A comparison of the loss of polycyclic hydrocarbons (PAHs) in soil and in the atmosphere

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Introduction: Polycyclic aromatic hydrocarbons

- Polycyclic aromatic hydrocarbons (PAHs) constitute a class of hazardous organic chemicals consisting of two or more aromatic rings
- PAHs, as persistent organic pollutants (POPs) are ubiquitous in soil and the atmosphere

- PAH are degraded in soil mostly by biodegradation and in atmosphere by oxidation reactions

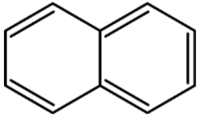
Research questions

- What PAH fraction is consumed in soil vs atmosphere

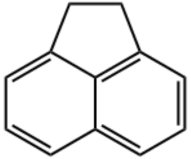
- How important are the transport processes (evaporation/absorption) of PAHs between soil vs atmosphere to determine their environmental loss

Most volatile

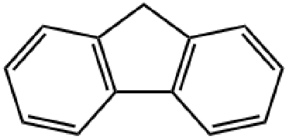
Least volatile



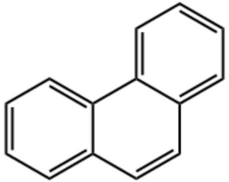
Naphtalene
NAP
128 g mol^{-1}



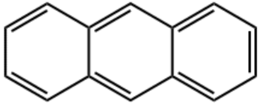
Acenaphtene
ACE
154 g mol^{-1}



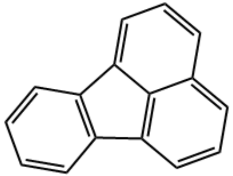
Fluorene
FLU
166 g mol^{-1}



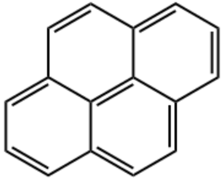
Phenanthrene
PHE
178 g mol^{-1}



Anthracene
ANT
178 g mol^{-1}

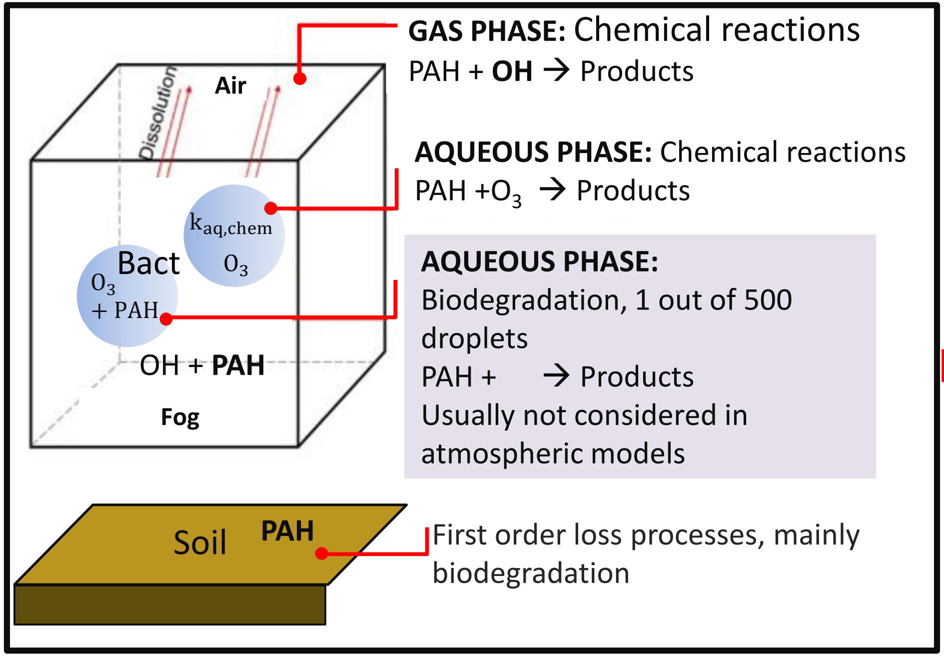


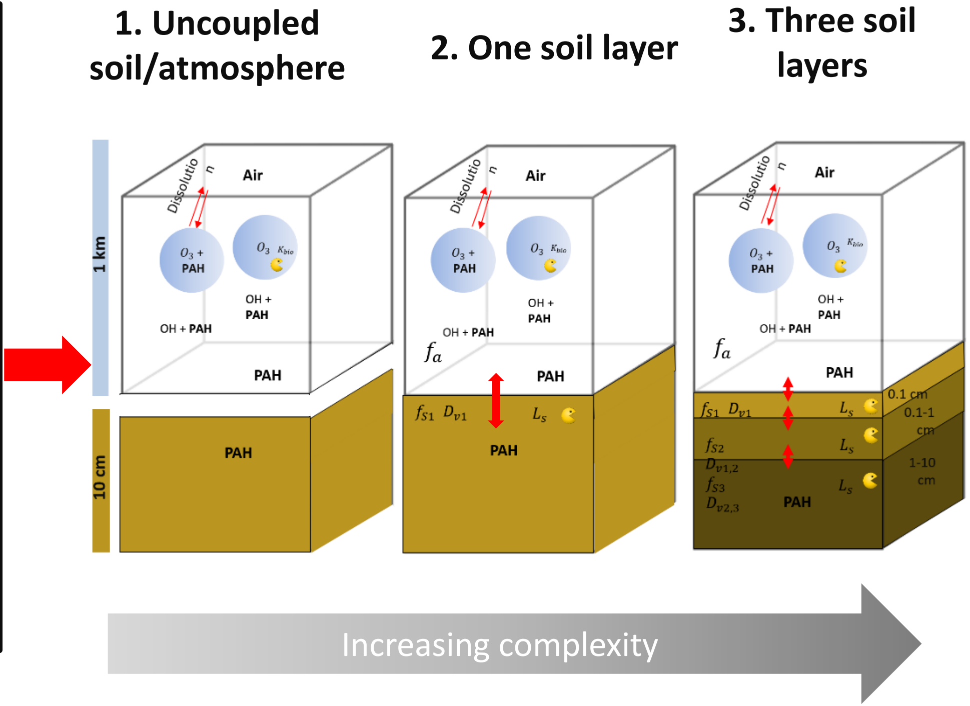
Fluoranthene
FLUT
202 g mol^{-1}



Pyrene
PYR
202 g mol^{-1}

3 box model approaches of soil and atmospheric losses





- Simulations: 12 h
- Volume(atmosphere) = 10 000 Volume(soil)
- Fog liquid water content: 1 g m^{-3}; N_{drop} = 250 cm^{-3}

PAH reactivity in different compartments and phases

Soil: PAH → products k^{1st} (lit)

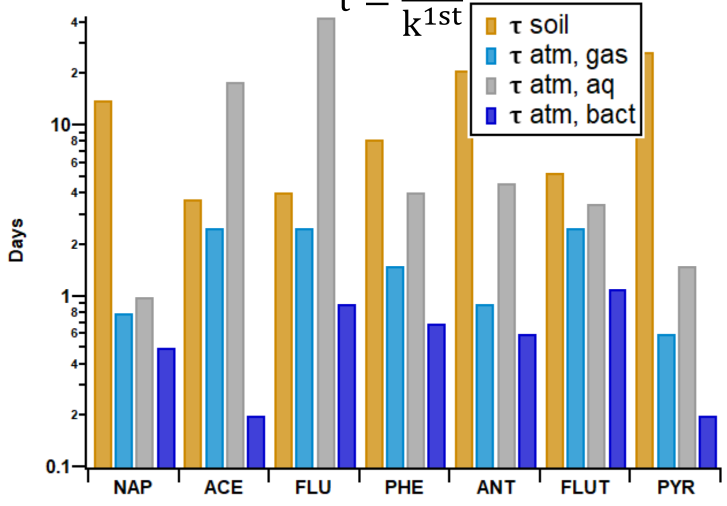
Atmosphere: gas phase: PAH + OH → Prod ; $k^{1st} = k^{2nd} \cdot 10^6\ cm^{-3}$

aq phase: PAH + O_3 → Prod ; $k^{1st} = k^{2nd}[5 \cdot 10^{-10}\ M]$

PAH + bacteria → Prod ; $k^{1st} = k_{bact} \cdot 5 \cdot 10^8$ cells L^{-1}]

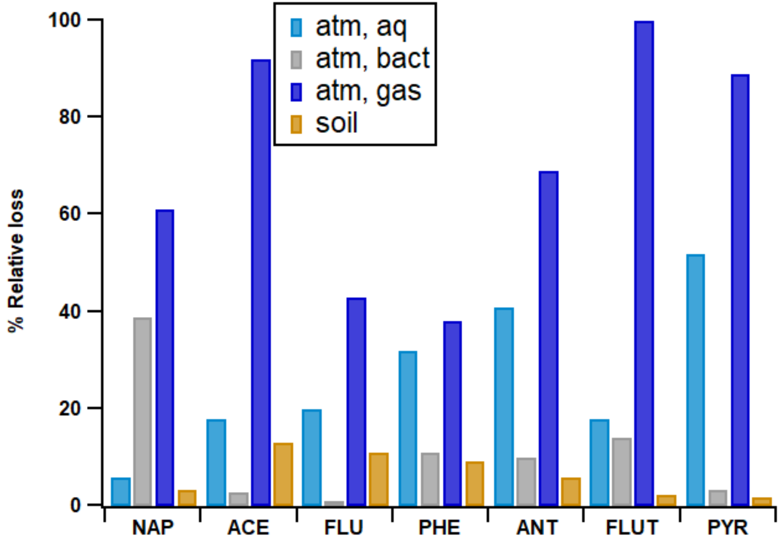
Lifetime τ [days]

$$\tau = \frac{1}{k^{1st}}$$



Lifetime in the atmospheric gas phase is the shortest compared to other processes

Relative loss [%] of concentration related to initial concentration in atmospheric gas and aqueous phase and in soil

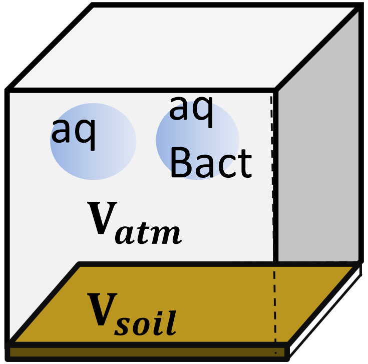


- Up to 100% of PAHs are lost in the atmospheric gas phase after 12 h
- Fraction lost in soil: ≤ 12%

Fractions in soil and the atmosphere

Volume fraction

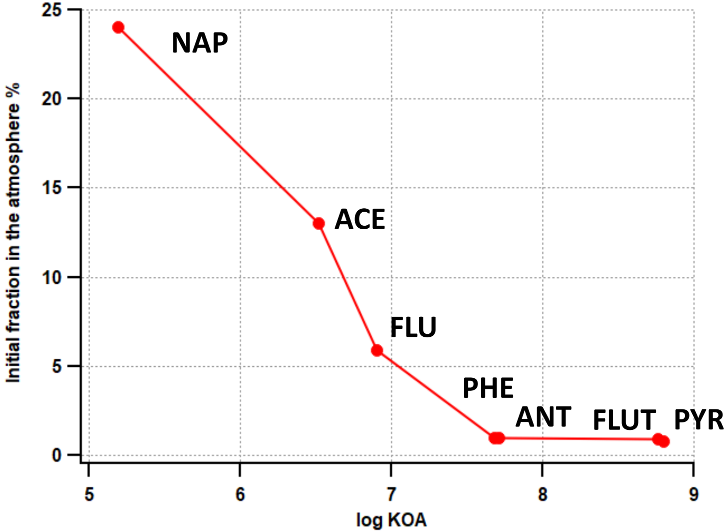
Volume (soil) = 10^{-4} Volume (atmosphere)



Volume (atmosphere)
= $10^6 \cdot$ Volume(droplets)
= $2 \cdot 10^{-9}$ = Volume (droplets w bacteria)

PAH fraction

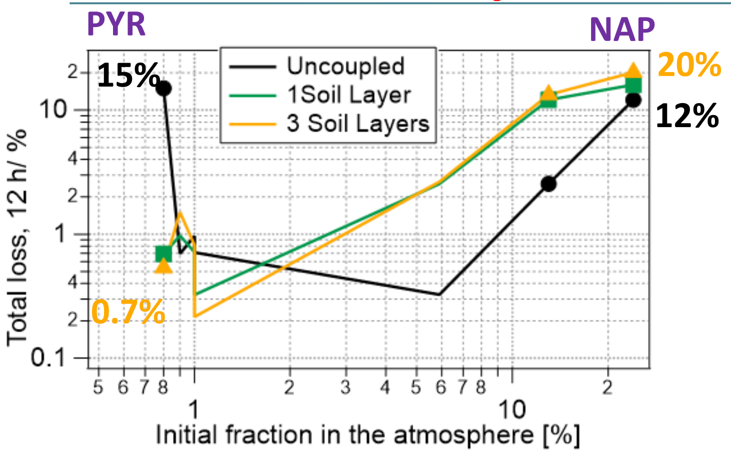
$$Fr_{atm}\,[\%] = \frac{C_{0,atm}}{C_{0,atm} + C_{0,soil}} \cdot 100\,\%$$

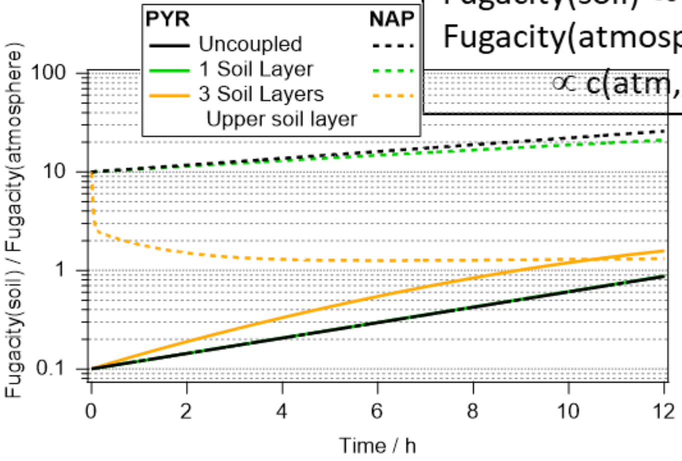


PAH fraction in soil ≥ 75 - 99 %
PAH fraction in droplets << 1% (not shown)

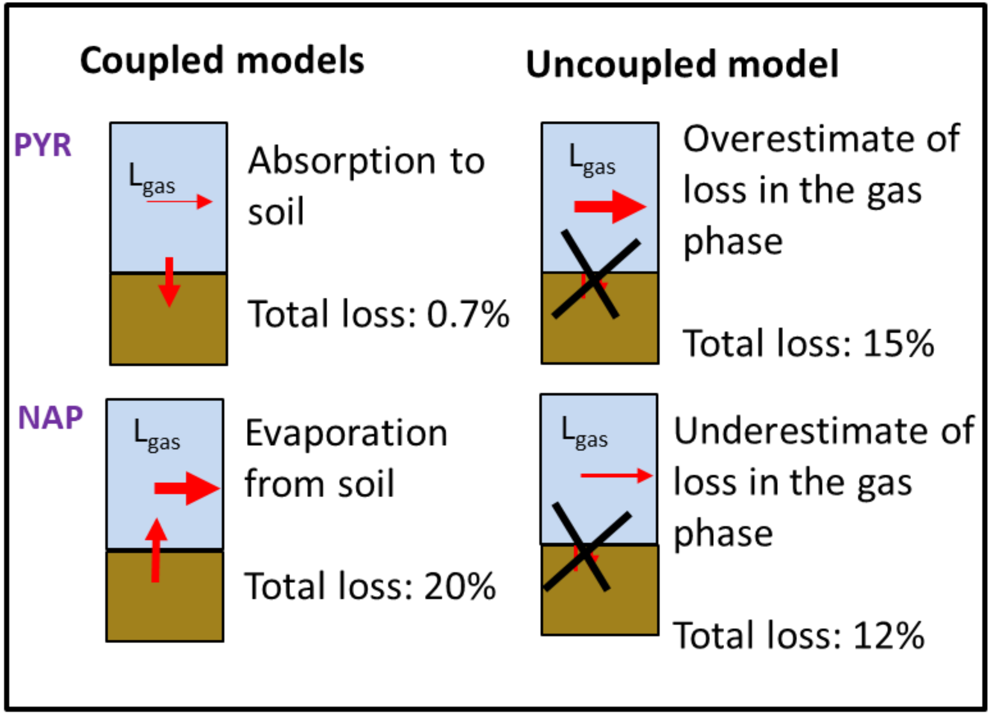
Total PAH loss (soil + atmosphere) and fugacities

$$L_{tot,12h}\,[\%] = \frac{C_{tot,0} - C_{tot,12}}{C_{tot,0}} \cdot 100\,\% \quad \text{where } C_{tot} = C_{soil} + C_{gas} + C_{aq} + C_{bio}$$



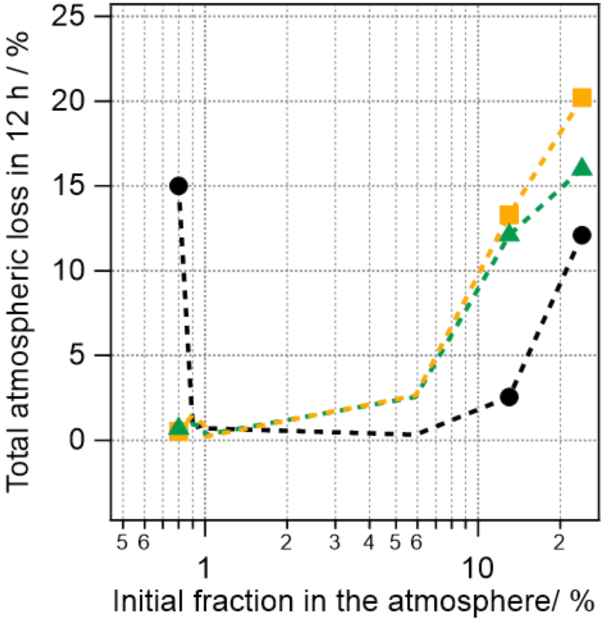


Fugacity(soil) $\propto$ c(soil)
Fugacity(atmosphere) $\propto$ c(atm,gas)

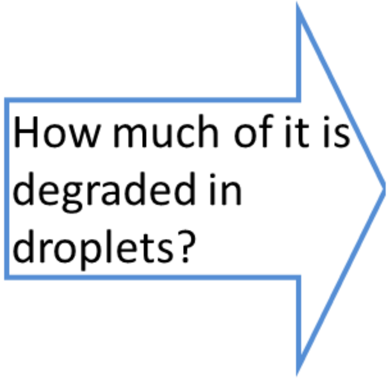


How much PAH is degraded in the atmosphere vs soil ?

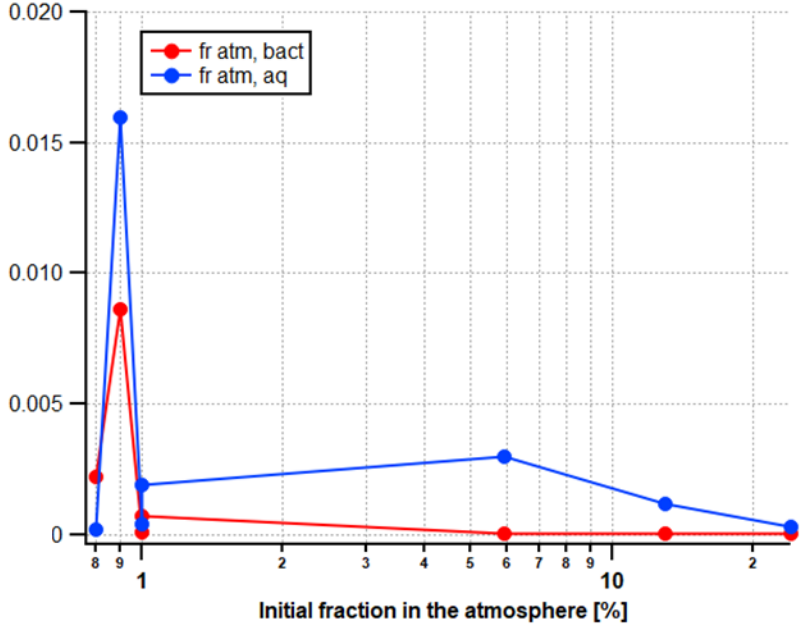
Fraction of total loss [%] in the atmosphere



≥ 85% of degradation of PAHs occurs in soil



Fr aqueous chemistry and biodegradation to loss



- The loss in the atmosphere aqueous phase is negligible (≤ 0.1%)
- Chemical processes and biodegradation contribute approximately equally, even though biodegradation only occurs in 0.2% of the droplets

Conclusions and outlooks

What PAH fraction is consumed in soil vs atmosphere ?

PAH fraction consumed in soil ranged between 14-96 % and in atmosphere from 4-85 %

How important are the transport processes (evaporation/absorption) of PAHs between soil and atmosphere to determine their environmental loss ?

For high volatility PAH (e.g. NAP), loss is underestimated if no evaporation considered

For low volatility PAH (e.g. PYR), loss is overestimated if no absorption considered

Outlook:

- Similar investigations for more soluble compounds → atmospheric biodegradation might be more important
- Sensitivity studies on soil composition
- Consideration of additional processes, e.g. advection, leaching, bioturbation, plants