Watershed-scale modeling of the Fate and Transport of Polycyclic Aromatic Hydrocarbons (PAHs)

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Polycyclic Aromatic Hydrocarbons:

Hydrocarbons-organic compounds that composed of multiple aromatic rings
Polycyclic Aromatic Hydrocarbons: Origins

- Industrial
- Forest fire
- Oil spill
- Volcano
Polycyclic Aromatic Hydrocarbons: Effects

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Conclusion

Deformation of aquatic fauna

Carcinogenesis endocrine disruption

Prenatal Exposures Adversely Affect Fetal Growth and Child Development in the US, Poland and China

PAHs/PAH-DNA adducts:
  a) reduction in birth weight and/or head circumference and child growth (Perera et al., Tang et al.)
  b) developmental deficits (Perera et al., Tang et al.)

ETS: reduction in birth weight and developmental deficits
(Raun et al., Jedrychowski et al.)

Chlorpyrifos (pesticide): reduction in birth weight (Whittem et al.) and developmental deficits (Raun et al.)

Affects fetal growth
Watershed-scale modeling with SWAT and Multimedia modeling

Methodology

SWAT

Multimedia modeling

Runoff

Sediment

Nutrients and pesticide

Bacteria transport

Air

Soil

Water

Fugacity Based Calculation

Wet deposit

Dry deposit

Input Flux

Output Flux
Fate and transport of PAHs

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Fate and transport of PAHs

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**Conclusion**

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**Dry deposition** (only particle)

\[
F_{dry,p} = V_D \times C_{air,p}
\]

- \(V_D\): the dry deposition velocity
- \(C_{air,p}\): the particle-bound concentration per volume of air [ng m\(^{-3}\)].

**Wet deposition (rain)** (gas and particle)

\[
F_{rain,g} = W_{rain,g} \times G_R \times C_{air,g}
\]

\[
F_{rain,p} = W_{rain,p} \times G_R \times C_{air,p}
\]

- \(W\): the washout ratio
- \(G_R\): the precipitation rate [m d\(^{-1}\)]
- \(C_{air}\): the concentration in air [ng m\(^{-3}\) of air]

The subscripts \(g\) and \(p\) stand for gas and particle-bound,
Air-soil exchange
(dry gaseous deposition and volatilisation)

The air-soil exchange fluxes are calculated here using the fugacity approach. Fugacity can also be seen as “escaping tendency” and depends on the concentration of the chemical in the different compartments as well as temperature and the properties of the chemical and the compartment

\[ C = Z \times f \]

Fugacity \( (f \text{[Pa]}) \) is related to concentration \( (C \text{[mol m}^{-3}]) \) through the Z-value (fugacity capacity) \( ([\text{mol m}^{-3} \text{ Pa}^{-1}]) \)
Fate and transport of PAHs

Air-soil exchange
(dry gaseous deposition and volatilisation)

Fugacity capacities for air ($Z_a$) and soil ($Z_s$) are calculated as follows:

\[
Z_a = \frac{1}{RT}
\]

\[
Z_s = f_{OC} K_{OC} \rho Z_w
\]

\[
Z_w = \frac{1}{H}
\]

$R$ : the ideal gas constant (Pa m$^3$ mol$^{-1}$ K$^{-1}$);
$T$ : the absolute temperature (K),
$f_{OC}$ : the fraction organic carbon in the soil,
$\rho$ : the soil density (kg L$^{-1}$).
$K_{OC}$ : the organic carbon-water partition coefficient (L kg$^{-1}$)
$Z_w$ : the fugacity capacity for water (mol m$^{-3}$ Pa$^{-1}$)
$H$ : the Henry’s Law constant (Pa m$^{-3}$ mol$^{-1}$)
Air-soil exchange
(dry gaseous deposition and volatilisation)

\[ N = D_v (f_s - f_a) \]

\( D_v \) (mol Pa\(^{-1}\) h\(^{-1}\)) : the overall D-value for transport across the soil/air interface.
\( N \) : net diffusive flux (mol h\(^{-1}\))
The PAH loading that ended up in the river was determined using the equation:

\[ C_{bs}^p = f_p \times W_{cp} \times \exp(-\mu_p) \]

\[ C_{bs}^{fd} = f_d^f \times W_{cf} \times \exp(-\mu_f) \]

\[ C_{bs}^{DOC} = f_d^{DOC} \times W_{cDOC} \times \exp(-\mu_{DOC}) \]

\[ \mu = \mu_i \times \theta^{(T-20)} \]

\[ f_p [-]: \text{fraction}, \ W_{cp}: \text{washoff load [kg-L}^{-1} \text{bulk soil]}, \ \mu_p: \text{rate constant [s}^{-1}] \ - \text{particle-bound PAH}, \]

\[ f_d^f [-], \ W_{cf}[\text{kg-L}^{-1} \text{bulk soil}], \ \mu_f[\text{s}^{-1}] \ - \text{freely-dissolved PAH}, \]

\[ f_d^{DOC} [-], \ W_{cf}[\text{kg-L}^{-1} \text{bulk soil}], \ \mu_{DOC}[\text{s}^{-1}] \ - \text{DOC-bound PAH}. \]
The fractions of particle-bound PAH, DOC-bound PAH, free-dissolved PAH

\[
fp = \frac{r_{sw}K_{sw}}{r_{sw}K_{sw} + 1 + [DOC]K_{DOC}} \quad fd = \frac{1}{r_{sw}K_{sw} + 1 + [DOC]K_{DOC}} \quad fd^{DOC} = \frac{[DOC]K_{DOC}}{r_{sw}K_{sw} + 1 + [DOC]K_{DOC}}
\]

\(r_{sw}\): the soil-to-water ratio [kg-m\(^{-3}\)], \(K_{sw}\): the soil-water distribution coefficient [L-kg\(^{-1}\)],
\(K_{DOC}\): the dissolved organic carbon-water partition coefficient [L-kg\(^{-1}\)],
\([DOC]\): concentration of DOC (kg/L)
PAH loadings of the model were computed by below equation:

\[ C_p = \frac{C_{bs}^p - C_{bs\_out}^p}{\rho} \quad C_w = C_{bs}^d + C_{bs\_out}^p \quad C_{w\_final} = \text{coeff}_{enratio,1} \times (C_w)^{\text{coeff}_{enratio,2}} \]

- \(C_p\): PAH loadings in soil (PAH per solid mass)
- \(C_w\): PAH loadings in water
- \(C_{w\_final}\): the final PAH loading in water, the two \(\text{coeff}_{enratio}\) : the enrichment ratio coefficients
Fate and transport of PAHs

The modified advection-dispersion equation

\[
\frac{\partial C}{\partial t} + u \frac{\partial C}{\partial x} = D_L \frac{\partial^2 C}{\partial x^2} - C \left( f \frac{v_s}{h} + aI \right) + N_{aw}
\]

- \( C \): concentration of PAH compounds in water \([g\cdot m^{-3}]\), \( t \): time \([t]\),
- \( x \): distance \([m]\), \( u \): the velocity of the water \([m\cdot s^{-1}]\),
- \( D_L \): the dispersion coefficient \([m^2\cdot s^{-1}]\), \( f \): the fraction of the particulate PAH in water,
- \( v_s \): the settling velocity \([m\cdot s^{-1}]\), \( h \): the depth of the channel \([m]\),
- \( a \): the photodegradation coefficient \([m^2\cdot MJ^{-1}\cdot s^{-1}]\), \( I \): the solar intensity \([MJ\cdot m^{-2}]\).
- \( N_{aw} \): the water-air exchange of PAH \([g\cdot m^{-3}\cdot s^{-1}]\).
Study area

Legend
- Air monitoring station
- Soil monitoring station
- Water monitoring station
- River
- Subbasin
- Deciduous Forest
- Water
- Urban
- Agriculture
- Pasture
- Mixed Forest
- Rice
- Crop

0 5 10 Kilometers
SWAT Model Streamflow

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# Sensitivity analysis of PAHs

<table>
<thead>
<tr>
<th>No.</th>
<th>Parameter</th>
<th>Definition</th>
<th>Unit</th>
<th>Soil phase</th>
<th>Water phase</th>
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<tr>
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</tbody>
</table>
PAHs in soil
PAHs in soil

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PAHs in soil

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2011

2012
PAHs in water

3 Rings

4 Rings

5 Rings

6 Rings

Load (g)

Load (g)

Load (g)

Load (g)
1. Sensitivity analyses of the PAH soil and PAH water parameters were able to determine the critical processes in TR watershed: degradation, deposition, volatilization, and washoff mechanism.

2. The simulated temporal pattern of the PAH compounds revealed that PAH loadings on soil peaked at colder seasons and dropped in summer. PAH loadings in water yielded varying peaks throughout the year but generally peaked in summer.

3. Spatial distribution of PAH concentrations in the watershed was mapped out. The model was able to reveal urbanized subbasins in the watershed by spatially distributing the simulated PAH concentrations of each subbasin in the map.
Thank you!