Supplementary Data

MANUSCRIPT TITLE: Fate estimation of polycyclic aromatic hydrocarbons in soils in a rapid urbanization region, Shenzhen of China

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Standard Materials

Standard mixtures: A standard mixtures containing naphthalene, 1-methylnaphthalene, 2-methylnaphthalene, 2,6-dimethylnaphthalene, 2,3,5-trimethylnaphthalene, biphenyl, acenaphthylene, acenaphthene, fluorene, phenanthrene, 1-methylphenanthrene, 2-methylphenanthrene, 2,6-dimethylphenanthrene, anthracene, fluoranthene, pyrene, 11H-benzo[b]fluorene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[e]pyrene, benzo[a]pyrene, perylene, and 9,10-diphenylanthracene at 1mg/mL each and a standard mixture including indeno[1,2,3-cd]pyrene, dibenzo[a, h]anthrancene and benzo[g,h,i]perylene at 2mg/mL each purchased from Accustandard (New Haven, CT) were used for identification and quantification.

Surrogates standards: Six deuterated PAHs (including naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, perylene-d_{12}, and benzo[g,h,i]perylene-d_{12}) (Cambridge Isotope Laboratories (Andover, MA)) were employed as surrogates standards. All solvents were redistilled using a glass system.

Internal standards: 2-fluoro-1,1-biphenyl, p-terphenyl-d_{14}, dibenzo[a,h]anthracene (Dr. Ehrenstorfer GmbH).

Σ_{27}PAHs List: 2-methylnaphthalene (2-Mn), 1-methylnaphthalene (1-Mn), Biphenyl

(Bip), 2,6-dimethylnaphthalene (2,6-Dn), Acenaphthylene (Acy), Acenaphthene (Acen), 2,3,5-trinaphthalene (Trn), Fluorene (Flo), Phenanthrene (Phe), Anthracene (Ant), 2-methylphenanthrene (2-Mp), 1-methylphenathrene (1-Mp), 2,6-dimethlyphenanthrene (2,6-Dp), Fluoranthrene (Fla), Pyrene (Pyr), 11H-benzo(b)fluorine (11H-B), Benzo(a)anthracene (BaA), Chrysene (Chr), Benzo(b)fluoranthene (BbF), Benzo(k)fluoranthene (BkF), Benzo(e)pyrene (BeP), Benzo(a)pyrene (BaP), Perylene (Per), 9,10-diphenylanthracen (9,10-Di), Iden(123-cd)pyrene (IP), Dibenzo(a,h)anthracene (DB*ah*A), Benzo(ghi)perylene (B*ghi*P)

Σ_{15}PAHs List: Acenaphthylene (Acy), Acenaphthene (Acen), Fluorene (Flo), Phenanthrene (Phe), Anthracene (Ant), Fluoranthene (Fla), Pyrene (Pyr), Benzo(a)anthracene (B*a*A), Chrysene (Chr), Benzo(b)fluoranthene (B*b*F), Benzo(k)fluoranthene (B*k*F), Benzo(e)pyrene (B*e*P), Iden(123-cd)pyrene (IP), Dibenzo(a,h)anthracene (DB*ah*A), Benzo(ghi)perylene (B*ghi*P)

Estimation procedure of mass inventories of PAHs in soils:

With the mean concentrations of 27 or 15 PAHs in each district and relative soil area, we estimated the mass inventories of PAHs by the equation (5). The mean concentration, soil area, and estimation are listed in Table S4.

Table S1
Calculation of transfer or reaction coefficients (*D*).

compartment	process	individual *D*	total *D*
air-soil	diffusion [a]	$D_S = 1/\{1/(k_{SA} \cdot A \cdot Z_A) + Y_S/[A \cdot (B_{MA} \cdot Z_A + B_{MW} \cdot Z_W)]\}$	$D_{AS}=D_s + D_{DS} + D_{WS} + D_{RS}$
	Rain washout	$D_{RS} = A/(U_R \cdot Z_W)$	
	wet deposition	$D_{WS} = A \cdot U_R \cdot Q \cdot v_Q \cdot Z_Q$	
	dry deposition	$D_{DS} = A \cdot U_Q \cdot v_Q \cdot Z_Q$	
soil-water	soil runoff	$D_{SS} = A \cdot U_{SS}\ Z_S$	$D_{soil\text{-}water} = D_{SS} + D_{SW}$
	water runoff	$D_{SW} = A \cdot U_{SW}\ Z_W$	
reaction	degradation	$D_{HL} = \ln 2 \cdot A \cdot d \cdot Z_S / HL$	

k_{SA} is air-side mass transfer coefficient (1 m/h [1, 2]), A is the interfacial area (soil area of Shenzhen 1.949×10^9 m^2), Z_A ($=1/RT$ [2]), Z_Q ($=Z_A \cdot 6\times10^6/P_{L,}$ P_L is liquid vapor pressure (Pa) [2]), Z_W ($=1/H$, H is Henry's law constant (Pa m^3/mol) [2]) are fugacity capacities for air, aerosol, and water (mol/m^3 · pa) and can be calculated by the method in literatures [1, 3-5], Y_S is the length of the pathway in soil (0.05 m) [2, 3], B_{MA} and B_{MW} are molecular diffusive coefficients for air and water (Table S3), U_Q and U_R are dry and wet deposition velocities, Q is atmosphere scavenging ratio (Table S3), v_Q is aerosol volume fraction [2, 3], d is depth of soil (0.1 m was taken as depth of soil in

the present study), *HL* is half lives of individual PAHs (in h, listed in Table S3).

Table S2

Estimated and assumed transport parameter.

Parameter	Value	Description
rain rate (U_R)	2.3×10^{-4} m/h	estimated with annual average rainfall 2000 mm in Shenzhen [6]
soil water runoff rate (U_{sw})	1.6×10^{-4} m/h	estimated with annual total surface runoff 27.06×10^8 m^3 in Shenzhen [7]
soil solids runoff rate (U_{ss})	3.3×10^{-8} m/h	estimated with soil erosion modulus 1.67×10^4 tons/km^2.year and total soil eroded area 60 km^2 in Shenzhen [8]
scavenging ratio Q	2×10^5	data was taken from Mackay et al study [1, 2]
molecular diffusivity in air (B_{MA})	0.04 m^2/h	data was taken from Mackay et al study [1, 2]
molecular diffusivity in water (B_{MW})	4.0×10^{-6} m^2/h	data was taken from Mackay et al study [1, 2]
dry deposition velocity (U_Q)	10.8 m/h	data was taken from Mackay et al study [1, 2]

Table S3
Physicochemical data, half-lives of PAHs.

Compounds	mol.wt.	lgK_{oa}	lgK_{ow} [c]	H (pa m^3/mol)	half lives (h)
Acy	152	6.23 [b]	3.98	146 [b]	240 [d]
Acen	154	6.28 [b]	4.07	402 [b]	240 [e]
Flo	166	6.58 [b]	4.18	10.1 [b]	1128 [e]
Phe	178	7.33 [b]	4.45	2.59 [b]	1440 [e]
Ant	178	7.09 [b]	4.45	179 [b]	6240 [e]
Fla	202	8.32 [b]	4.90	0.64 [b]	10560 [e]
Pyr	202	8.80 [a]	4.88	4.93 [b]	45600 [e]
BaA	228	9.10 [b]	5.61	0.10 [b]	10320 [e]
Chr	228	9.40 [b]	5.16	0.11 [b]	24000 [e]
BbF	252	10.7 [b]	6.04	1.23 [b]	14640 [e]
BkF	252	10.7 [b]	6.06	3.91 [b]	33600 [e]
BaP	252	10.7 [b]	6.06	0.05 [b]	6960 [e]
IP	276	11.6 [b]	6.58	0.01 [b]	17520 [e]
DBahA	278	13.7 [b]	6.84	0.01 [b]	18000 [e]
BghiP	276	11.8 [b]	6.50	0.01 [b]	14400 [e]

[a] data from [9] and therein; [b] data were taken from [10]; [c] data source [11]; [d] according to Coover et al. report [12], the half life of Naph and Acy in soil shorter than 60 days, therefore we assumed both of them half life in soil are as the same of Acen's half life; [e] data source [12].

Table S4

Mean concentration of PAHs in soil from different districts of Shenzhen or from different land use types.

Compounds	Acronym	Districts of Shenzhen							Land use types							
		LH	FT	NS	YT	LG	BA	SZ	Ind	Agr	Com	Tra	Res	Orc	For	Gre
2-methylnaphthalene	2-Mn	14	13	22	71	12	33	28	15	17	31	30	14	33	29	19
1-methylnaphthalene	1-Mn	7.7	9.0	13	43	6.7	19	16	9.3	8.4	19	17	7.8	19	17	12
Biphenyl	Bip	2.6	2.8	3.0	7.5	2.7	6.1	4.1	3.1	4	7.3	6.5	2.6	4.6	3.6	2.5
2,6-dimethylnaphthalene	2,6-Dn	14	20	18	69	12	44	30	17	17	53	35	17	36	24	20
Acenaphthylene	Acy	1.0	1.1	1.4	3.9	2.3	2.8	2.1	1.5	1.9	4.1	6.2	1.0	1.8	1.6	1.1
Acenaphthene	Acen	0.8	0.7	0.9	1.7	1.3	1.5	1.2	1.0	1.2	2.3	2.6	0.7	0.9	0.9	0.7
2,3,5-trinaphthalene	Trn	7.7	9.6	7.6	33	4.6	16	13	6.5	7.9	23	16	6.9	12	9.5	9.2
Fluorene	Flo	4.2	5.4	4.7	14	6.7	8.5	7.3	3.8	4.9	14	17	3.4	6.7	5.1	4.3
Phenanthrene	Phe	14	12	13	16	57	33	24	22	26	72	142	12	10	9.7	9.8
Anthracene	Ant	2.3	2.3	2.1	2.3	9.0	5.0	3.8	2.9	4.1	11	20	2.6	2.3	2.0	2.5
2-methylphenanthrene	2-Mp	4.0	3.3	4.0	4.6	10	8.7	5.8	4.7	4.8	15	30	3.9	2.3	2.1	2.5
1-methylphenathrene	1-Mp	2.7	1.9	2.5	2.5	6.0	5.5	3.5	3.0	3.3	9.6	17	2.5	1.3	1.4	1.6
2,6-dimethlyphenanthrene	2,6-Dp	0.7	0.3	0.5	0.5	1.3	1.3	0.8	0.6	0.5	2.7	4.1	0.4	ND	ND	ND
Fluoranthene	Fla	18	8.7	14	10	97	35	31	30	30	110	235	13	4.2	5.1	7.3
Pyrene	Pyr	14	6.9	11	8.2	68	28	23	25	28	76	172	9.9	2.8	3.4	5.5

11H-benzo(b)fluorine	11H-B	1.7	0.7	1.2	1.1	18	5.7	4.7	2.9	1.6	19	49	1.7	0.3	0.4	0.6
Benzo(a)anthracene	B*a*A	6.5	2.5	5.0	4.0	45	14	13	9.5	7.6	51	112	4.6	0.6	0.9	2.2
Chrysene	Chr	16	7.9	14	12	67	35	26	24	17	96	180	11	2.8	3.7	5.8
Benzo(b)fluoranthene	B*b*F	22	10	19	17	99	46	36	33	21	141	252	15	3.0	4.2	8.4
Benzo(k)fluoranthene	B*k*F	6.4	3.6	5.0	5.0	30	15	11	9.5	7.1	42	77	5.0	1.1	1.5	2.8
Benzo(e)pyrene	B*e*P	17	6.9	16	14	56	32	24	23	15	92	149	9.7	1.7	2.3	5.4
Benzo(a)pyrene	B*a*P	9.2	3.5	6.9	6.5	43	17	14	13	8.4	60	105	5.3	0.7	1.4	3.2
Perylene	Per	3.6	3.4	2.8	3.0	13	5.6	5.2	4.4	3.0	20	32	2.6	0	0.3	1.9
9,10-diphenylanthracen	9,10-Di	ND	ND	ND	ND	0.5	ND	ND	ND	ND	1.4	0.6	ND	ND	ND	ND
Iden(123-cd)pyrene	IP	14	4.8	10	11	58	29	21	22	16	89	148	7.3	1.4	2.0	4.6
Dibenzo(a,h)anthracene	DB*ah*A	3.0	1.4	3.1	2.8	18	8.0	6.1	4.1	3.4	23	50	1.9	0.2	0.3	1.0
Benzo(ghi)perylene	B*ghi*P	22	8.9	20	18	70	44	31	33	24	116	190	12	2.3	3.0	7.0
Σ_{27}PAH		230	151	220	383	813	498	383	325	282	1200	2093	174	151	135	140
Σ_{15}PAH		155	80	129	132	670	321	248	235	200	906	1708	104	41	45	66

ND: not detected.

LH: Luohu, FT: Futian, NS:Nanshan, YT: Yantian, LG: Longgang, BA: Baoan, SZ: Shenzhen.

Ind: industry, Agr: agricultural, Com: commerce, Tra: traffic, Res: residential, Orc: orchard, For: forestry, Gre: greenbelt.

Table S5
Estimated mass inventories of PAHs in soils.

		LH	FT	NS	YT	LG	BA	SZ
C (μg/kg) [a]	Σ_{27}PAH	230	151	220	383	813	498	383
	Σ_{15}PAH	155	80	129	132	670	321	248
A (km^2) [b]		79	76	173	73	845	704	1949
Σ_{27}PAH (ton)		3	2	7	5	124	63	204
Σ_{15}PAH (ton)		2	1	4	2	102	41	152
R.A.[c]	Σ_{27}PAH	2	1	3	2	61	31	
	Σ_{15}PAH	1	1	3	1	67	27	

[a] Concentration in μg/kg
[b] Soil area of each district of Shenzhen, data are taken from [13].
[c] Relative abundance of inventory in soil from different district (%).
LH: Luohu, FT: Futian, NS: Nanshan, YT: Yantian, LG: Longgang, BA: Baoan, SZ: Shenzhen.

Fig. S1. Administrative divisions of Shenzhen. The Special Economic Zone comprises of Luohu, Futian, Nanshan, and Yantian but not include Baoan, Guangming, and Longgang district.

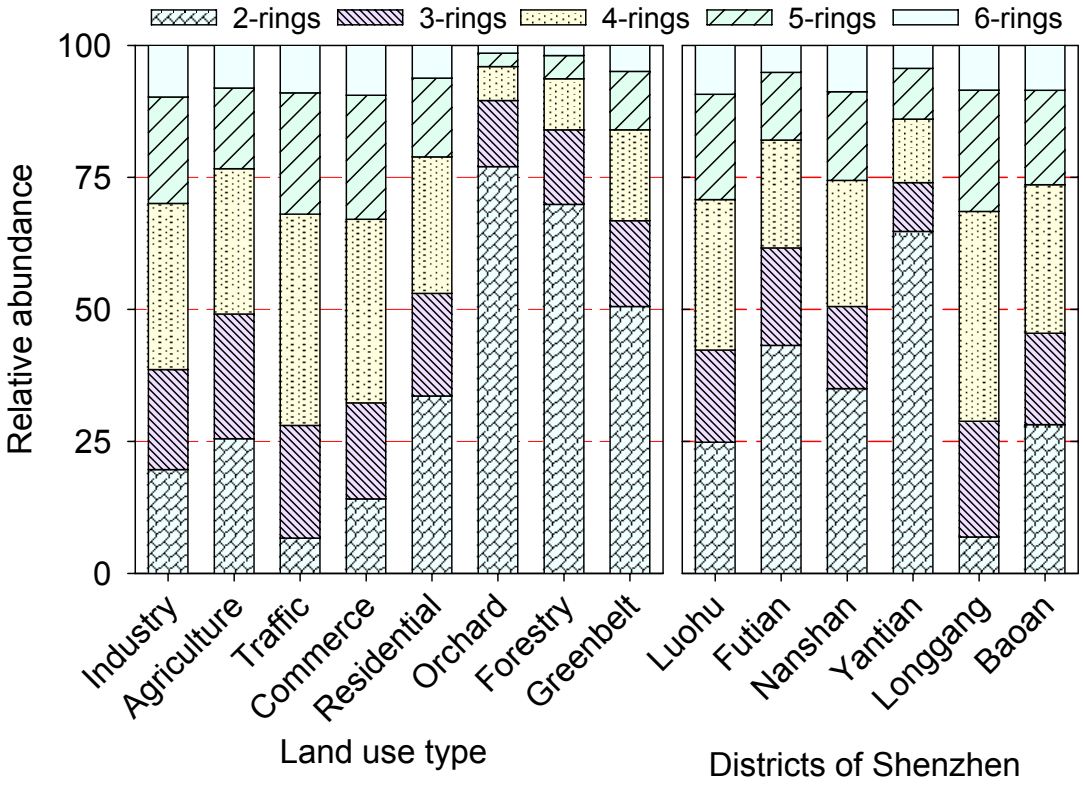

Fig. S2. Percentage composition of 2,3,4,5,6-ring PAHs in the soils of Shenzhen. (2-ring PAHs include naphthalene, 2-methylnaphthalene, 1-methylnaphthalene, biphenyl, 2,6-dimethylnaphthalene, acenaphthylene, acenaphthene, 2,3,5-trinaphthalene, fluorene; 3-ring PAHs include phenanthrene, anthracene, 2-methylphenanthrene, 1-methylphenathrene, 2,6-dimethlyphenanthrene, fluoranthrene; 4-ring PAHs include pyrene, 11H-benzo(b)fluorine), benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene; 5-ring PAHs include benzo(e)pyrene, benzo(a)pyrene, perylene, 9,10-diphenylanthracen, iden(123-cd)pyrene, dibenzo(a,h)anthracene; 6-ring include benzo(ghi)perylene.

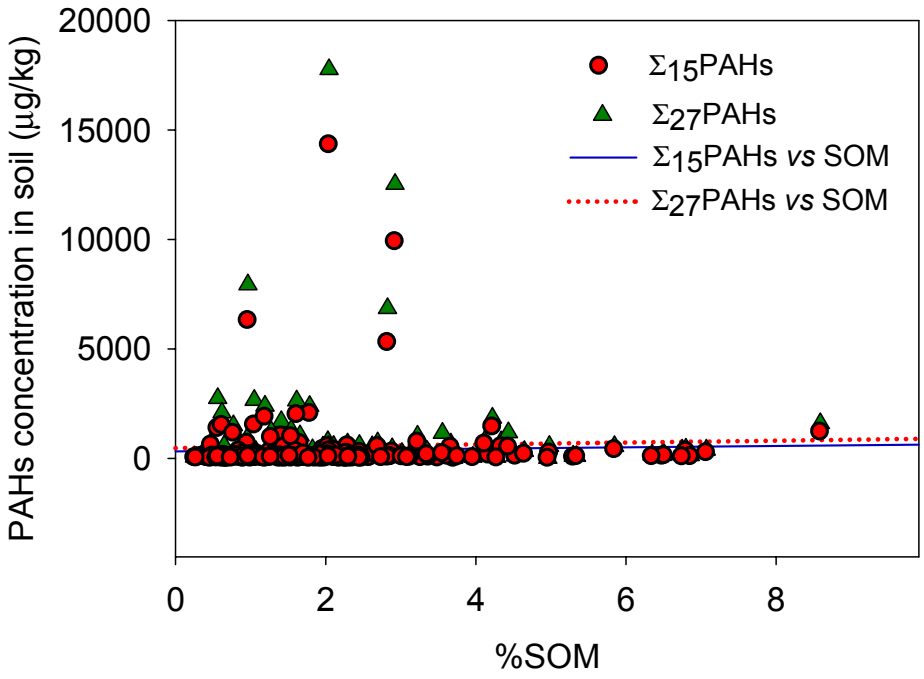

Fig. S3 Regression analysis between concentration of PAHs and fraction of soil organic matter.

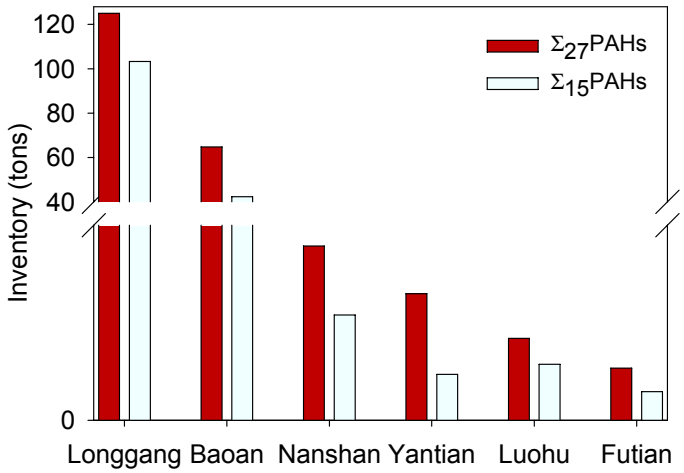

Fig. S4. Inventories of Σ_{27}PAHs and Σ_{15}PAHs in soil of Shenzhen. Longgang, Baoan Nanshan, Yantian, Luohu, Futian are districts of Shenzhen.

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