Occurrence and Distribution of Oxygenated Polycyclic Aromatic Hydrocarbons (Oxy-PAHs) in Soils of an Australian Industrial City

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Presentation Outline

- Introduction
- Methods
- Results
- References
Introduction

Ubiquitous in the Environment

Toxic to Biota

Focus of Environmental Regulatory Agencies
Polycyclic Aromatic Compounds (PACs)

Polar Polycyclic Aromatic Compounds (POLAR PACs)

- Oxygenated PAHs
- Oxy-PAHs

- Nitrated PAHs (NPAHs)

Other Polycyclic Aromatic Compounds

- N/S/O heterocycles

Not Only PAHs…
Polycyclic Aromatic Compounds

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Time to Say Goodbye to the 16 EPA PAHs? Toward an Up-to-Date Use of PACs for Environmental Purposes

Jan T. Andersson & Christine Achten
Greater mobility and bioavailability...

...Volatilisation

Diffusion of more hydrophobic polar PAHs into rubbery and glassy soil organic matter (Non-bioavailable fraction)

Microbial Degradation

Leaching of less hydrophobic/bioavailable polar PAHs into sub-soil and underground water

Increased environmental and human health risk?

Idowu et al., 2019a
Direct toxic effects...

Absorption
- Skin and lungs
- Gastrointestinal tract

Distribution
- Cells
- Tissues

Storage
- Kidneys, liver and adipose tissues
- Spleen adrenal glands and ovary

Metabolism
To increase contaminant polarity and facilitate excretion

Excretion
Final stage of the elimination process of polar and non polar PAHs from the body

Direct toxic effects (Oxy-PAHs and N-PAHs)

Indirect toxic effects (Homocyclic and Heterocyclic PAHs)

Oxidative Protein Damage
DNA Damage
Lipid Peroxidation
DNA Adducts Formation

Idowu et al., 2019a
Aerobic Bioremediation of PAH Contaminated Soil Results in Increased Genotoxicity and Developmental Toxicity

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Supporting Information

ABSTRACT: The formation of more polar and toxic polycyclic aromatic hydrocarbon (PAH) transformation products is one of the concerns associated with the bioremediation of PAH-contaminated soils. Soil contaminated with coal tar (prebioremediation) from a former manufactured gas plant (MGP) site was treated in a laboratory scale bioreactor (postbioremediation) and extracted using pressurized liquid extraction. The soil extracts were fractionated, based on polarity, and analyzed for 88 PAHs (unsubstituted, oxygenated, nitrated, and heterocyclic PAHs). The PAH concentrations in the soil treated, postbioremediation, were lower than their regulatory maximum allowable concentrations (MACs), with the exception of the higher molecular weight PAHs (BaA, BbF, BbF, BaP, and IcdP), most of which did not undergo significant biodegradation. The soil extract fractions were tested for genotoxicity using the DT40 chicken lymphocyte bioassay and developmental toxicity using the embryonic zebrafish (Danio rerio) bioassay. A statistically significant increase in genotoxicity was measured in the unfraccionated soil extract, as well as in four polar soil extract fractions, postbioremediation (p < 0.05). In addition, a statistically significant increase in developmental toxicity was measured in one polar soil extract fraction, postbioremediation (p < 0.05). A series of morphological abnormalities, including peculiar caudal fin malformations and hyperpigmentation in the tail, were measured in several soil extract fractions in embryonic zebrafish, both pre- and postbioremediation. The increased toxicity measured postbioremediation is not likely due to the 88 PAHs measured in this study (including quinones), because most were not present in the toxic polar fractions and/or because their concentrations did not increase postbioremediation. However, the increased toxicity measured postbioremediation is likely due to hydroxylated and carboxylated transformation products of the 3- and 4-ring PAHs (PHE, 1MPHE, 2MPHE, PRY, BaA, and FLA) that were most degraded.
Soil sampling Locations

Idowu et al., 2019b
Exhaustive Extraction

Fractionation and Clean-up

Soil Sampling

Consult Idowu et al., 2019b for detailed methodology

GC/MS Analysis
RESULTS AND DISCUSSION
<table>
<thead>
<tr>
<th>Soil ID</th>
<th>pH(CaCl₂)</th>
<th>EC(μS/cm)</th>
<th>TOC%</th>
<th>Sand%</th>
<th>Clay %</th>
<th>Silt%</th>
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<tbody>
<tr>
<td>RI</td>
<td>5.86</td>
<td>150.4</td>
<td>5.20</td>
<td>87.6</td>
<td>4.1</td>
<td>8.3</td>
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<tr>
<td>R2</td>
<td>5.58</td>
<td>491</td>
<td>12.29</td>
<td>49.6</td>
<td>18.1</td>
<td>32.4</td>
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<tr>
<td>R3</td>
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<td>467</td>
<td>3.43</td>
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<td>8.3</td>
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<td>S1</td>
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<td>267</td>
<td>5.27</td>
<td>71.1</td>
<td>10.1</td>
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<td>7.13</td>
<td>97.8</td>
<td>1.13</td>
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<tr>
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<tr>
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<td>1.46</td>
<td>81.6</td>
<td>12.3</td>
<td>6.1</td>
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Percent contribution of PAHs and oxy-PAHs to total concentrations per land use
Concentrations (µg/g) of oxy/parent PAHs in Newcastle soils

<table>
<thead>
<tr>
<th></th>
<th>$\Sigma 7\text{oxy-PAHs}$</th>
<th>$\Sigma 13\text{PAHs}$</th>
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</thead>
<tbody>
<tr>
<td>Industrial</td>
<td>3.9</td>
<td>94.5</td>
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<tr>
<td>Recreational</td>
<td>1.5</td>
<td>20.5</td>
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<tr>
<td>Smoking</td>
<td>0.6</td>
<td>4.7</td>
</tr>
<tr>
<td>Residential</td>
<td>3.1</td>
<td>5.4</td>
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</table>
Concentration profile of oxy/parent PAHs
## Reported occurrence levels of oxy-PAHs (mean concentrations ng/g d.w.)

<table>
<thead>
<tr>
<th>Analyte</th>
<th>This study</th>
<th>Other studies</th>
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<tbody>
<tr>
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<td>Industrial soil</td>
<td>Smoking zone soil</td>
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<tr>
<td>1,4-NQ</td>
<td>705</td>
<td>163</td>
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<td>9-FLO</td>
<td>783</td>
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<td>9,10-ANQ</td>
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<td>2-EAQ</td>
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<td>2-MAQ</td>
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<td>7H-BANT</td>
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</table>
Conclusion

• Concentrations of oxy-PAHs in soils were much lower than that of parent PAHs across all the land uses.
• Analysed soil concentrations of oxy-PAHs were comparatively higher than concentrations from agricultural, urban and industrial areas of other parts of the world.
• Analysed soil concentrations of oxy-PAHs were lower than concentrations in historically contaminated soils such as former gaswork and superfund sites.
• High oxy-PAH concentrations in soils across land uses may have high implications from the perspective of human health risks.
References


5. Wei, C.; Bandowe, B. A. M.; Han, Y.; Cao, J.; Zhan, C.; Wilcke, W., Polycyclic aromatic hydrocarbons (PAHs) and their derivatives (alkyl-PAHs, oxygenated-PAHs, nitrated-PAHs and azaarenes) in urban road dusts from Xi'an, Central China. *Chemosphere* 2015, 134, 512-520.


Acknowledgement
Thank you for listening.