

Air-Surface Exchange of Persistent Substances

by

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Phases in the Atmosphere

What phases do organic chemicals associate with in the atmosphere?

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- Gas phase
- Particulate matter
- Water
- Ice/Snow

Surfaces in the Environment

Which surfaces are important for exchange of organic chemicals with the atmosphere?

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- Water
- Soil
- Vegetation
- Snow/Ice

Exchange Processes

What processes can transfer organic chemicals from the atmosphere to surfaces?

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What processes can transfer organic chemicals from the atmosphere to surfaces?

- Deposition of water (wet deposition of dissolved chemical)
- Deposition of ice/snow
- Wet deposition of particulate matter
- Dry deposition of particulate matter
- Gaseous deposition

Exchange Processes (II)

What processes can transfer organic chemicals from surfaces to the atmosphere?

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What processes can transfer organic chemicals from surfaces to the atmosphere?

- Aerosol generation
- Volatilisation

Phase Distribution in the Atmosphere

Between the gas phase and water

Phase Distribution in the Atmosphere

Between the gas phase and water

- according to the Henry's Law constant ($K_{AW} = H/RT$)
- Dependent on temperature
- Equilibrium generally reached, but perhaps not locally
- Surface adsorption can contribute to levels in very small water droplets (fog)

Phase Distribution in the Atmosphere (II)

Between the gas phase and particulate matter

Phase Distribution in the Atmosphere (II)

Between the gas phase and particulate matter

- Combination of dissolution, surface adsorption, and absorption in organic matter
- Absorption believed to dominate for POPs, described by $K_{PA} = f_{OC}K_{OC}/K_{AW}$
- Temperature dependent
- Equilibration believed to be rapid, but not much experimental evidence

Phase Distribution in the Atmosphere (III)

Between the gas phase and snow

Phase Distribution in the Atmosphere (III)

Between the gas phase and snow

- Surface adsorption
- Dependent on surface area of snow
- Little experimental evidence on magnitude and kinetics of partitioning

Deposition of Rain and Snow

Dissolved/sorbed chemical

Deposition of Rain and Snow

Dissolved/sorbed chemical

- Surface independent (exception fog)
- Flux is the product of concentration in rain/snow and the rain rate
e.g. $N_{RD} \text{ (mol m}^{-2} \text{ h}^{-1}) = v_R C_{RD} = v_R C_G / K_{AW}$
- What is the relevant temperature?
- Steady state may be a good assumption for compounds with high K_{AW}

Deposition of Rain and Snow

Chemical associated with particulate matter

Deposition of Rain and Snow

Chemical associated with particulate matter

- Surface independent
- Flux is the product of concentration on PM, the rain rate, and the scavenging efficiency Q
e.g. $N_{RP} \text{ (mol m}^{-2} \text{ h}^{-1}\text{)} = v_R QC_P = v_R QC_G K_{PA}$
- Q depends on particle size, cloud physics
- Steady state not a good assumption!
- "bulk" Q often used (20,000 – 200,000)

Dry Deposition of Particulate Matter

Dry Deposition of Particulate Matter

- Surface dependent!
- Flux is the product of concentration on PM and a dry particle deposition velocity v_p
e.g. N_p ($\text{mol m}^{-2} \text{h}^{-1}$) = $v_p C_p = v_p C_G K_{PA}$
- v_p depends on particle size, surface, turbulence
- Mechanisms: diffusion, impaction, sedimentation
- C_p also depends on particle size
- Steady state does not exist but may be a good approximation over long time scales

Gaseous Deposition

Gaseous Deposition

- Surface dependent!
- Thermodynamically governed phase distribution/partitioning
- Flux can be calculated from Fick's Law using the concentration gradient between the gas phase and surface and a dry gaseous deposition velocity v_G
e.g. $N_G \text{ (mol m}^{-2} \text{ h}^{-1}) = v_G(C_G - C_S/K_{SA})$

Gaseous Deposition

Partition Coefficients

Gaseous Deposition

Partition Coefficients

- For water from Henrys Law Constant, affected by POM, DOM, temp., salinity
- For soil from K_{OC}/K_{AW} for neutral species, K_{OC} can be predicted from K_{OW} , affected by quality of OM, temp., relative humidity, concentration (non-linearity!)
- For vegetation few data, non-linear function of K_{OA} , function of species, age, temp.

Gaseous Deposition

Deposition Velocity

Gaseous Deposition

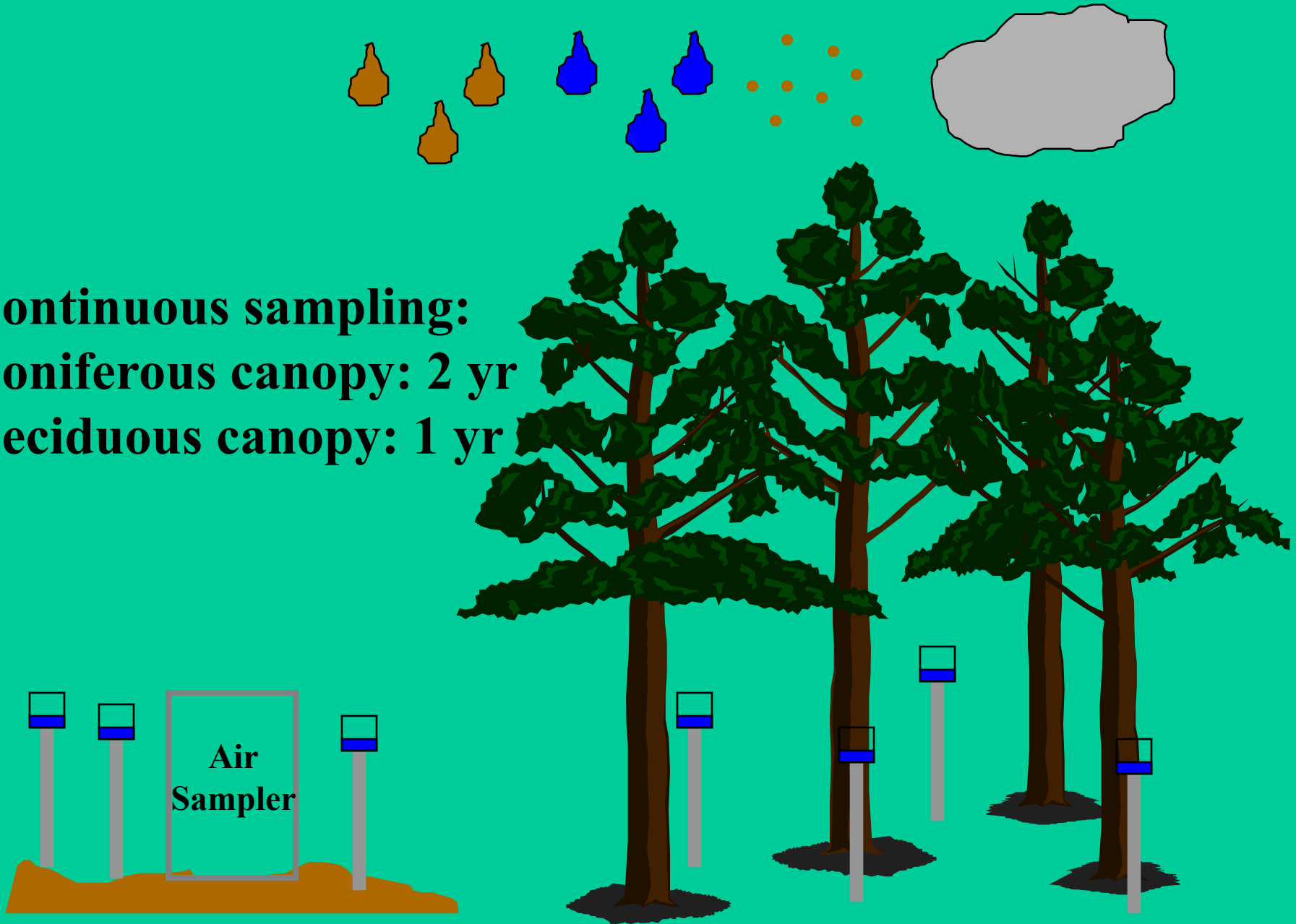
Deposition Velocity

- Two film resistance model
- Air-side resistance depends on meteorology, surface roughness, diffusion coefficient in air
- Surface-side resistance to major reservoir
 - water: surface film, turbulence, diff coeff.
 - soil: diffusion in soil air and soil water, vertical sorbed phase transport
 - vegetation: diffusion through cuticle, stomata
- Dominant resistance depends on partition coeff.

Part II: An Example using Field Data

- Continuous monitoring of atmospheric deposition over 12 months
- Sampling with glass jars, collection every month
- One set of jars in a beech/oak forest, one in a clearing

**Continuous sampling:
Coniferous canopy: 2 yr
Deciduous canopy: 1 yr**



Sampling Characteristics of the Sampler

Do the glass jars collect the different forms of deposition *in the clearing* a representative manner?

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Do the glass jars collect the different forms of deposition *in the clearing* a representative manner?

- Deposition of rain/snow: Yes for both dissolved and particle associated
- Dry deposition of particulate matter: Yes for sedimentation, no for impaction and diffusion
- Dry gaseous deposition: No

Sampling Characteristics of the Sampler II

Do the glass jars collect the different forms of deposition *in the forest* a representative manner?

Sampling Characteristics of the Sampler II

Do the glass jars collect the different forms of deposition *in the forest* a representative manner?

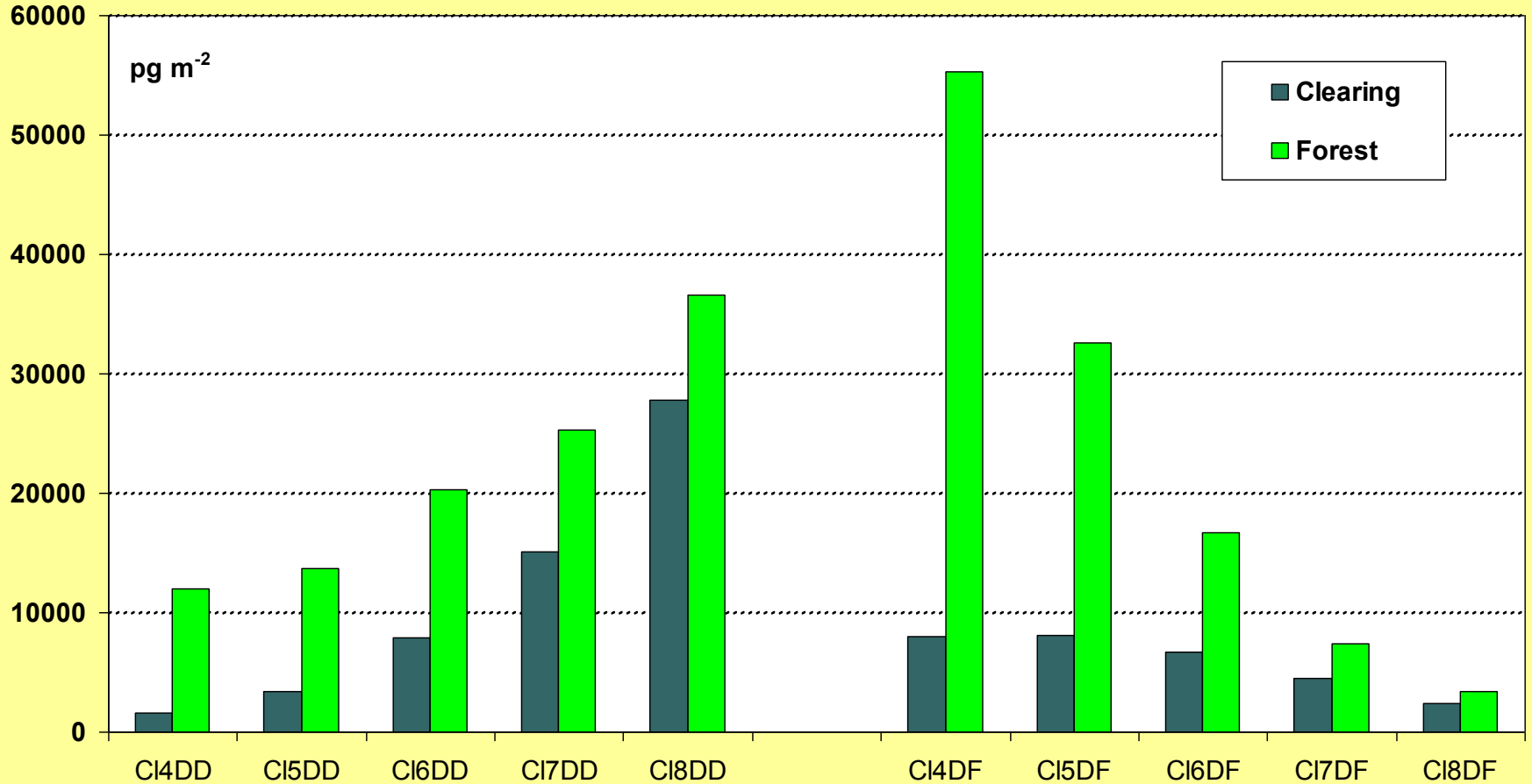
- Deposition of rain/snow: Yes for both dissolved and particle associated
- Dry deposition of particulate matter: Yes for sedimentation, yes for impaction and diffusion to the canopy, no for impaction and diffusion to the forest floor
- Dry gaseous deposition: Yes for the canopy, no for the forest floor

Sampling Characteristics of the Sampler III

In summary, the difference between the samplers in the forest and in the clearing represents the gaseous deposition and the dry particle bound deposition via diffusion and impaction/interception (i.e. of small particles) to the canopy.

We call this difference the “interception”.

Comparison of the Bulk Deposition of PCDD/Fs to a Clearing and Two Forest Canopies during 1 Year



Estimate Dry Particle Bound Deposition Velocity of Chemical to Canopy v_P

Divide canopy interception (I)
by average particle bound
concentration in the atmosphere
and exposure time (6 months).

$$v_P = N_P/C_P = I_P/C_P\Delta t$$

Similar values for most
involatile PAHs

$$(v_P = 0.0073 \text{ m/s})$$

Higher values for more volatile
PAHs indicates other deposition
mechanism ($I > I_P$)

	v_P (m/s)
Phenanthrene	0.2000
Fluoranthene	0.0870
Pyrene	0.0641
Benz[a]anthracene	0.0220
Triphenylen/Chrysene	0.0280
Benzo[b]fluoranthene	0.0088
Benzo[k]fluoranthene	0.0095
Benzo[e]pyrene	0.0078
Benzo[a]pyrene	0.0088
Indeno[cd]pyrene	0.0060
Benzo[ghi]perylene	0.0074
Dibenzo[ah]anthracene	0.0073
Coronene	0.0065

Estimate Gaseous Deposition Velocity of Chemical to Canopy v_G

Divide canopy gaseous interception ($I_G = I - I_p$) by average gaseous conc. in the atmosphere and exposure time.

$$v_G = N_G/C_G = I_G/C_G\Delta t$$

Similar values for PCDDs, involatile PCBs

$$v_G = 0.035 \text{ m/s}$$

(compare to <0.001 to soil)

Higher values for more volatile PCBs indicates deposition limited (equilibrium reached)

	v_G (m/s)
HCB	0.0004
PCB-28	0.0021
PCB-52	0.0038
PCB-101	0.0115
PCB-153	0.026
PCB-138	0.036
PCB-180	0.053
2,3,7,8-Cl ₄ -DD:	0.043
1,2,3,7,8-Cl ₅ -DD:	0.032
1,2,3,4,7,8-Cl ₆ -DD:	0.026
1,2,3,6,7,8-Cl ₆ -DD:	0.031
1,2,3,7,8,9-Cl ₆ -DD:	0.036

Estimate Partition Coefficients (K_{VA}) of the Chemicals between Canopy and Atmosphere

Divide canopy gaseous interception by gaseous conc. in autumn and specific canopy volume (V_V).

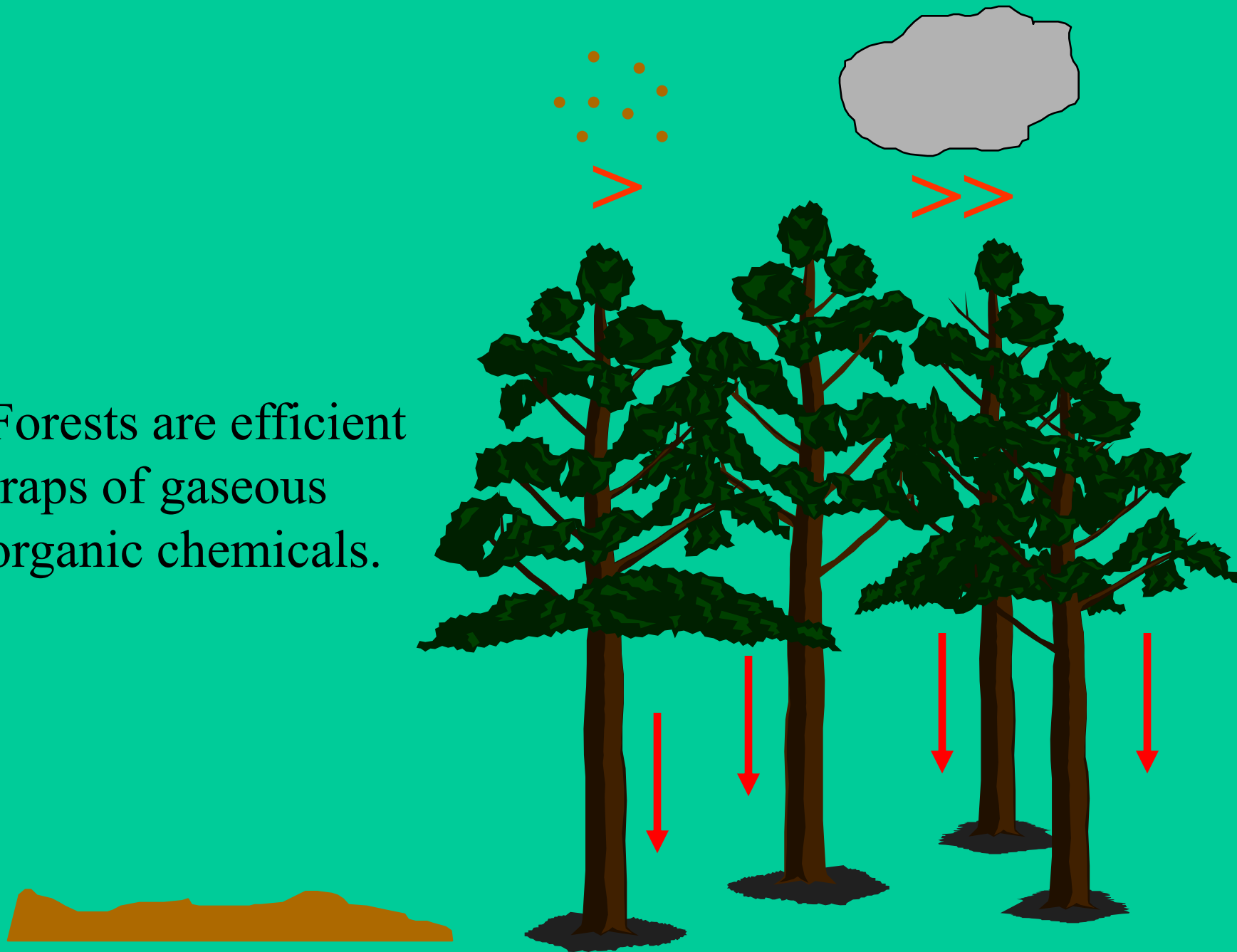
$$K_{VA} = C_V/C_G = I_G/V_V C_G$$

Yields a correlation between K_{VA} and K_{OA}

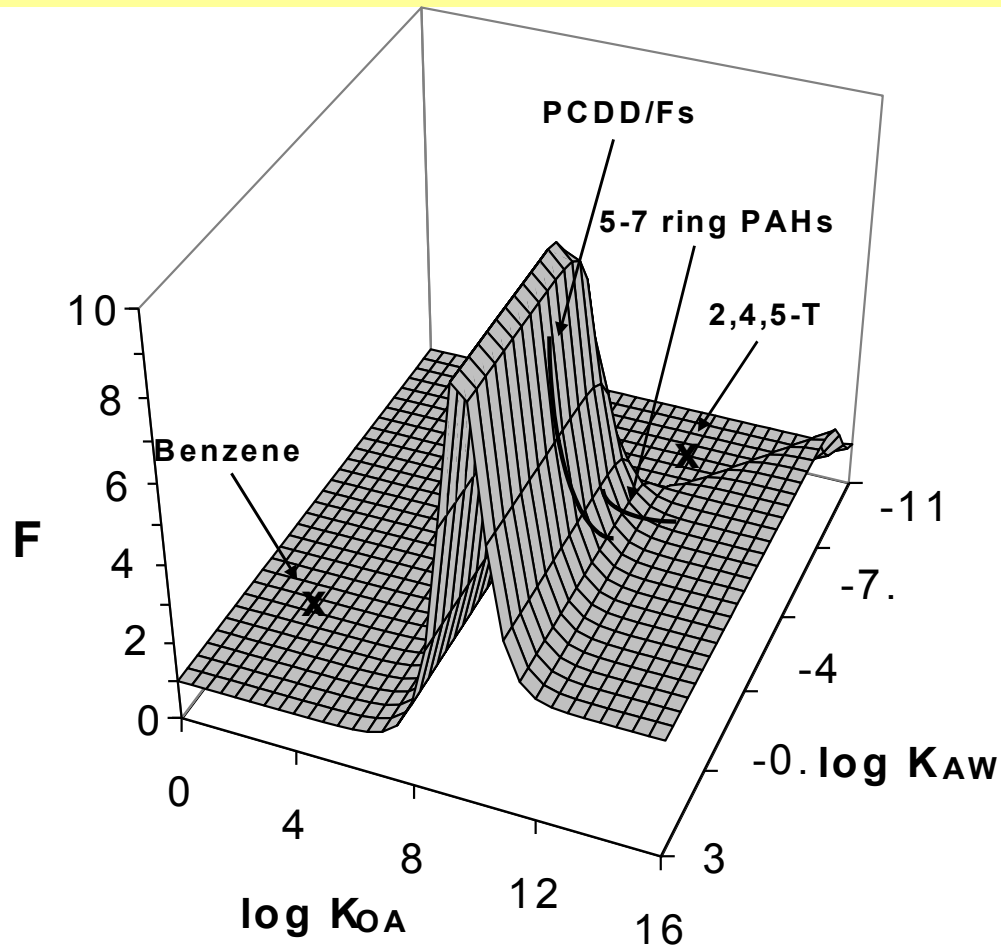
$$K_{VA} = 14 K_{OA}^{0.76}$$

	log K_{PA}	log K_{OA} (11°C)
HCB	6.72	7.55
Phenanthrene	7.57	8.25
PCB-28	7.77	8.61
PCB-52	7.95	8.94
Fluoranthene	8.23	9.46
Pyrene	8.24	9.46
PCB-101	8.45	9.52

Forests are efficient traps of gaseous organic chemicals.



Forest Filter Effect plotted as a Function of the Octanol-Air (K_{OA}) and Air-Water Partition (K_{AW}) coefficient of the Chemical



Horstmann and McLachlan (1998) Atmos. Environ. 32, 1799-1809
McLachlan and Horstmann (1998) Environ. Sci. Technol. 32, 413-420

Applying Process Understanding in Monitoring

How would you monitor atmospheric deposition of PCBs and PCDD/Fs?

- For higher chlorinated PCDD/Fs, wet particle bound deposition dominates (a bulk deposition sampler in a field may be adequate)
- For PCBs, gaseous deposition must be quantified (a bulk deposition sampler in a clearing will not work. Perhaps in a forest ...)