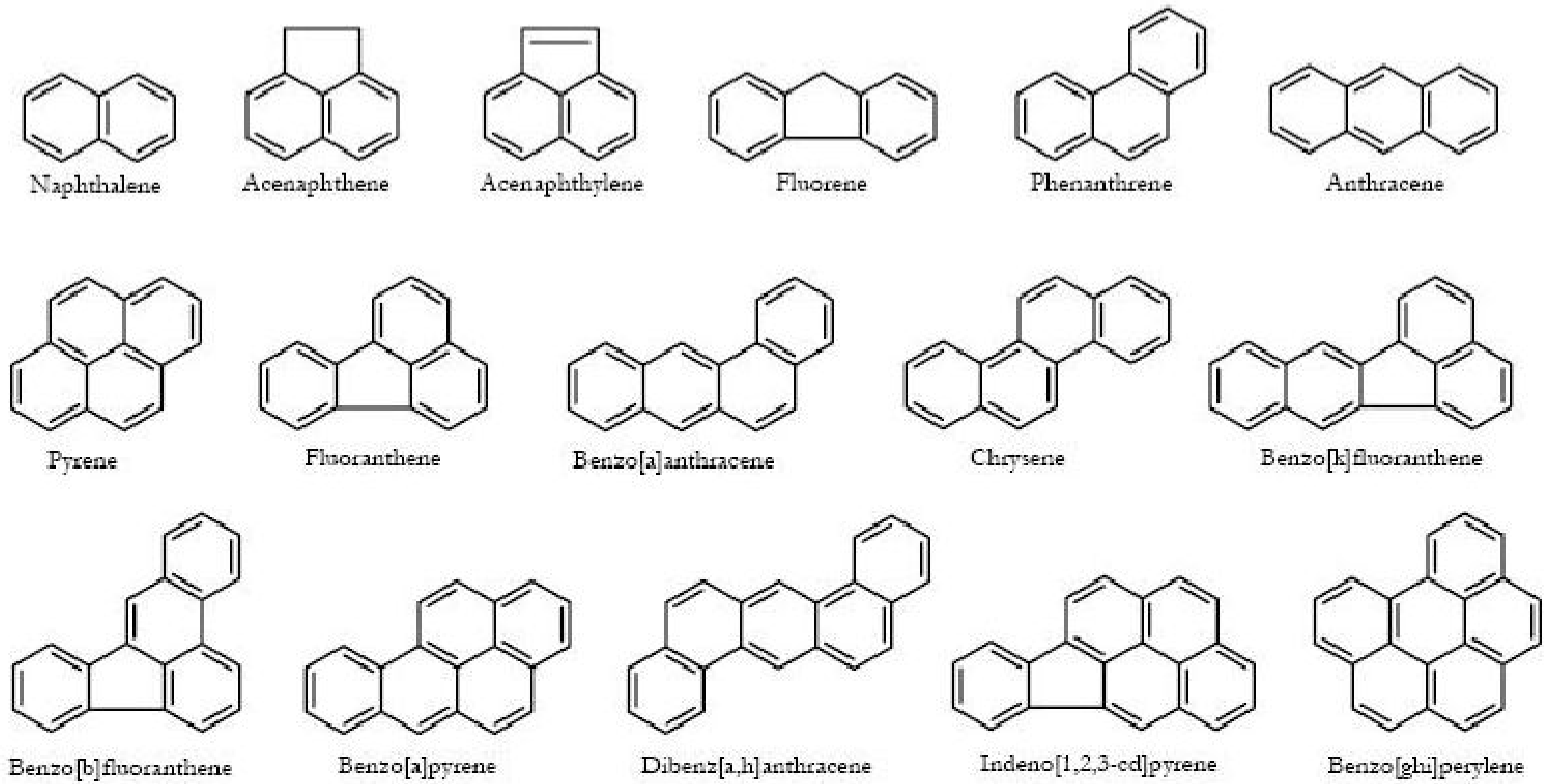
Watershed-scale modeling of the Fate and Transport of Polycyclic Aromatic Hydrocarbons (PAHs)

Sang Soo Baek, Mayzonee Ligaray, Hye-Ok Kwon, Sung-Deuk Choi, Kyung Hwa Cho†

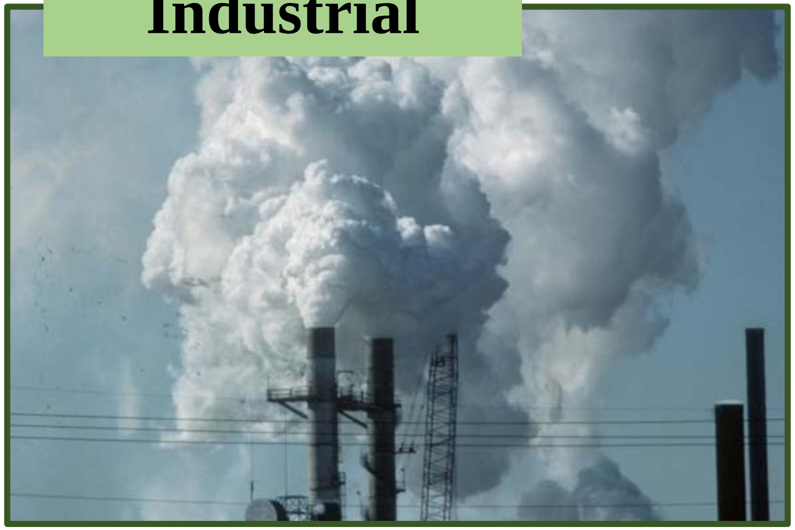
Polycyclic Aromatic Hydrocarbons



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

Polycyclic Aromatic Hydrocarbons : Origins

Industrial

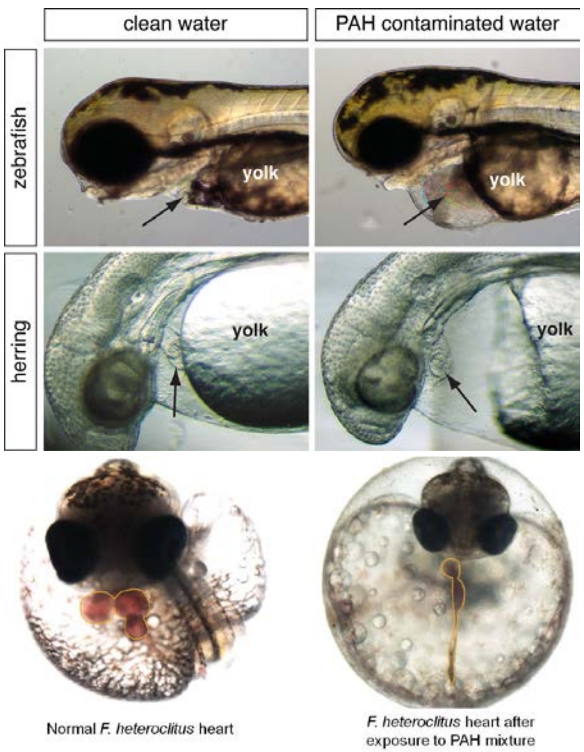


Forest fire

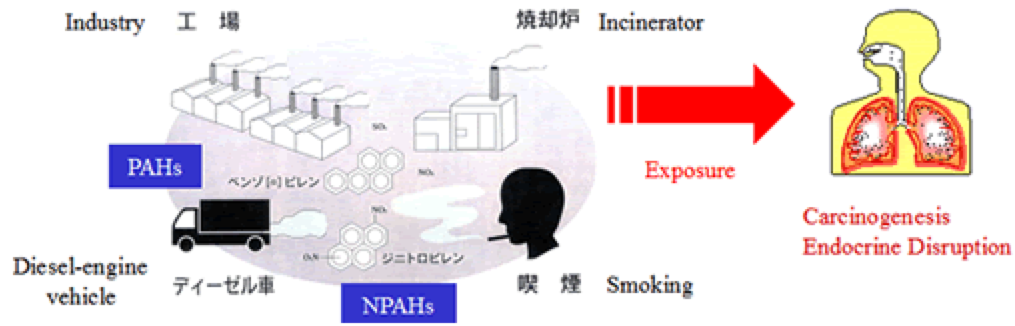
Oil spill

Volcano

Polycyclic Aromatic Hydrocarbons : Effects



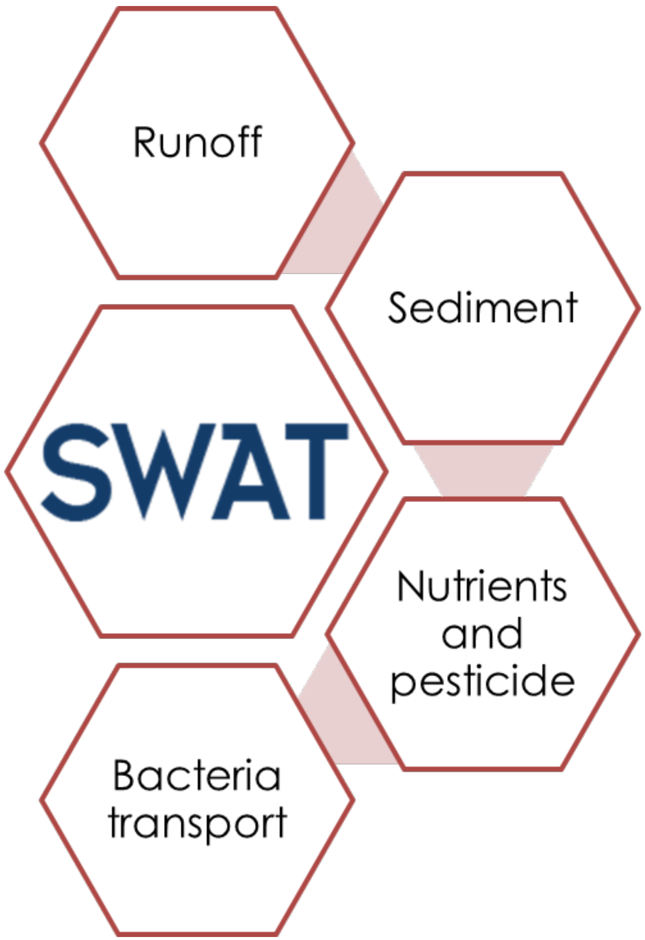
Deformation of aquatic fauna

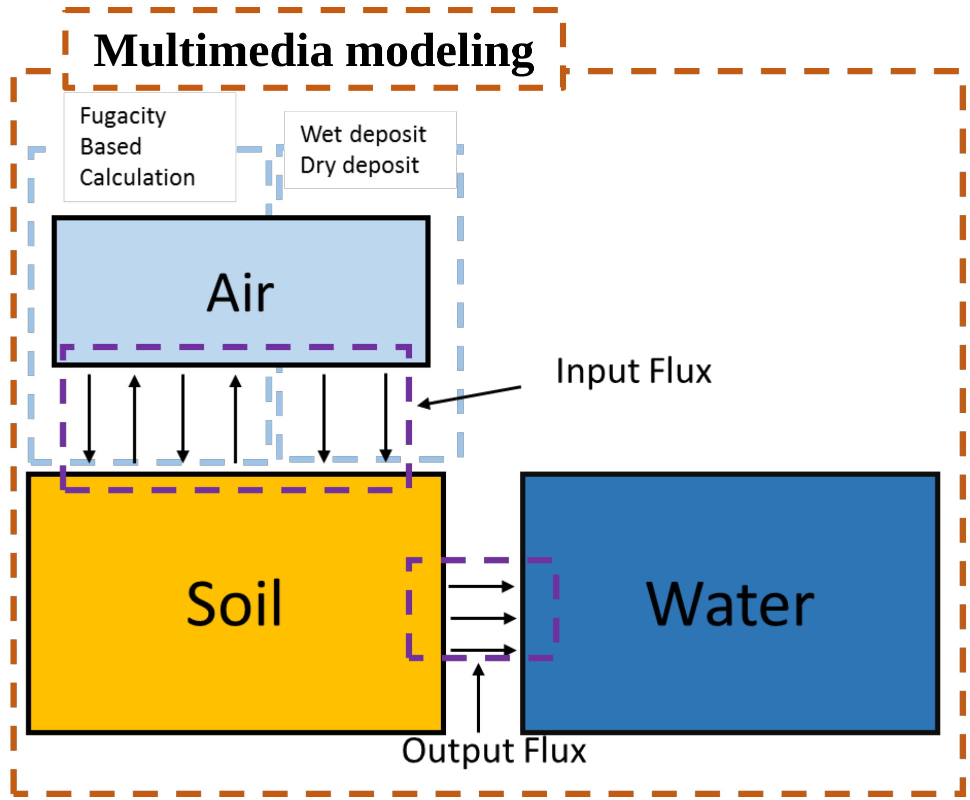


Carcinogenesis endocrine disruption

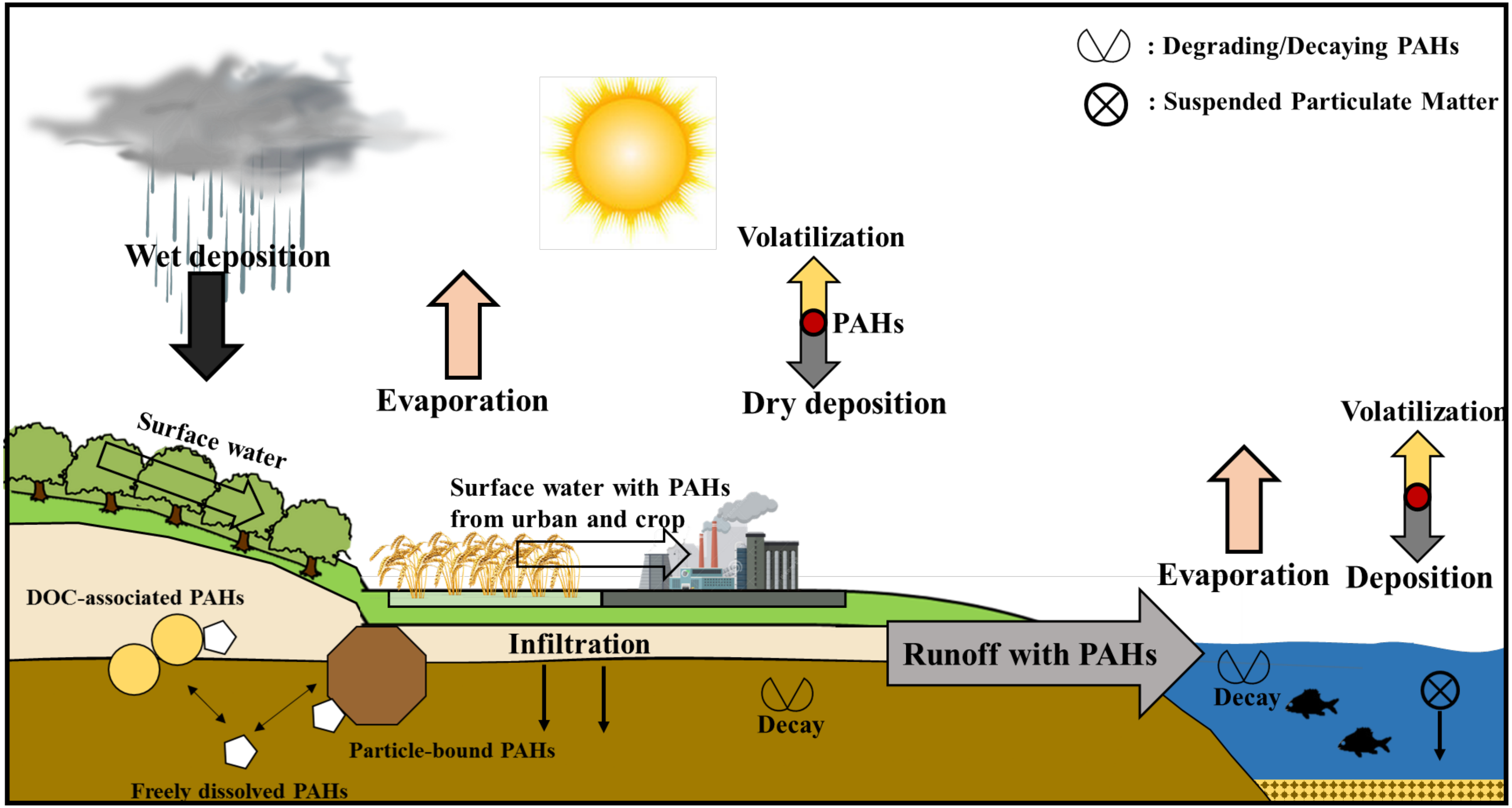
Affects fetal growth

Watershed-scale modeling with SWAT and Multimedia modeling

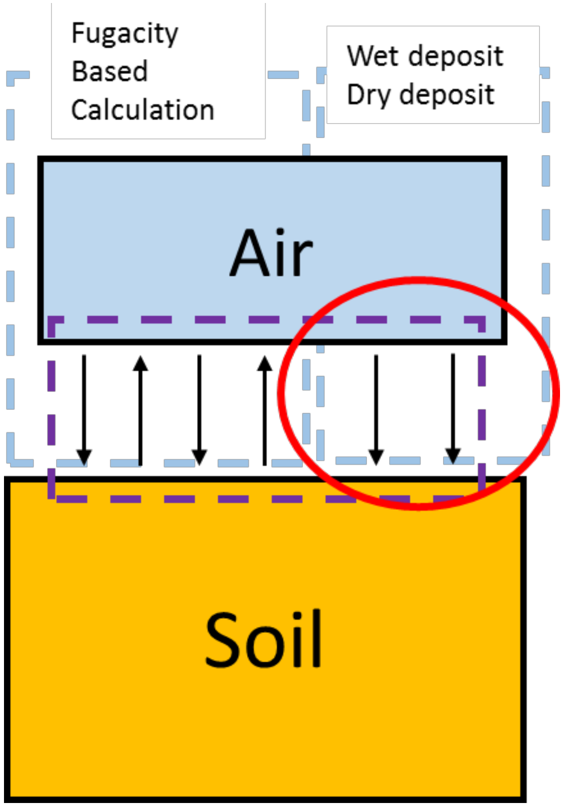




Fate and transport of PAHs



Fate and transport of PAHs



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}].

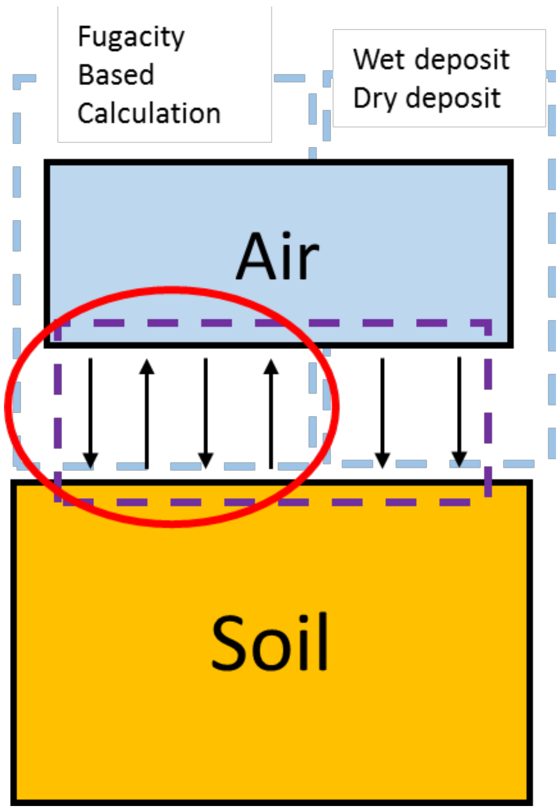
Wet deposition(rain) (gas and particle)

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

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

W is the washout ratio; G_R is the precipitation rate [m d^{-1}];
C_{air} is the concentration in air [ng m^{-3} of air].
The subscripts g and p stand for gas and particle-bound,

Fate and transport of PAHs



Air-soil exchange

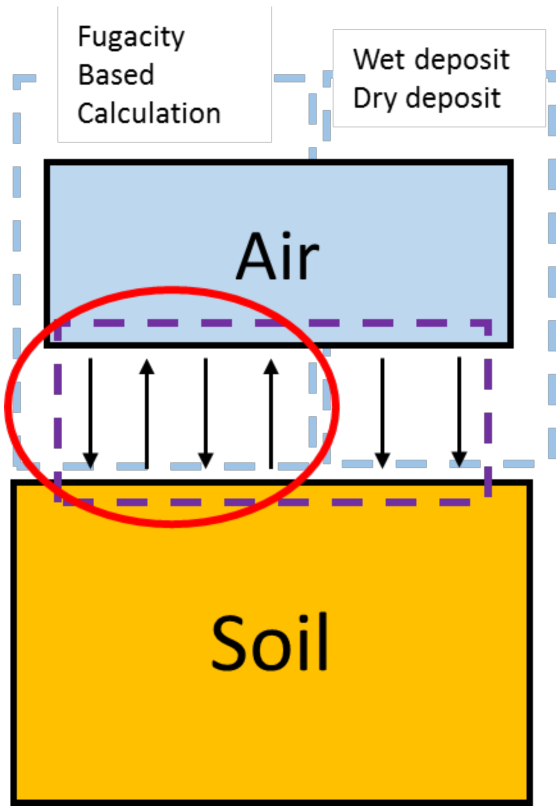
(dry gaseous deposition and volatilisation)

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 [Pa]) is related to concentration (C [mol m^{-3}]) through the Z-value(fugacity capacity) ([mol m^{-3} 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

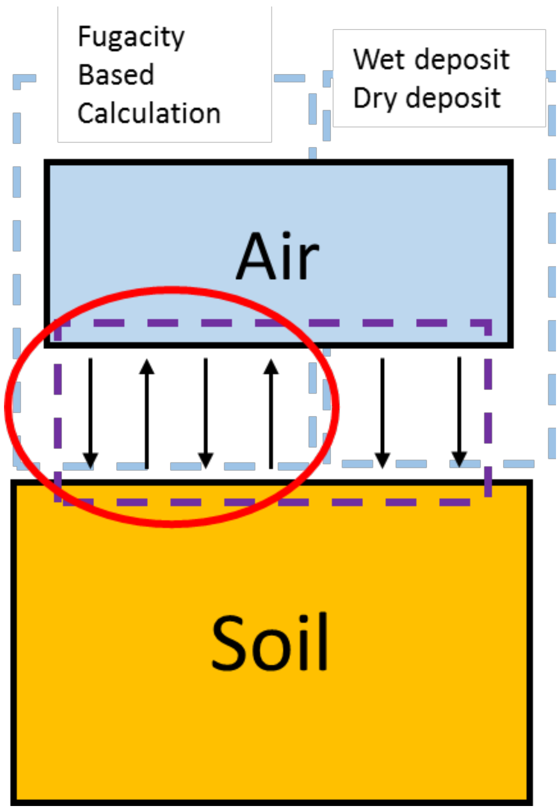
$$Z_a = 1/RT$$

$$Z_s = f_{OC} K_{OC} \rho Z_w$$

$$Z_w = 1/H$$

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,
ρ : 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})

Fate and transport of PAHs



Air-soil exchange

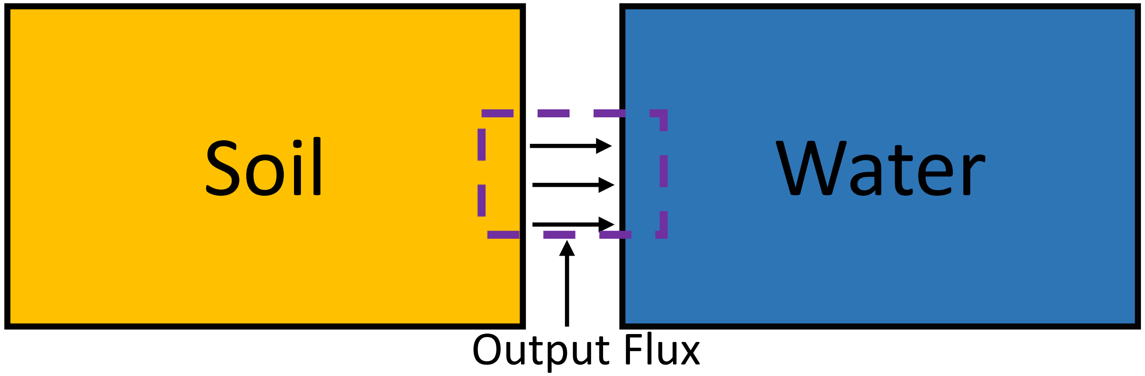
(dry gaseous deposition and volatilisation)

$$N = D_v(f_s - f_a)$$

D_v (mol Pa^{-1} h^{-1}) : the overall D-value for transport across the soil/air interface.

N : net diffusive flux N (mol h^{-1})

Fate and transport of PAHs



The PAH loading that ended up in the river was determined using the equation:

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

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

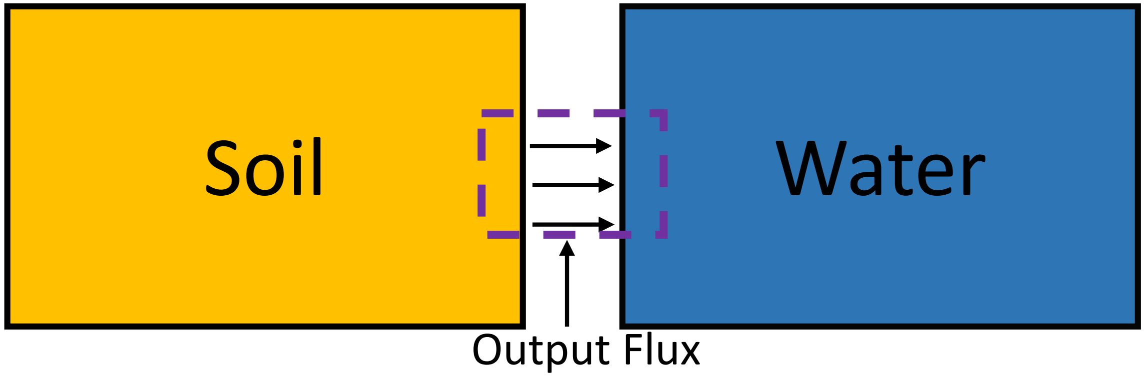
$$C_{bs}^{DOC} = f_d^{DOC} \times W_{cDOC} \times \exp(-\mu_{DOC})$$

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

μ_i : the initial rate constant for the PAH compounds [s^{-1}],
θ : the temperature adjustment factor for PAH compounds [-],
T : the temperature [°C]

f_p [-] : fraction, W_{cp} : washoff load [kg-L^{-1} bulk soil], μ_p : rate constant [s^{-1}] - particle-bound PAH,
$f_d{}^f$ [-], W_{cf} [kg-L^{-1} bulk soil], μ_f [s^{-1}] - freely-dissolved PAH,
$f_d{}^{DOC}$ [-], W_{cf} [kg-L^{-1} bulk soil], μ_{DOC} [s^{-1}] - DOC-bound PAH.

Fate and transport of PAHs

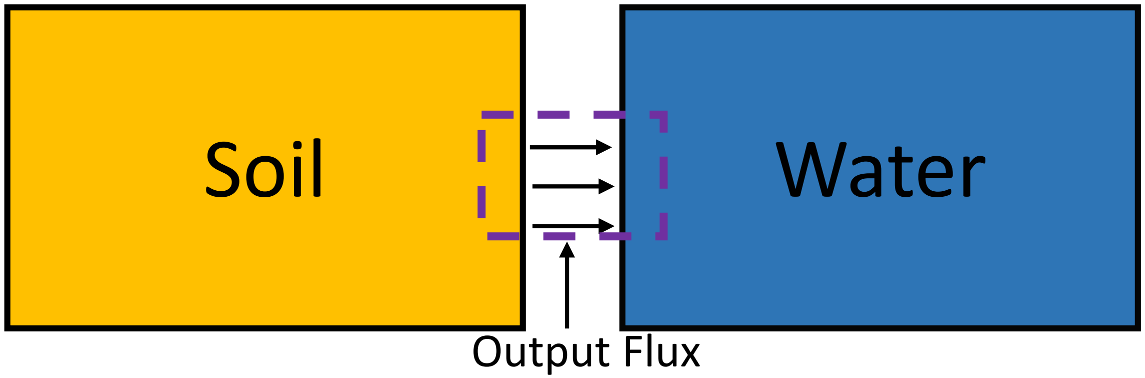


The fractions of particle-bound PAH, DOC-bound PAH, free-dissolved PAH

$$f_p = \frac{r_{sw}K_{sw}}{r_{sw}K_{sw}+1+[DOC]K_{DOC}} \qquad f_d^f = \frac{1}{r_{sw}K_{sw}+1+[DOC]K_{DOC}} \qquad f_d^{DOC} = \frac{[DOC]K_{DOC}}{r_{sw}K_{sw}+1+[DOC]K_{DOC}}$$

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)

Fate and transport of PAHs

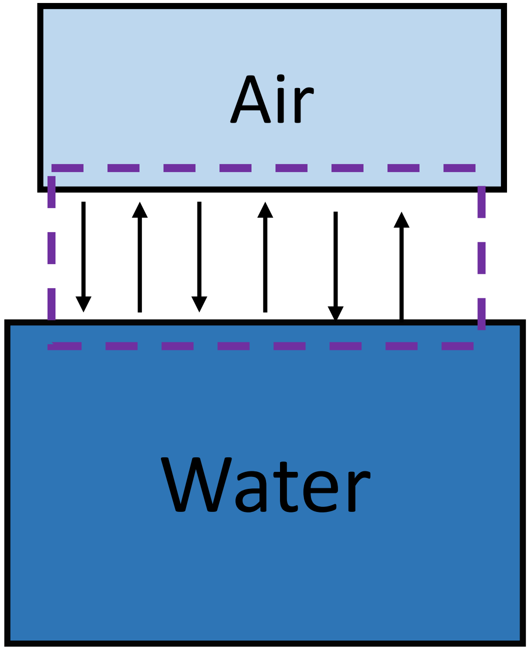


PAH loadings of the model were computed by below equation

$$C_p = \frac{C_{bs}^{p} - C_{bs\_out}^{p}}{\rho} \qquad C_w = C_{bs}^{d} + C_{bs\_out}^{p} \qquad C_{w_{final}} = coeff_{enratio,1} \times (C_w)^{coeff_{enratio,2}}$$

C_p : PAH loadings in soil (PAH per solid mass) C_w : PAH loadings in water
C_{wfinal} : the final PAH loading in water, the two $coeff_{enratio}$: the enrichment ratio coefficients

Fate and transport of PAHs

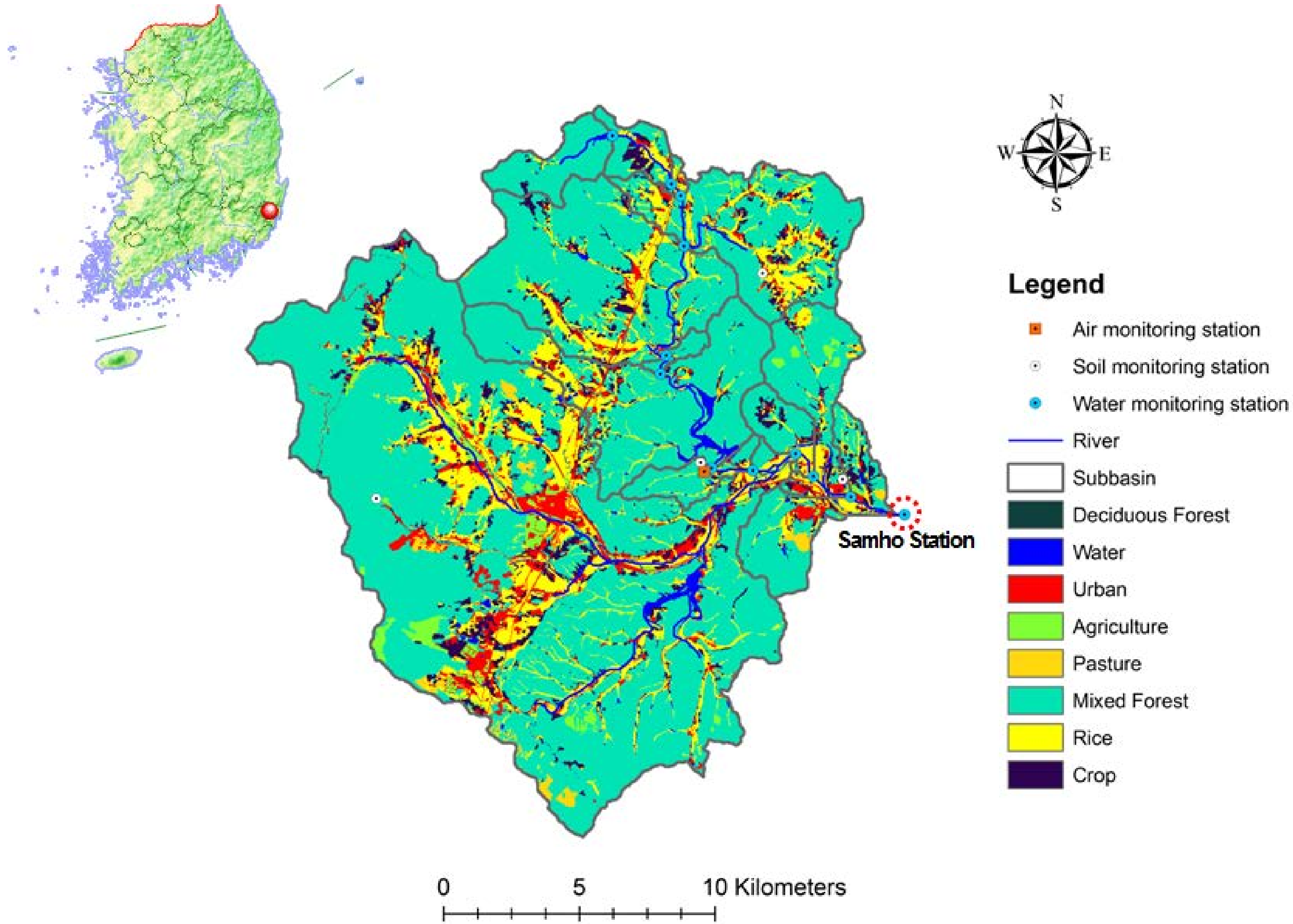


The modified advection-dispersion equation

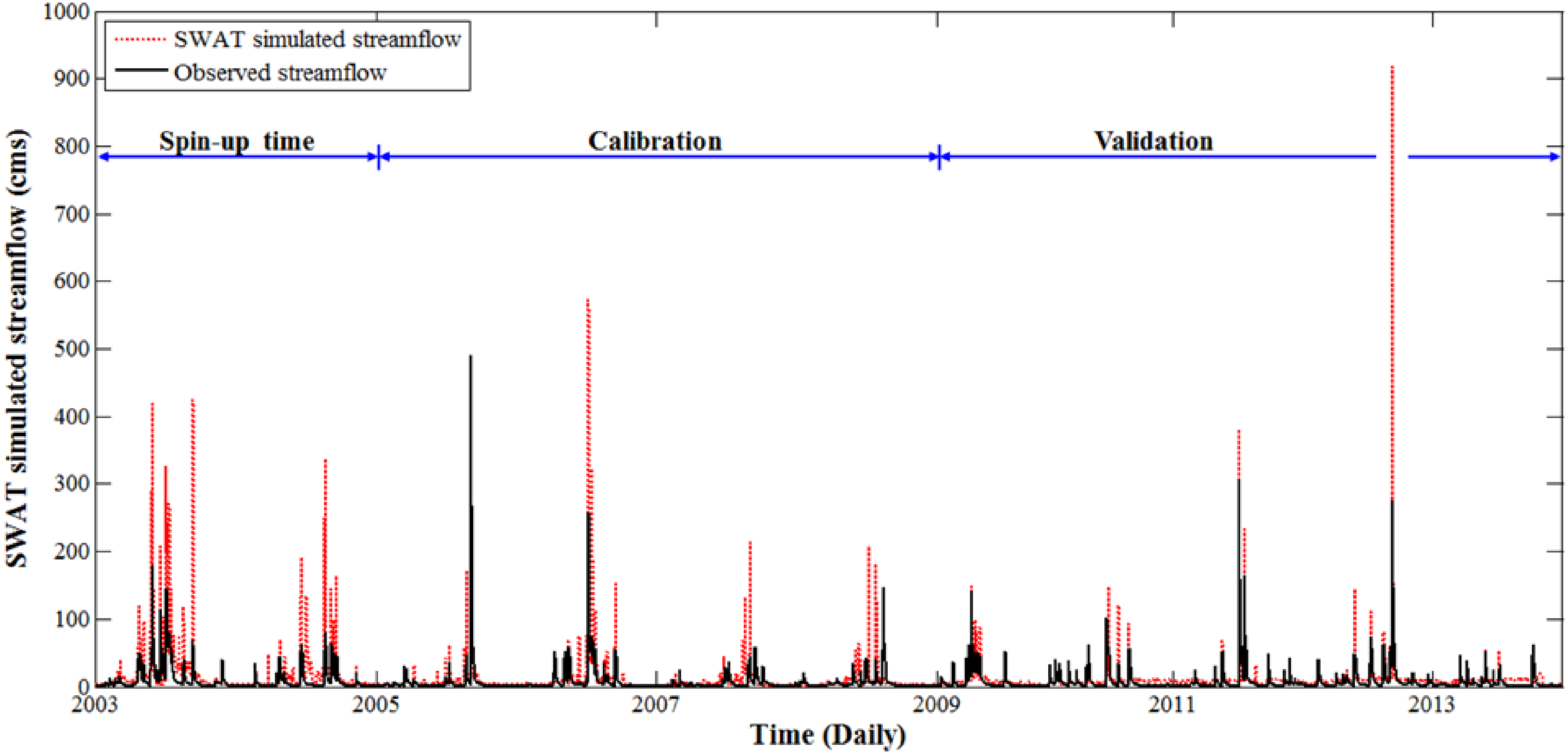
$$\frac{\partial C}{\partial t} + u\frac{\partial C}{\partial x} = D_L\frac{\partial^2 C}{\partial x^2} - C\left(f\frac{v_s}{h} + aI\right) + N_{aw}$$

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

Study area


N
W
E
S
Legend
Air monitoring station
Soil monitoring station
Water monitoring station
River
Subbasin
Deciduous Forest
Water
Urban
Agriculture
Pasture
Mixed Forest
Rice
Crop
Samho Station
0
5
10 Kilometers

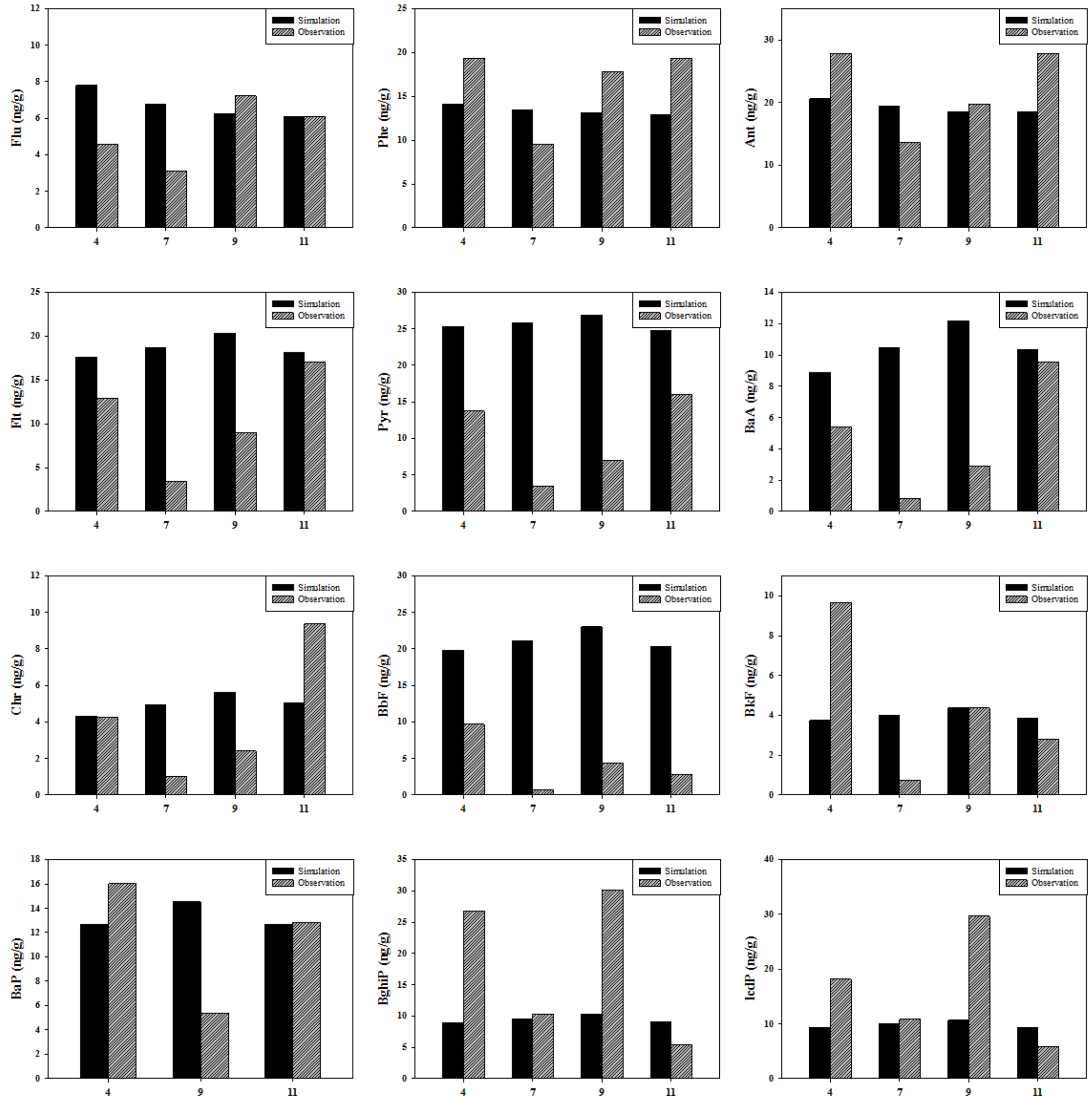
SWAT Model Streamflow



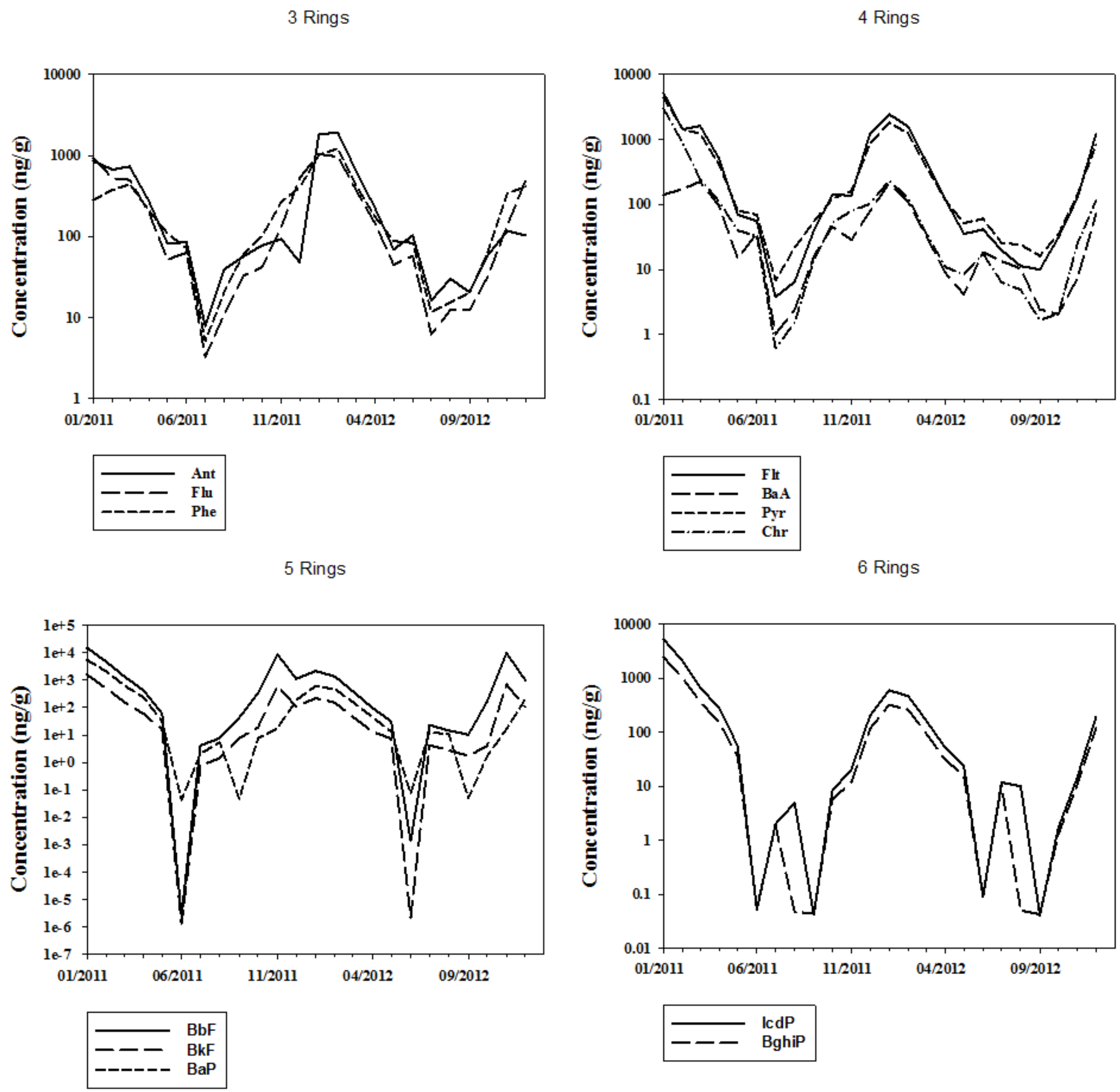
Sensitivity analysis of PAHs

No.	Parameter	Definition	Unit	Soil phase	Water phase
1	f_{oc}	Organic carbon fraction in soil	-	13	15
2	ρ	Soil density	kg-m^{-3}	11	25
3	$W_{rain,g}$	Washout ratio for gaseous PAH	-	14	16
4	$W_{rain,p}$	Washout ratio for particulate PAH	-	15	13
5	f_{DOC}	Fraction of the dissolve organic carbon	-	12	10
6	$coeff_{enratio,1}$	Enrichment ratio coefficient 1	-	21	23
7	$coeff_{enratio,2}$	Enrichment ratio coefficient 2	-	1	19
8	$D_{v,aw}$	Overall D-value for PAH transport across the air/water interface	mol-Pa^{-1}-h^{-1}	-	14
9	$D_{v,wa}$	Overall D-value for PAH transport across the water/air interface	mol-Pa^{-1}-h^{-1}	-	4
10	$D_{v,as}$	Overall D-value for PAH transport across the air/soil interface	mol-Pa^{-1}-h^{-1}	4	1
11	$D_{v,sa}$	Overall D-value for PAH transport across the soil/air interface	mol-Pa^{-1}-h^{-1}	2	11
12	C_{p1}	Washoff coefficient for particle-bound PAH	-	5	12
13	C_{f1}	Washoff coefficient for free-dissolved PAH	-	8	7
14	C_{p2}	Washoff exponent for particle-bound PAH	-	9	21
15	C_{f2}	Washoff exponent for free-dissolved PAH	-	3	20
16	a	Decay coefficient in water due to solar intensity	-	-	2
17	F	Fraction of particulate PAH in water	-	-	3
18	C_{DOC1}	Washoff coefficient for DOC-associated PAH	-	19	5
19	C_{DOC2}	Washoff exponent for DOC-associated PAH	-	18	8
20	μ_p	Rate constant for the particle-bound PAH	s^{-1}	7	22
21	θ_p	Temperature adjustment factor for particle-bound PAH	-	10	9
22	μ_f	Rate constant for the free-dissolved PAH	s^{-1}	6	18
23	θ_f	Temperature adjustment factor for free-dissolved PAH	-	20	24
24	μ_{DOC}	Rate constant for the DOC-associated PAH	s^{-1}	17	17
25	θ_{DOC}	Temperature adjustment factor for DOC-associated PAH	-	16	6

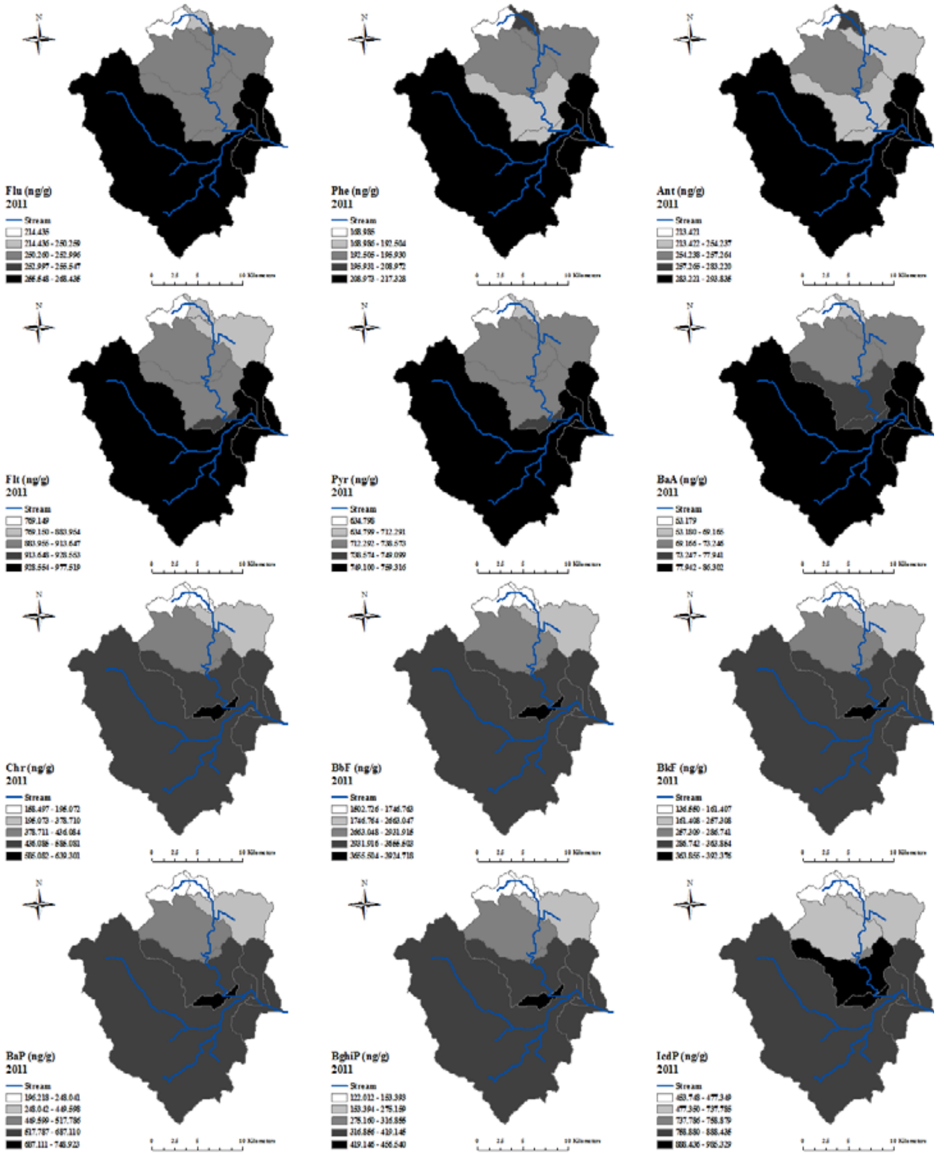
PAHs in soil


Simulation
Observation
Flu (ng/g)
Phe (ng/g)
Ant (ng/g)
Flt (ng/g)
Pyr (ng/g)
BaA (ng/g)
Chr (ng/g)
BbF (ng/g)
BkF (ng/g)
BaP (ng/g)
BghiP (ng/g)
IcdP (ng/g)
4
7
9
11

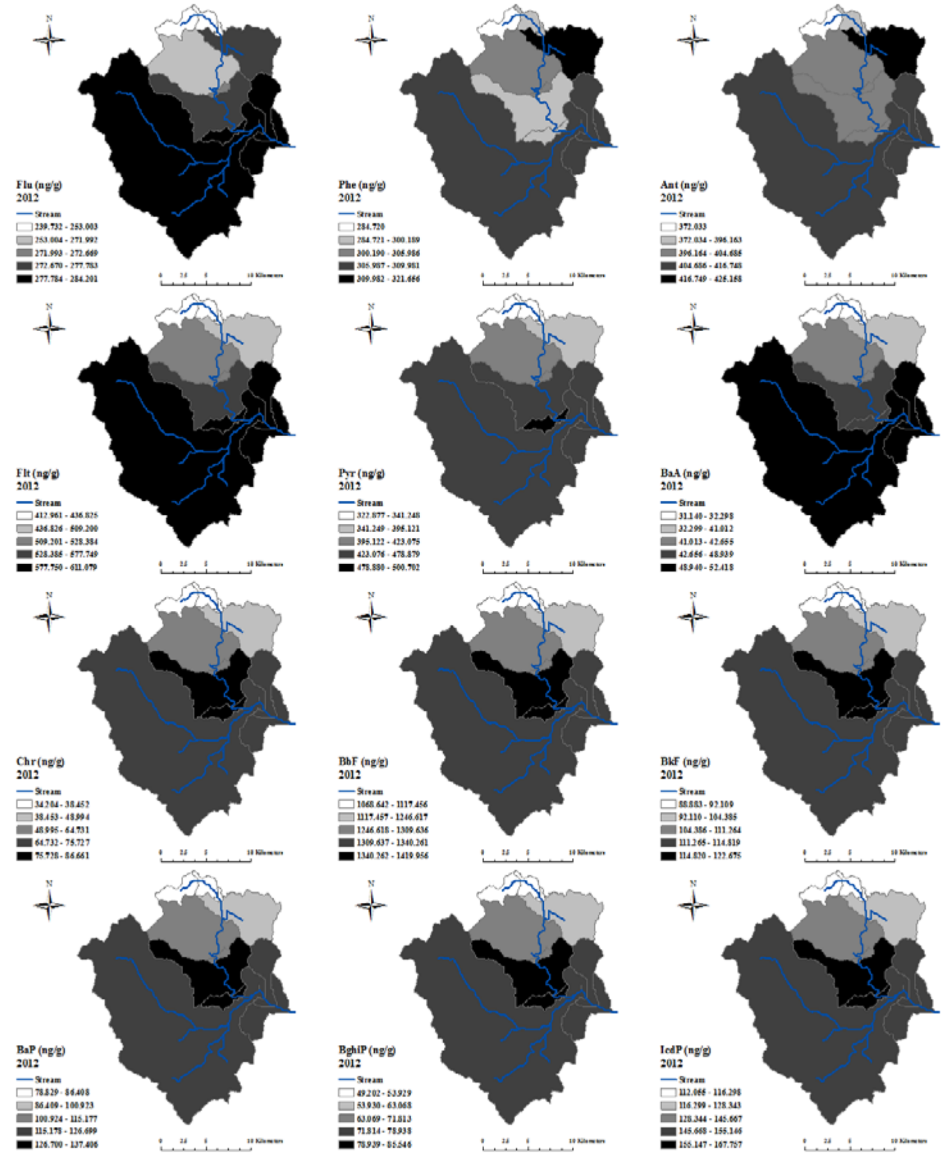
PAHs in soil


3 Rings
Concentration (ng/g)
10000
1000
100
10
1
01/2011
06/2011
11/2011
04/2012
09/2012
Ant
Flu
Phe
4 Rings
Concentration (ng/g)
10000
1000
100
10
1
0.1
01/2011
06/2011
11/2011
04/2012
09/2012
Flt
BaA
Pyr
Chr
5 Rings
Concentration (ng/g)
1e+5
1e+4
1e+3
1e+2
1e+1
1e+0
1e-1
1e-2
1e-3
1e-4
1e-5
1e-6
1e-7
01/2011
06/2011
11/2011
04/2012
09/2012
BbF
BkF
BaP
6 Rings
Concentration (ng/g)
10000
1000
100
10
1
0.1
0.01
01/2011
06/2011
11/2011
04/2012
09/2012
IcdP
BghiP

PAHs in soil

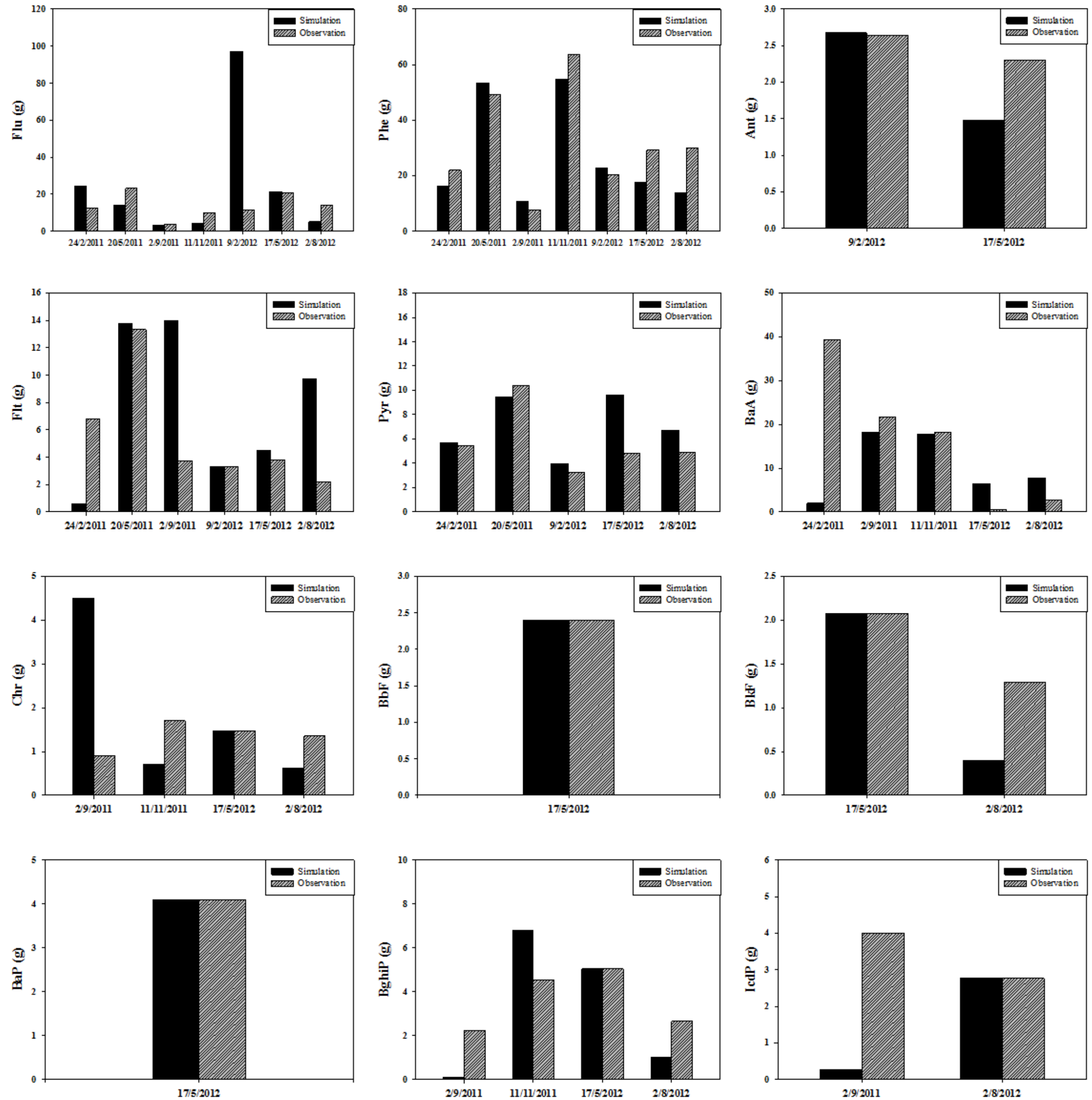


2011

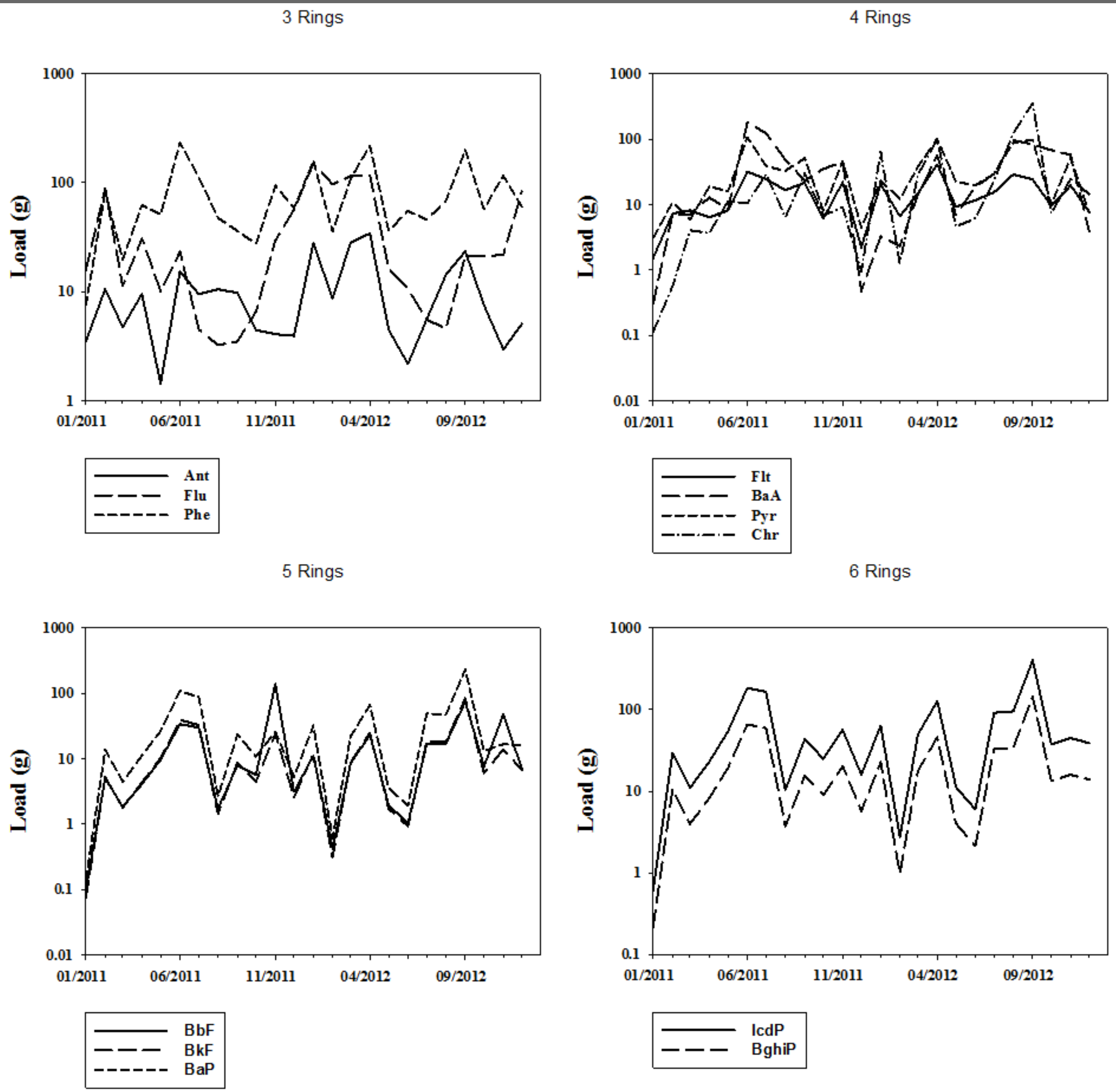


2012

PAHs in water



PAHs in water



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!