Revisit the Fate of Halogenated Organic Pollutants in the Environment in the Presence of Pyrogenic Carbon Matter

Kai Ding and Wengqing Xu
The Final Sink for Pollutants: Soil and Sediment

Strong affinity toward black carbon

Black carbon constitutes 10 ~ 30% of organic carbon in soil and sediment (Middleburg et al. 1999)
Black Carbon **Shields** Pollutants from Reactions

- Photolysis
- Abiotic transformation
- Not BIOAVAILABLE
Natural Attenuation with Black Carbon and Sulfide

Black Carbon (10% ~30% OC)

Lower Toxicity Products

H₂S / HS⁻ (~ 5mM, pKₐ=7)
Products from sulfate reducing bacteria

Pollutants
Black Carbon Foster Nitrogenous Pollutants Decay

RDX, nitroglycerin, 2,4-dinitrotoluene, nitrobenzene, 3-chloronitrobenzene, 4-nitrophenol, 3-bromonitrobenzene, hexachloethane (Kemper et al. 2008; Xu et al, 2010, 2013, and 2015; Oh et al, 2009 and 2012; Fu et al., 2013; Gong et al., 2014; Amezquita-Garcia et al., 2013)

(Pignatello et al. 2017, submitted)
DDT is a halogenated insecticide, Persistent Organic Pollutants (POPs)

Persistent in the environment and often detected in soils and sediments as **DDX (DDT, DDD, and DDE)**

- Up to 45 ng/g of DDX in soil and 252 μg/g in sediment have been reported (Kannan *et al.*, 2003)
- $t_{1/2}$ of DDX is 2 to 15 years in soil (Sudharshan *et al.*, 2012)

Extremely hydrophobic, bioaccumulative, bioaugmentative, and toxic

- log $K_{ow}$ values above 6.0, probable human carcinogen (EPA, 2002)
Objectives

Objective 1: To evaluate the feasibility of pyrogenic carbon matter in promoting DDX degradation by sulfide

Objective 2: To characterize the reaction pathways

Objective 3: To differentiate the important characteristics of pyrogenic carbon matter in promoting the observed reactions
Batch Reactor Experiments

Experimental conditions: 10 μg DDX, 5 mM sulfide, and 21 g/L at pH 7
DDX Degradation Kinetics

Degradation Kinetics: DDT > DDD ≥ DDE
20 times faster than reported half-life values for DDX in soils

(Sudharshan et al., 2012)
The Formation of Products from DDX Degradation

Lower toxicity products are formed (DDD, DDMU, and Cl⁻)
Reaction Pathways in Batch Reactors

Concurrent solution reaction and surface-mediated pathways

Aqueous Phase Reaction

DDX + H₂S

BC as Electron Shuttle

H₂S(ads) → e⁻

DDX(ads)

BC Reacts with Sulfides

DDX(ads) → "S""S"
Only permits electron transfer via an anode to a cathode constructed from sheet graphite
Reaction Pathways for Sulfide Treated Carbon

Step 1

BC + H₂S

Step 2

DDT + Sulfide treated BC

DDX + H₂S

H₂S(ads)

DDX(ads)

DDX(ads) "S" "S"

ln(C/C₀)

Sulfide treated BC

Control

t (d)
DDT Decay by Surface-bound S Species

55.7% ==

0% ==

54.4% ==

0% ==
Proposed Reaction Pathway for DDT

BC Reacts with Sulfide Forming Surface-bound S Species

DDD + Cl⁻ ⇌ DDT(ads) “S” “S”

X-philic reaction: DDT to DDD

E1CB reaction: DDT to DDE

(DDD, X-philic) (DDE, E1CB)
DDD Decay by Surface-bound S Species

![Diagram showing the decay of DDD by surface-bound S species in Batch and EC conditions. The diagram includes bars for DDD + Graphite + Sulfides, DDD + Sulfide treated Graphite + Sulfides, and DDD + Graphite + Sulfides. The percentages and chemical species are indicated as follows:

- **32.6%** \(\Rightarrow\) DDD + \(\text{H}_2\text{S}\)
- **0%** \(\Rightarrow\) DDD + \(\text{H}_2\text{S}\)
- **34.3%** \(\Rightarrow\) DDD(ads)
- **0%** \(\Rightarrow\) \(\text{H}_2\text{S(ads)}\)

The diagram also shows the transfer of electrons from DDD(ads) to \(\text{H}_2\text{S(ads)}\).]
Proposed Reaction Pathway for DDD

BC Reacts with Sulfide Forming Surface-bound S Species

DDD + Cl⁻ $\overset{S}{\rightleftharpoons}$ DDT(ads)

DDMU + Cl⁻ $\overset{S}{\rightleftharpoons}$ DDD(ads)

X-philic reaction: DDD to product E

E1CB reaction: DDD to DDMU

(DDMS: X-philic)

(DDMU: E1CB)
DDE Decay by Surface Reduction

![Bar chart showing the final mass of DDE for different conditions:](image)

- **Batch** conditions:
  - DDE + Graphite + Sulfides: 31.9% reduction
  - DDE + Sulfide treated Graphite: 0% reduction
  - DDE + Graphite + Sulfides: 29.7% reduction

- **EC** conditions:
  - DDE + H$_2$S: 0% reduction

Chemical reactions:

\[
\text{DDE(ads)} + \text{H}_2\text{S} \rightarrow \text{DDE+ H}_2\text{S} \quad 31.9\%
\]

\[
\text{DDE(ads)} \quad 0\%
\]

\[
\text{DDE(ads)} + \text{e}^{-} \rightarrow \text{DDE(ads)} \quad 29.7\%
\]
Proposed Role of Pyrogenic Carbon Materials

BC Reacts with Sulfide Forming Surface-bound S Species

BC as Electron Shuttle

H₂S(ads)

DDE(ads) → DDMU + Cl⁻

Reductive dechlorination: DDE to DDMU
Redox Properties of Pyrogenic Carbon Matter

Cao et al., 2012; Klüpfel et al., 2014; Pignatello et al., submitted
# Physical Properties of Pyrogenic Carbon Matter

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Biochar</th>
<th>Graphite Powder</th>
<th>Element Analysis (By weight)</th>
<th>BET Surface Area (m$^2$/g)*</th>
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</thead>
<tbody>
<tr>
<td>550°C</td>
<td>79.32%</td>
<td>100.20%</td>
<td>Carbon</td>
<td>428.5</td>
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<tr>
<td></td>
<td>12.74%</td>
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<td>Oxygen</td>
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<td>3.36%</td>
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<td>&lt;1.0%</td>
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<td>Nitrogen</td>
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<td>700°C</td>
<td>84.64%</td>
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<td>Carbon</td>
<td>291.17</td>
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<td>7.53%</td>
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<td>900°C</td>
<td>90.59%</td>
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<td>Carbon</td>
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<td>0.99%</td>
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<td>Hydrogen</td>
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<tr>
<td></td>
<td>1.00%</td>
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<td>Nitrogen</td>
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</table>

<table>
<thead>
<tr>
<th>Functional Groups ($\mu$mol/g)</th>
<th>Conductivity (S/mm)</th>
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<tbody>
<tr>
<td>Phenolic</td>
<td>550°C</td>
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<tr>
<td>700°C</td>
<td>900°C</td>
</tr>
<tr>
<td>Biochar</td>
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<td>9.65</td>
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</tbody>
</table>
Physical Properties of Pyrogenic Carbon Matter

![Bar chart showing reaction rates of DDT, DDD, and DDE for 550 °C Biochar, 700 °C Biochar, 900 °C Biochar, and Graphite Powder.]

- **550 °C Biochar**
- **700 °C Biochar**
- **900 °C Biochar**
- **Graphite Powder**

14 g/L of biochars and graphite and 5 mM sulfide.

Reaction rates follow the same trend as conductivity.
Environmental Relevance: Natural Organic Matter

Natural Organic Matter (Suwannee River NOM, 2 mg/L) slowed down the DDX degradation:

- 61% for DDT
- 33% for DDD
- 18% for DDE
Conclusions

Pyrogenic carbon matter can promote DDX decay by sulfide and generate lower toxicity products.

DDT/DDD and DDE underwent two different reaction pathways.

Conductivity of black carbon is important in the observed reaction.

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