ values with depth (Figure 1 and Table 4 of the Supporting Information).

Over the last ~200 years (0–30 cm), BC concentrations declined significantly, from ~0.60% to ~0.40% dw (Figure 3 of the Supporting Information). During the same period, OC concentrations also declined, albeit with a weaker correlation (Table 4 of the Supporting Information). For both OC and BC, $\delta^{13}C$ values became more depleted in $^{13}C$ (i.e., lighter) over the last 200 years (0–30 cm), but not in preindustrial sediments (39–60 cm) (Table 4 of the Supporting Information).

Overall, the OC and BC profiles suggest that there were two distinct periods captured in the sediments of Oriole Lake. There was an almost constant background signal from OC and BC prior to 1800, in terms of their $\delta^{13}C$ values (Figure 1). Both OC and BC displayed a sharp decrease at 50 cm, probably indicating dilution by a mineral phase. Since 1800, there was evidence for increasing (atmospheric) deposition of BC and OC during the industrialization of the northern hemisphere, leading to enhanced C deposition to Oriole Lake (Figure 3 of the Supporting Information). Presumably, the high background concentrations of OC in Oriole Lake masked the impact of C-deposition, resulting in weaker correlations. Additional evidence for long-term changes of carbon residing in Oriole Lake can be gleaned from the carbon fractions’ $\delta^{13}C$ values. The overall $\delta^{13}C$ values of OC and BC were consistent with C$_T$-vegetation (~23% to 28%), dominating C-influx into Oriole Lake, in line with the vegetation present in its watershed. The enrichment of $\delta^{13}C$ values of OC and BC in the recent sediment (Figure 1) could be due to the deposition of carbon from fossil fuel emissions.

With the high amount of OC present, there is potential of charring, leading to erroneously high values of BC. There was a significant intercorrelation of OC and BC concentrations from 1630 to 2007 ($r^2 = 0.58$) over the whole time span analyzed, but a much weaker correlation was found over last 200 years ($r^2 = 0.19$). Conversely, the correlation between OC and BC was highly significant for the deepest 39–60 cm section ($r^2 = 0.87$) (Table 4 of the Supporting Information). As reported above, $\delta^{13}C$ values were offset between the two carbon pools, suggesting that different fractions of carbon were involved. Density plots (Figure 2 of the Supporting Information) suggested that the influx of OC and BC into Oriole Lake might have been coupled. Nevertheless, in the preindustrial time horizon it seems possible that charring of OC might have inflated BC values.

### Bulked Sediment Layers. Sediment PAH Concentrations.

The three sediment layers displayed vastly different PAH concentrations and profiles (Figure 2, Table 4 of the Supporting Information). All PAHs were summed and reported as $\Sigma_{18}$PAH, except for perylene and retene, which can have a biological origin (see below). The depth distribution of $\Sigma_{18}$PAHs was consistent with natural fires having influenced the middle (2000 ng/g dw) and deep layer (300 ng/g dw), but not the top layer. Even though there was an increase of BC in the top sediment layer, it displayed the lowest PAH concentrations, at 50 ng/g dw. This suggested that natural fires constituted a more important source of PAHs to Oriole Lake than other local sources or their long-range transport to the lake.

We investigated the distribution of different PAHs ("molecular ratios") to assess whether the PAHs stemmed from petroleum spills or the combustion of fossil fuels or wood.
Wood combustion should be characterized by ratios of fluoranthenes over fluoranthene and pyrene (fl/([fl + pyr]) > 0.5, anthracene over anthracene and phenanthrene (an/([an + phen]) > 0.1 and indeno[1,2,3-c,d]pyrene over indeno[1,2,3-c,d]pyrene and benzo[gh,i]pyrene (ip/([ip + b(ghi)p])) > 0.5. A petrogenic source would be indicated by elevated methylphenanthrenes relative to phenanthrene and by an/([an + phen] < 0.1. All PAH ratios established here suggested a pyrogenic origin of the PAHs (fl/([fl + pyr]) ratio 0.5–0.65; an/([an + phen]) ratio 0.17–0.5; ip/([ip + b(ghi)p]) ratio 0.47–0.55; methylphenanthrenes < phenanthrene). The fl/([fl + pyr] and ip/([ip + b(ghi)p]) ratios suggested grass/wood/coal combustion as sources.

Unexpectedly, retene and perylene concentrations displayed inverse trends with total PAHs (Figure 2). Retene (and perylene) concentrations were highest in the top layer, at 830 ng/g (520 ng/g), elevated in the deepest layer, at 410 ng/g (280 ng/g), but very low in the middle layer, at merely 63 ng/g (91 ng/g). Retene was proposed as a marker molecule for coniferous (soft) wood combustion in air, but very low in the middle layer (530 ng/g). BC related to forest fire was highest in the top layer (210 ng/g), but displayed similar concentrations of ∼110–130 ng/g in the other layers (Figure 2).

Petrographical Analysis of Sediments. The three samples were rich in organic matter (OM) (Table 5 of the Supporting Information) and were dominated by humified plant fragments (retene and perylene were formed (upper layer). In contrast, perylene was highest in the top layer (530 ng/g), but displayed similar concentrations of ∼110–130 ng/g in the other layers (Figure 2).
layer, 2.1% in the middle, to 2.3% in the top layer) with results by petrography (Table 1). Natural chars formed at low temperatures are generally oxidized during CTO-375. We included risotto char, chestnut char, and melanoïdin in the CTO-375 runs, all of which were completely removed. Most likely, chars formed during natural fires in Oriole Lake were resistant to CTO-375, possibly due to their formation at higher temperatures. It is also conceivable that the very high OC content of the sediments resulted in preferential oxidation of huminites and liptinites first, resulting in the preservation of natural chars, charcoals, and soots.

**Sedimentary Evidence for the Presence of Natural Fires in Oriole Lake.** While PAH results suggested natural fires affected the deeper layers, there was no indication of increases in natural chars in these layers. Presumably, as indicated by their constant concentrations among all three layers, there is a continuous flux of these particles into the lake. A major fire would leave topsoil vulnerable to erosion during strong rains. This could possibly explain unchanged char and charcoal concentrations after a natural fire, as the fire signal would be diluted with soil richer in minerals, but lower in OC and BC. Indeed, there was a major change in magnetic susceptibility from ca. 15–25 cm, coupled with a gentler increase in sediment density (Figure 2 of the Supporting Information). In fact, there are also smaller increases apparent in the lowest (28–36 cm) layer, supporting the existence of a smaller scale natural fire recorded in the deepest sediment layer analyzed. This agrees with the tree-based fire history of numerous natural fires in Oriole Lake Grove prior to 1850.15

**Sorption Models.** Concentrations of the PAHs in the PEs that were incubated with the different sediment layers displayed a much narrower range of concentrations compared to the sediments (Table 4 of the Supporting Information). This reflects upon different availabilities of the PAHs or the extent to which sorption was holding PAHs in the sediments, as discussed below. Concentrations of $\sum_{18}$PAHs in PE did not mirror its sediment profile, while retene’s PE concentrations changed with depth similar to its sediment profile (Figure 2).

**OC-Absorption Model.** Values of $K_{oc}$ taken from the literature (Table 1 of the Supporting Information) have an uncertainty of a factor of $2^{2} \pm 3^{2}$ The OC-absorption model strongly underestimates the partitioning of PAHs (Figure 4a), by $\sim 1$ order of magnitude for the deepest layer and by $\sim 2$ to $3$ orders of magnitude for the upper layers. These results imply that additional sorption to the sediments is occurring, most likely to reduced carbonaceous geosorbents such as soot black carbon and chars, as detected both by petrography and CTO-375 in all layers.

**Combined OC-Adsorption and OC-Absorption Model.** The combined OC-Adsorption and OC-Absorption model explained the observed distributions well for the most recent sediment layer, with most values within a factor of $3^{2}$ of predictions (Figure 4b). In contrast, using $n = 0.7$, $K_{d,meas}$ of the deepest layer were still underpredicted by factors of $5$ to $10$, while the middle layer was

![Microscopic examples of organic and black carbon particles.](image-url)
underpredicted 10–1000 times (Figure 4 of the Supporting Information). Sootlike black carbon seems to be able to account for additional sorption present in the most recent sediment, but is insufficient to explain sorption in the deeper layers. If soot BC values were artificially elevated due to charring, real sorption due to BC would be further underestimated. These results strongly suggest the presence of additional sorption beyond the phases considered above, most likely due to the presence of natural charcoals throughout the sediment core.

Explaining the Observed Sorption of PAHs in Oriole Lake Sediments. We investigated whether the addition of a separate lipid-phase (based on the presence of liptinites at around 5% of TOC) could account for the additional sorption. Yet partitioning to lipids (assuming log $K_{lipid-w} = 0.91 \log K_{ow} + 0.50$) is not enough to account for the missing sorption. Any further subdividing of the BC phases (into chars, charcoals, coke, coals, or soot) would not help either, as soot is thought to be among the strongest natural geosorbents (i.e., excluding activated carbon or NAPL phases). Enhanced PAH Sorption to Chars. The only way to explain the observed enhanced sorption of PAHs in the deeper sediment layers affected by natural fires is to use a different value for the Freundlich coefficient $n$. The value of 0.7 is based on sorption isotherms derived for soot black carbon in urban/industrialized sediments, with strong competition from other hydrophobic organic contaminants. Furthermore, these anthropogenically affected sediments typically contain PAHs at much higher concentrations than encountered in Oriole Lake. A Freundlich coefficient of $n = 0.7$ gave a good fit for the most recent sediment layer. In contrast, we needed to use $n = 0.3$ for the middle layer and 0.5 for the deepest layer to reconcile predicted and measured $K_d$ values (Figure 4b).

**Freundlich Coefficient of Phenanthrene Sorption to Chars.** Phenanthrene is the PAH most commonly used for sorption isotherms; hence, we compared sorption results from Oriole Lake with literature values (Table 2). We obtained $n = 0.54$ (top), 0.21 (middle), and 0.38 (deepest layer) for phenanthrene, using a log $K_F = 5.0$. Other sorption studies using natural wood chars resulted in similar $n$-values (Table 2). Sorption to artificial wood chars and charred kerogens also yielded $n$-values $<0.5$, albeit with increasing $K_F$ values. In contrast, in a review of phenanthrene sorption onto black carbon, coal, and kerogen, all black carbon sorbents displayed $n > 0.5$. The difference in Freundlich coefficients could represent a means of distinguishing between sorption to soots and charcoals in situ.

### Table 2. Comparison of Freundlich Coefficients $n$ and Freundlich Sorption Constants $K_F [\text{µg/kg char}/(\text{µg/L})^n]$ for Phenanthrene Sorption onto Natural Chars and Black Carbon

<table>
<thead>
<tr>
<th>natural char/charcoal</th>
<th>Freundlich $n$</th>
<th>$\log K_F$</th>
<th>ref</th>
<th>black carbon</th>
<th>Freundlich $n$</th>
<th>$\log K_F$</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.40 ± 0.009 (natural wood char)</td>
<td>4.6</td>
<td>36</td>
<td>0.52 ± 0.01 (hexane soot)</td>
<td>4.4</td>
<td>37</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.39 ± 0.002 (extracted natural wood char)</td>
<td>4.7</td>
<td>36</td>
<td>0.41 (SRM 2975 diesel soot)</td>
<td>4.3</td>
<td>37</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.13 – 0.42 (artificial wood chars at 300–820 °C)</td>
<td>0.24 – 0.60 (natural wood chars)</td>
<td>5.0 – 6.11</td>
<td>39</td>
<td>0.60 (SRM 1650b diesel soot)</td>
<td>45.47</td>
<td>37</td>
<td></td>
</tr>
<tr>
<td>0.30 – 0.35 (charred kerogen at 450 °C)</td>
<td>0.24 – 0.32 (charred kerogen at 500 °C)</td>
<td>5.8</td>
<td>0.58 – 0.64 (black carbon substrates)</td>
<td>5.6 – 6.3</td>
<td>38</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.47 (artificial wood char, unknown temperature)</td>
<td>6.1</td>
<td>41</td>
<td>0.51 – 0.64 (natural kerogens)</td>
<td>5.0 – 5.4</td>
<td>41</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.42 – 0.47 (charred sawdust at 400 °C)</td>
<td>7.1 – 8.0</td>
<td>42</td>
<td>0.24 – 0.32 (presumably natural charcoal)</td>
<td>5.0</td>
<td>this work</td>
<td>0.55 (presumably black carbon, top layer)</td>
<td>5.0</td>
</tr>
</tbody>
</table>

Figure 4. Measured sediment–porewater distribution ($K_{d,meas}$) of PAHs versus predictions based on (a) absorption into OC and (b) combined OC and BC adsorption.

Table 2. Comparison of Freundlich Coefficients $n$ and Freundlich Sorption Constants $K_F [\text{µg/kg char}/(\text{µg/L})^n]$ for Phenanthrene Sorption onto Natural Chars and Black Carbon
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REFERENCES


