



Inter-calibrating passive sampling and dosing polymers

based on polymer-polymer partition ratios of PCBs, PAHs and organo-chlorine pesticides

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Equilibrium sampling & passive dosing

> $K_{\text{polymer:water}}$ required to determine $C_{\text{free}} = \frac{C_{\text{polymer}}}{K_{\text{polymer,water}}}$



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- > $K_{\text{polymer:water}}$ not always available
- > $K_{\text{polymer:water}}$ often limits accuracy & precision
 - (1) experimental errors
 - (2) polymer:polymer partitioning differences



Inter-calibration of polymers

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Inter-calibration of polymers

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 - > connect passive sampling & passive dosing
- > calibration of new polymers
 - > monitoring with new polymeric materials of unknown $K_{\text{polymer,water}}$



Calibration

$$\log K_{pol.y,medium} = \log K_{pol.x,medium} + \log K_{pol.y,pol.x}$$

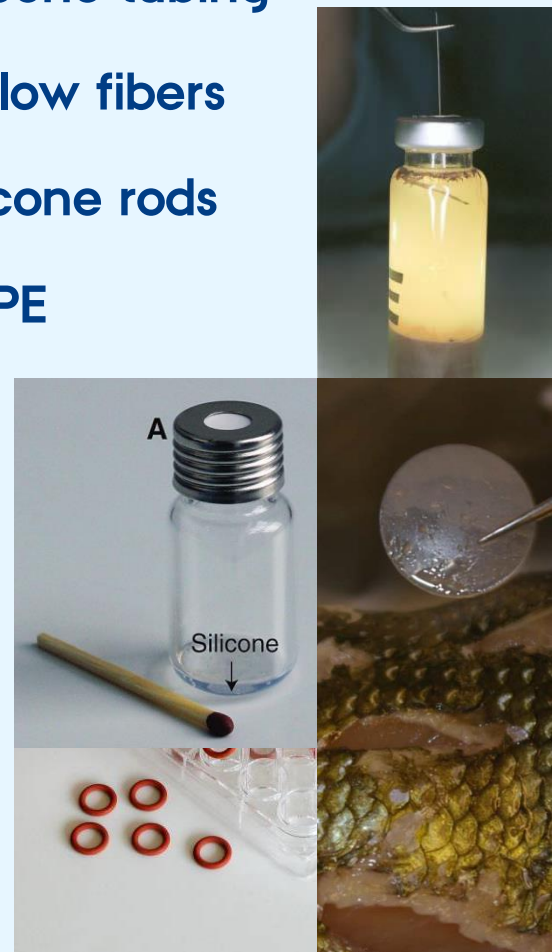
medium: e.g. water, air, lipid

pol.x: reference polymer

pol.y: test polymer

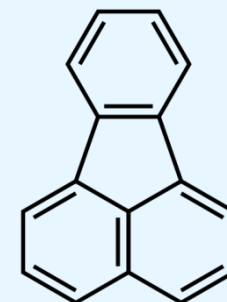
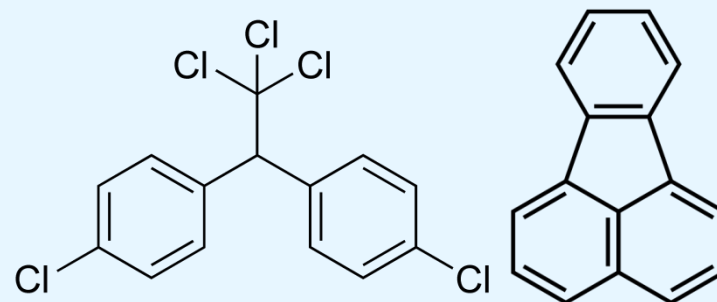
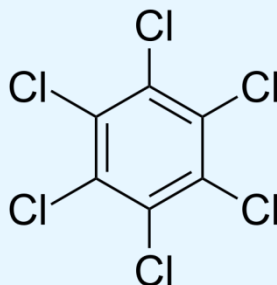
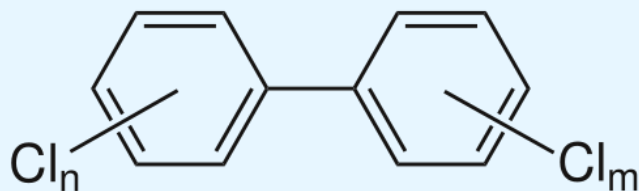
Polymers in passive sampling & dosing

- > **30- μ m PDMS fiber** (Polymicro Techn.)
- > **10- μ m PDMS fiber** (Fiberguide Ind.)
- > **AlteSil silicone sheet** (Altec)
- > **SSP-M823** (Speciality Silicone Products)
- > **BiscaSil PDMS coated fabric** (Biscor)
- > **PDMS MDX4-4210** (Dow Corning)
- > **PDMS DC1-2577** (Dow Corning)
- > **silicone O-rings** (Altec)
- > **silicone tubing**
- > **hollow fibers**
- > **silicone rods**
- > **LDPE**



Chemicals in this study

- > **25 PCBs + HCB**
- > **HCHs (α , β , γ), o'p-DDT, p'p-DDT, DDEs, p'p-DDD, TNC**
- > **10 PAHs in separate experiment**





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 - > **mass balance for confirmation**



Partitioning experiments

- > **individual silicone pieces (10-500 mg) equilibrated**
 - > $V_{\text{PDMS}(\text{total})} \approx 1 \text{ mL}$
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- > $K_{\text{pol.x,pol.y}} = \frac{C_{\text{pol.x}}}{C_{\text{pol.y}}}$



High precision & accuracy of $K_{\text{PDMS,PDMS}}$

> including all $K_{\text{pol.x,pol.y}}$: **70 % with RSD < 5 % (RSE < 2.1 %)**

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- > large RSDs associated with
 - > β -HCH & DDTs (omitted)
 - > $K_{pol:fiber(PM)}$, $K_{pol:fiber(FG)}$!,
 $K_{pol:Biscasil}$!, $K_{pol:hollow fiber}$

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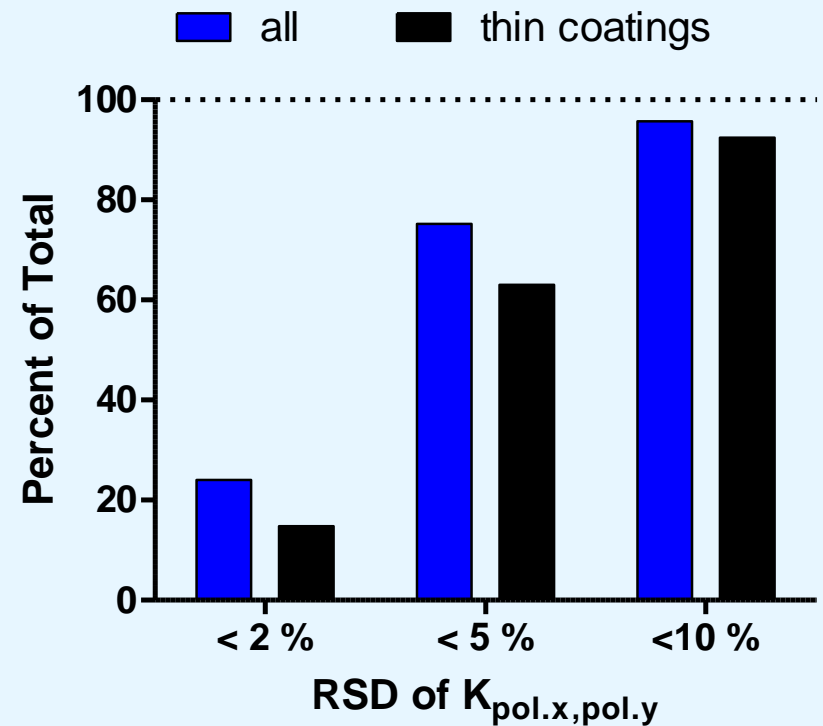
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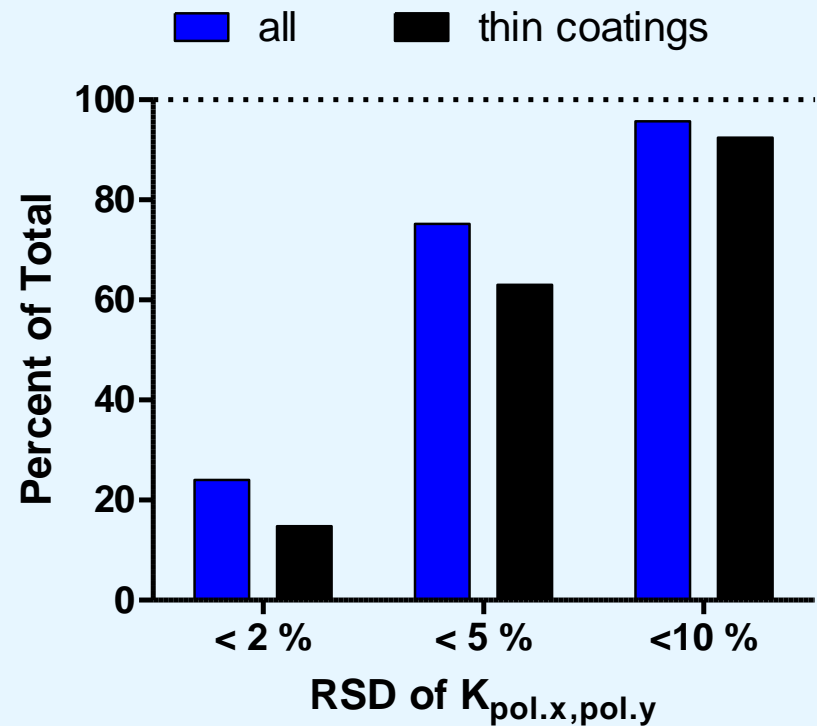
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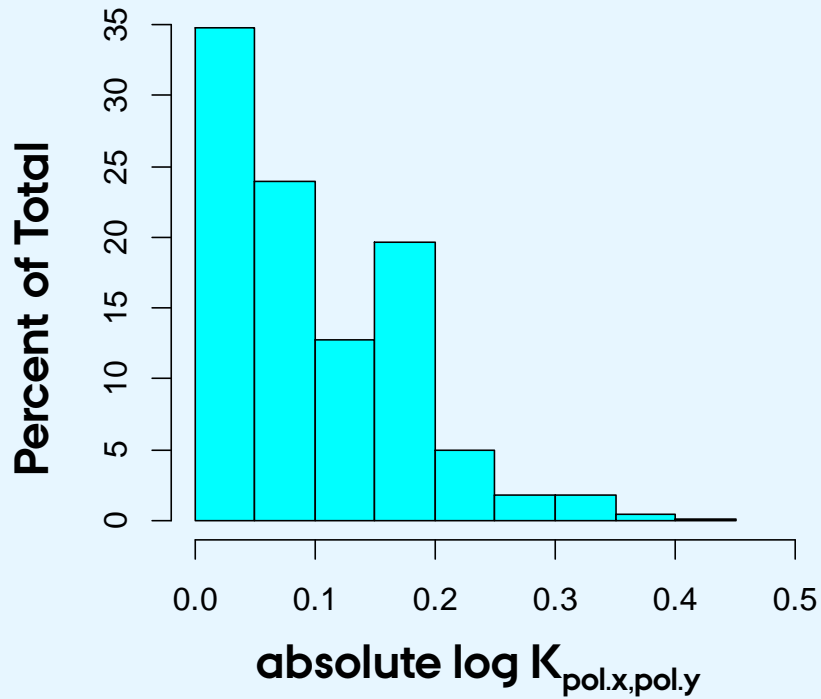
$K_{pol:Biscasil}$!, $K_{pol:hollow fiber}$

> SE of $K_{pol.x,pol.y} \leq \log 0.005$



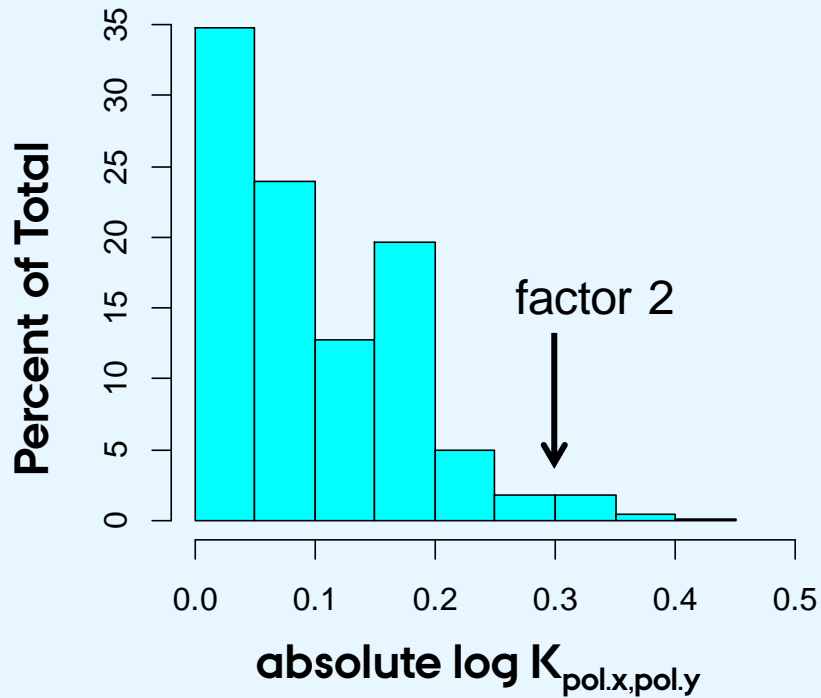


$K_{\text{PDMS,PDMS}}$





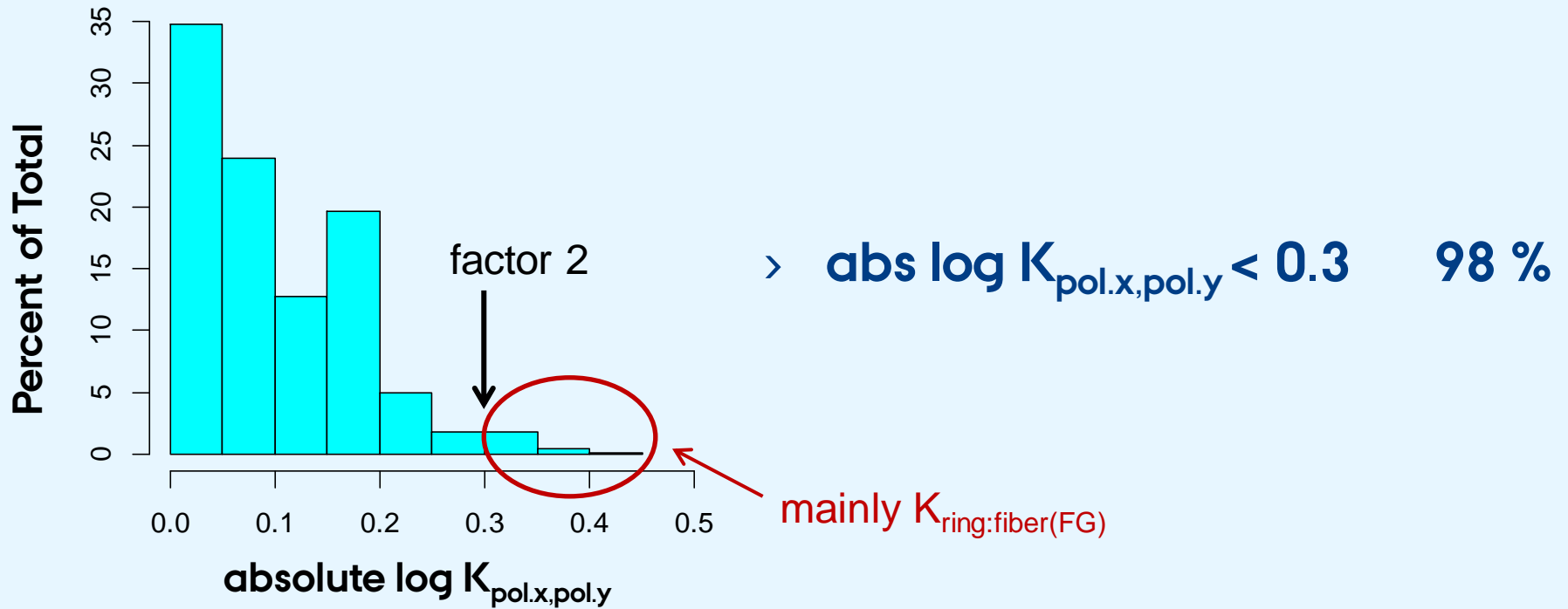
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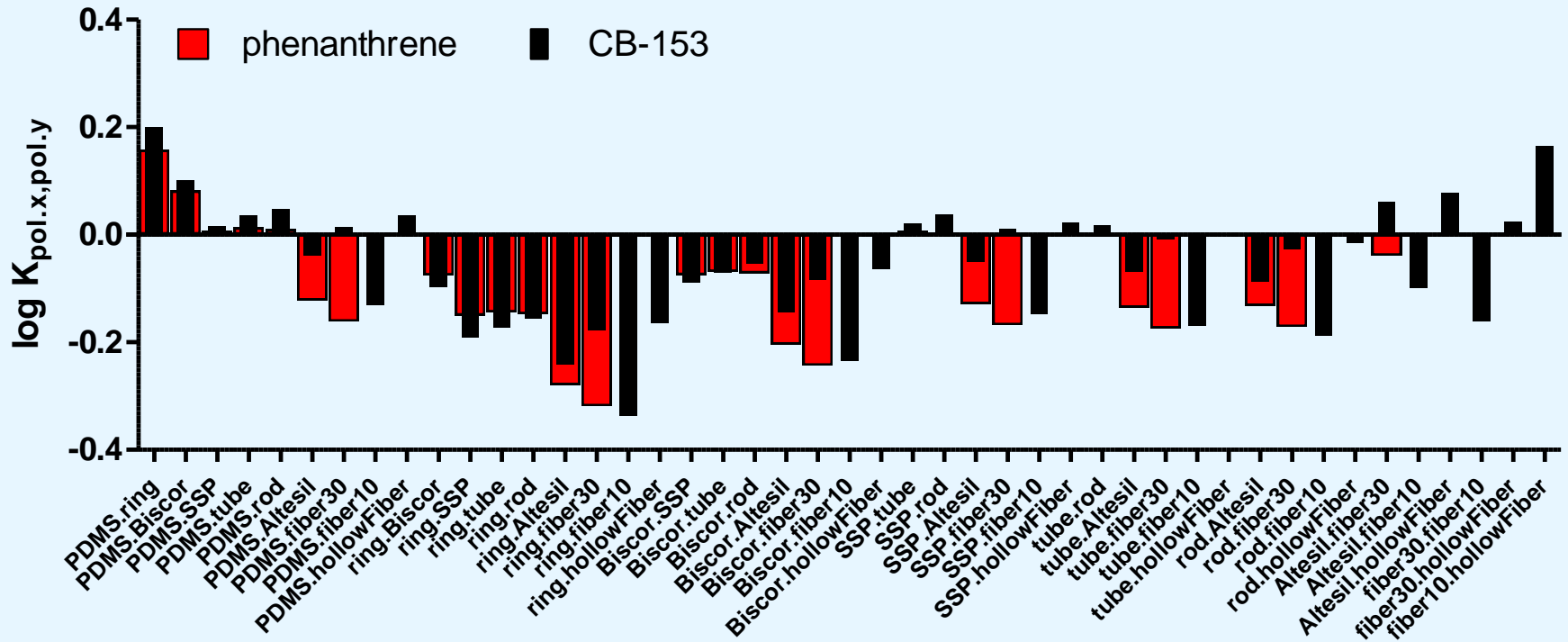
> **$\text{abs log } K_{\text{pol.x,pol.y}} < 0.3$** **98 %**



$K_{PDMS,PDMS}$



Example: phenanthrene & PCB153

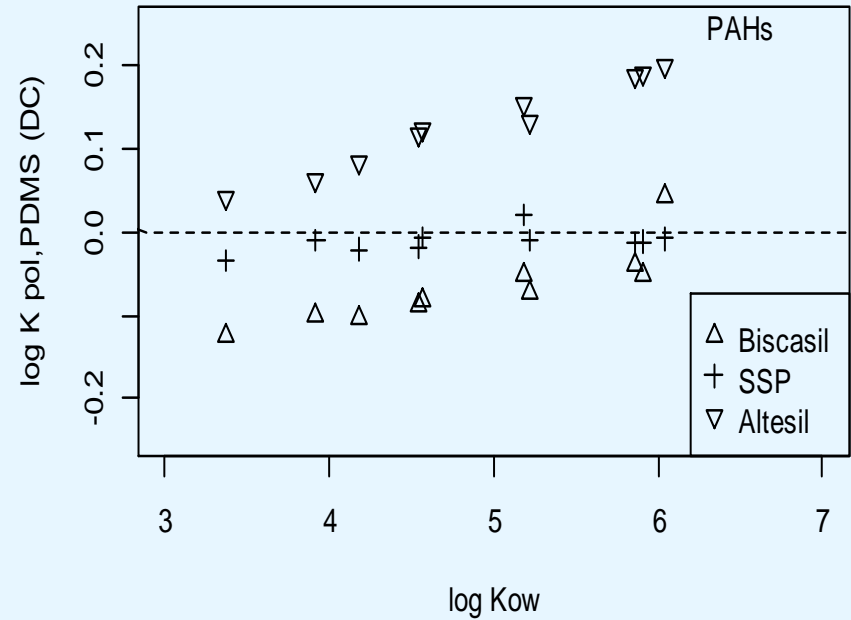
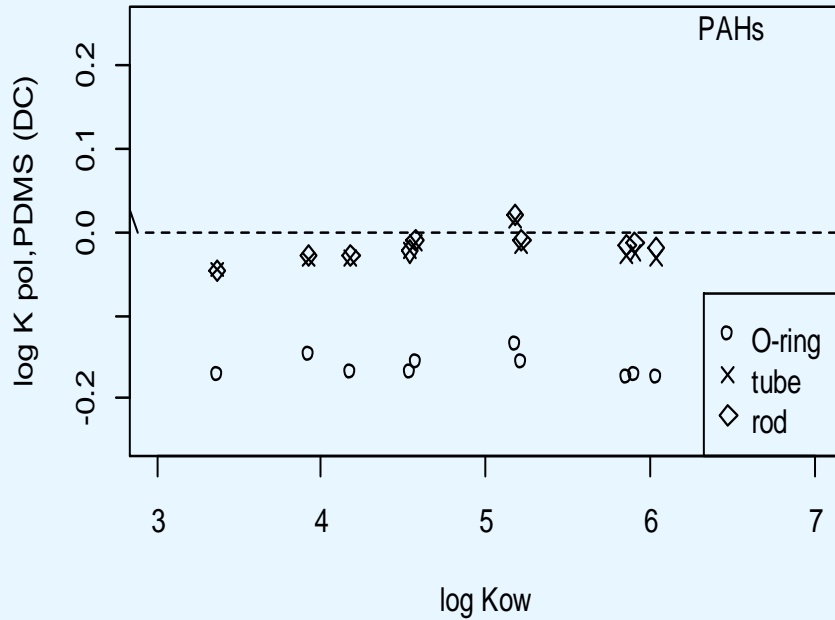




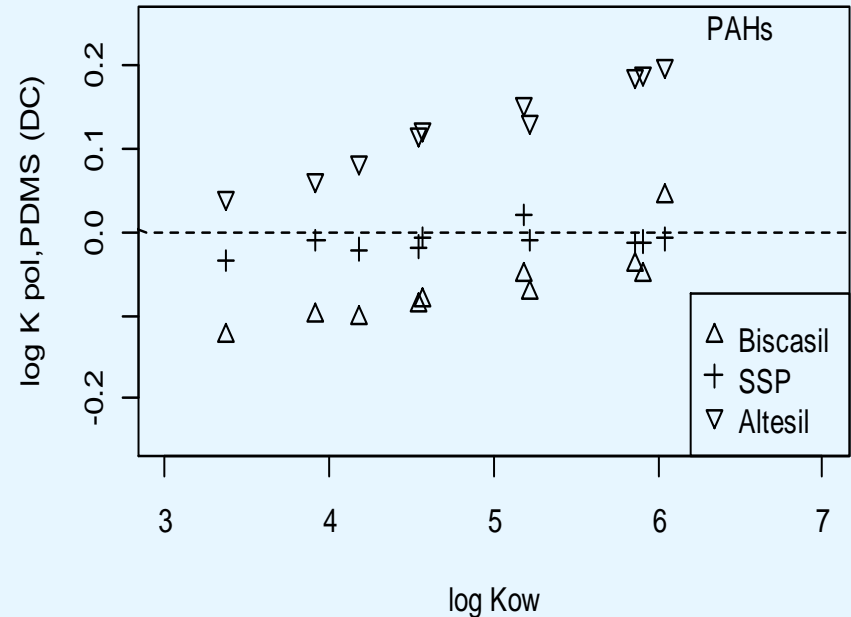
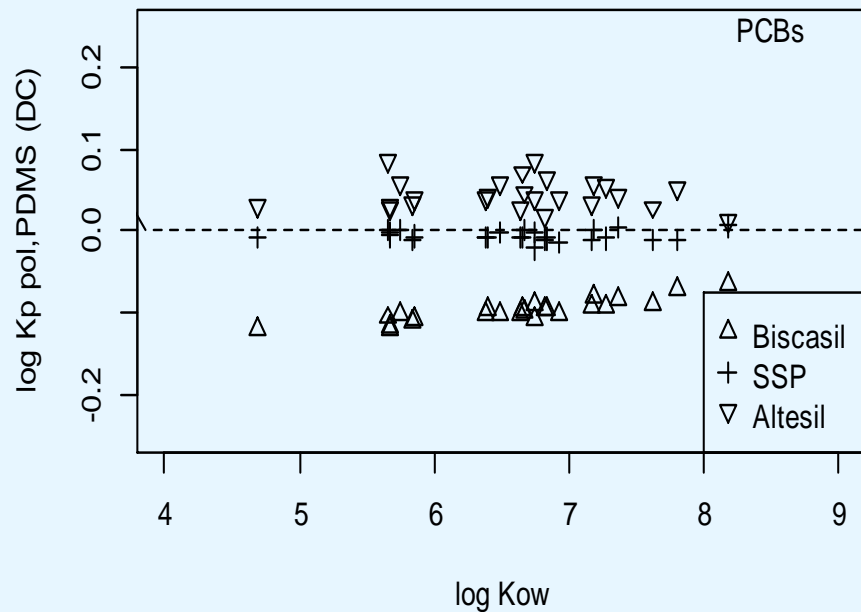
$$K_{\text{PDMS,PDMS}} \neq 1$$

- > **different polymer** → substance-specific
- > **fillers** → not substance-specific
- > **uncertainty in V_{polymer}** → not substance specific

$\log K_{\text{pol.x,pol.y}} - \log K_{\text{ow}}$ relationship

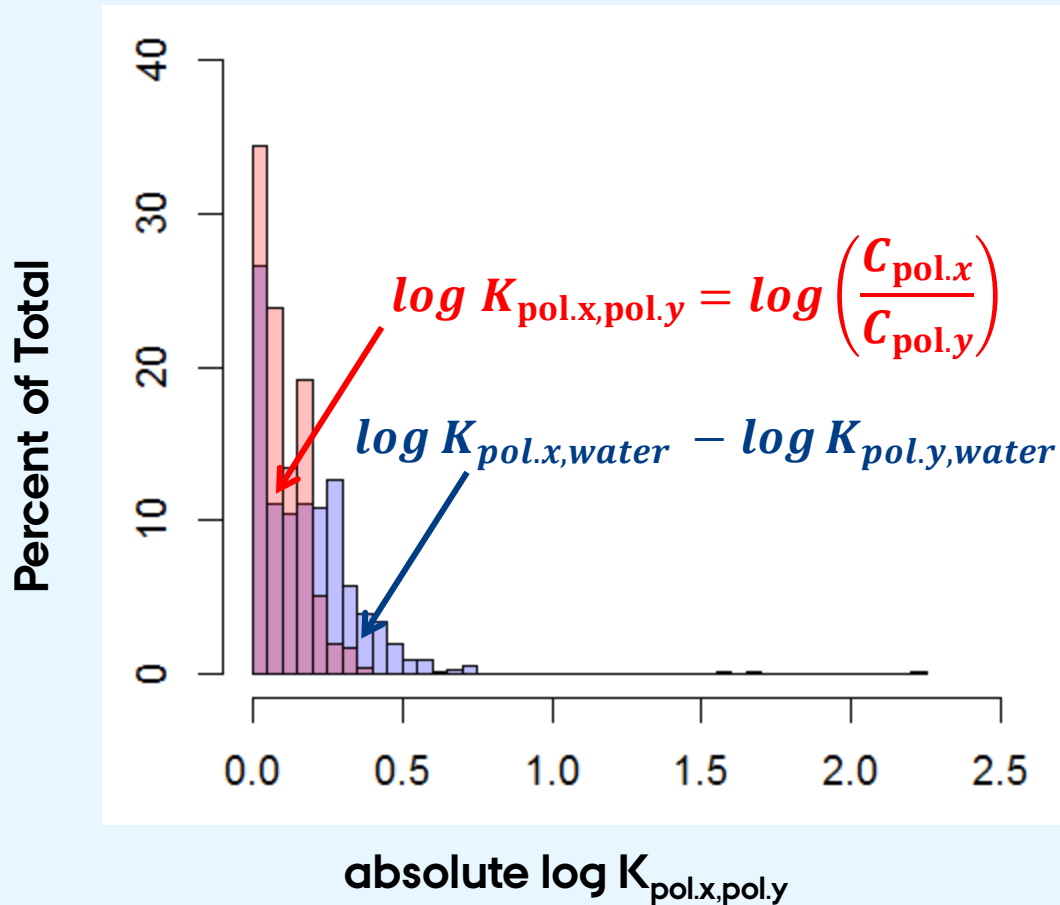


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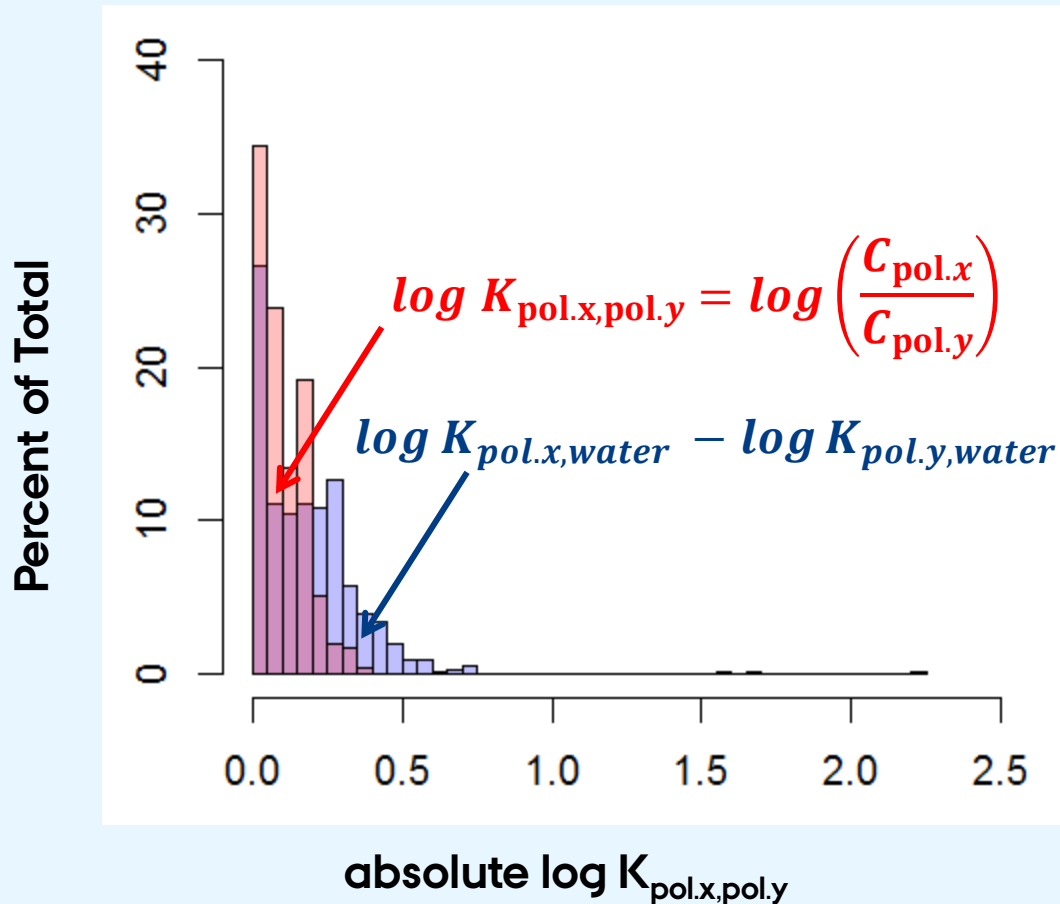


- > diatomic fillers in silicone O-rings
- > higher affinities of some materials for more hydrophobic PAHs

Relevance & implications

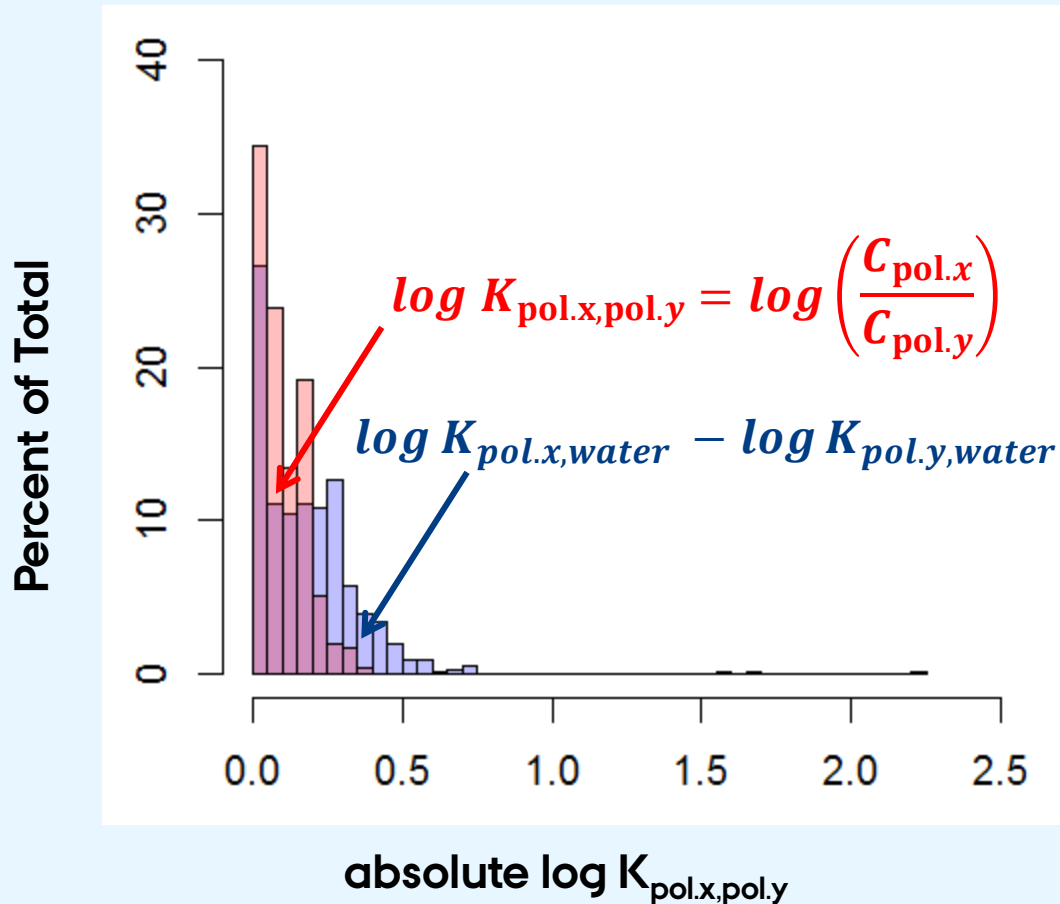


Relevance & implications



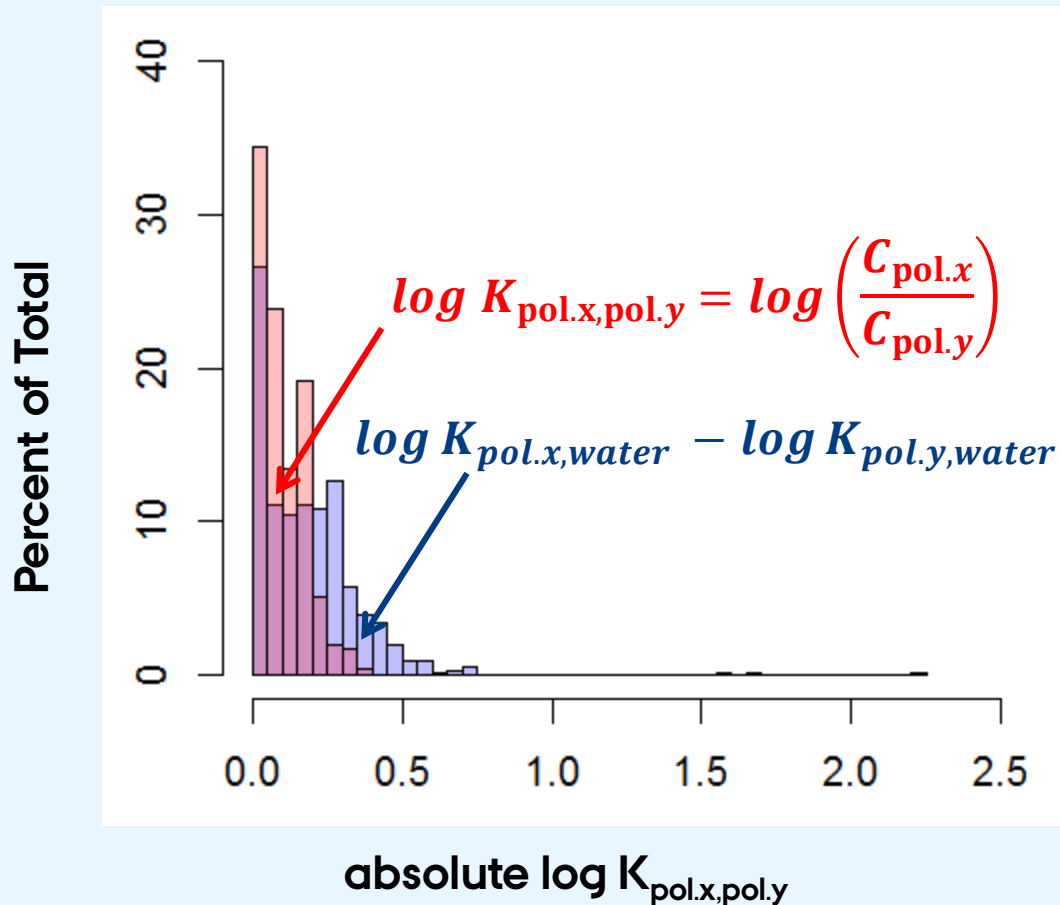
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Relevance & implications



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- > $K_{\text{pol.x,pol.y}}$ allows correction of existing $K_{\text{polymer,water}}$

Relevance & implications



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- > $K_{\text{pol.x,pol.y}}$ allows correction of existing $K_{\text{polymer,water}}$
- > cross-consistency check now possible



Conclusions

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- > **for PDMS $0.5 < K_{\text{pol.x,pol.y}} < 2$ (PAHs, PCBs, OCPs)**



Conclusions

- > **high precision & accuracy of $K_{\text{pol.x,pol.y}}$**
- > **for PDMS $0.5 < K_{\text{pol.x,pol.y}} < 2$ (PAHs, PCBs, OCPs)**
- > **little contribution of $K_{\text{pol.x,pol.y}}$ to uncertainty in $K_{\text{polymer:water}}$**



Thank you for your attention.

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