Supporting Information to the Article:

Comparison of polycyclic aromatic hydrocarbon uptake pathways and risk assessment of vegetables from waste-water irrigated areas in northern China

By

Yanchun Wang[1,2], Min Qiao[1], Yunxia Liu[1], Hans Peter Arp[3], Yong-Guan Zhu[1,4]*

1 Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Shuangqing Road 18, Haidian District, Beijing 100085, PR China

2 Beijing institute of landscape gardening, Huajiadi Street 7, Chaoyang District, Beijing, 100102, PR China

3 Norwegian Geotechnical Institute (NGI), PO Box 3930 Ullevål Stadion, 0806 Oslo, Norway

4 Institute of Urban Environment, Chinese Academy of Sciences, Xiamen, China

Material and methods

Sample extraction and cleanup

Soil samples were extracted by accelerated solvent extraction (ASE) (Dionex ASE 300). Ten grams of soil samples blended with 15g anhydrous sodium sulfate were extracted in 34 mL stainless steel vessels. Extractions were performed with 1:1 mixture of dichloromethane and acetone (pesticide grade, Fisher Company, USA) at 120 °C and 1500 psi for a 5 min heat-up followed by a 10 min static extraction. The vessels were then rinsed with 17 mL of the same solvent and the extracts were purged from the sample cell using pressurized nitrogen at 1500 psi.

The ASE extracts were concentrated using a vacuum rotary evaporator (R-201, Shanghai Shenshen) at 38°C before being transferred to a silica gel/alumina column for sample cleanup. A glass column (20 mm outside diameter,450 mm length) was first filled with 120 mm of silica gel (pre-rinsed with n-hexane), then packed with 60 mm of alumina (pre-rinsed in n-hexane). 20 mm of anhydrous sodium sulfate was added to the top of alumina. During the process, n-hexane was added to ensure the column remained soaked. Columns were pre-eluted with 15 mL of hexane, followed by introduction of the extract an elution of 70 mL of methylene chloride/hexane (v/v=3:7). All elutions were carried out at 2 mL/min. The eluates collected from the silica column were concentrated to 1.0 mL with a rotary evaporator and nitrogen blowdown (SHE812, Beijing Shuaien). The samples were sealed in vials and stored at -18 °C before analysis. The vegetable samples were subjected to similar extraction, involving circa 0.2 g dried shoot samples and circa 0.4 g root samples were used. Solvent blanks were analyzed within each batch.

Sample analysis

Soil and vegetable extracts were analyzed by an Agilent 7890 GC equipped with an Agilent 5975 mass spectrometer under the selected ion monitoring mode (SIM). Total 16 PAHs including naphthalene (Nap), acenaphthylene (Any), acenaphthene (Ace), fluorene (Fle), phenanthrene (Phe), anthracene (Ant), pyrene (Pyr), fluoranthene (Flu), benz[a]anthracene (BaA), chrysene (CHR), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IncdP), benzo[ghi]perylene (BghiP) and dibenzo[a,h]anthracene (DahA) were determined in all samples. A 30 mm×0.25 mm i.d.×0.25 mm film thickness HP 5MS capillary column (Agilent Technology) was used with helium as the carrier gas at a constant flow rate of 1 mL / min. Splitless injection of 1 μL of the sample was conducted with a 7683 autosampler (Agilent Technology). The GC oven temperature was programmed from 50 °C (2 min) to 200 °C (2 min) at 20 °C /min, then to 240 °C (2 min) at 5

°C min before reaching 290 °C at 3 °C min and held for 15 min. The injector and detector temperatures were 280 °C and 300 °C, respectively.

PAHs in the samples were identified by the retention time and the abundance of quantification ions/confirmation ions with respect to authentic PAH standards. Automated library searching was performed using the National Institute of Standards and Technology (NIST) Mass Spectral Database. Quantization was performed using the five-point calibration curve for individual components. Detection limits were 1.5-3.6 μg kg^{-1} dry weight for PAHs. Results were expressed on a dry weight basis.

Table S1. Abraham Solvent Descriptors, Experimental and Predicted Log Dimensionless Octanol-Water (Log Kow) and Air-Water Partition Coefficients (log Kaw) for the EPA-16 PAHs

	E	L	V [a]	A	B	S	log K_{OW} (-) 25°C	log Kaw (-) 25°C
Nap	1.340 [b]	5.161 [d]	1.085	0.00 [b]	0.20 [b]	0.92 [b]	3.33 [g]	-1.73 [g]
Any	1.750 [c]	6.175 [c]	1.216	0.00 [c]	0.20 [f]	1.14 [c]	3.84 [l]	-2.20 [m]
Ace	1.604 [d]	6.469 [c]	1.259	0.00 [d]	0.20 [d]	1.04 [d]	3.94 [g]	-2.63 [j]
Fle	1.588 [d]	6.922 [c]	1.357	0.00 [d]	0.20 [d]	1.03 [d]	4.68 [g]	-2.57 [g]
Phe	2.055 [b]	7.632 [c]	1.454	0.00 [b]	0.29 [b]	1.29 [b]	4.57 [g]	-2.92 [g]
Ant	2.290 [b]	7.568 [c]	1.454	0.00 [b]	0.28 [b]	1.34 [b]	4.63 [h]	-3.34 [m]
Flu	2.377 [e]	8.827 [c]	1.585	0.00 [e]	0.20 [e]	1.55 [e]	5.23 [g]	-3.35 [g]
Pyr	2.808 [d]	8.833 [c]	1.585	0.00 [d]	0.29 [d]	1.71 [d]	4.79 [i]	-4.38 [g]
BaA	2.992 [b]	10.291 [c]	1.823	0.00 [b]	0.35 [b]	1.70 [b]	5.91 [h]	-4.68 [j]
Chr	3.027 [b]	10.334 [c]	1.823	0.00 [b]	0.36 [b]	1.73 [b]	5.91 [g]	-4.56 [j]
BbF	3.194 [c]	11.609 [c]	1.954	0.00 [c]	0.44 [f]	1.82 [c]	5.81 [g]	-4.68 [g]
BkF	3.194 [c]	11.607 [c]	1.954	0.00 [c]	0.44 [f]	1.91 [c]	6.11 [g]	-4.75 [g]
BaP	3.625 [e]	11.715 [c]	1.954	0.00 [e]	0.44 [e]	1.98 [e]	6.13 [g]	-5.58 [g]
IcdP	3.610 [c]	12.690 [c]	2.084	0.00 [f]	0.44 [f]	1.90 [f]	6.64 [l]	-4.92 [k]
DahA	4.000 [c]	12.960 [c]	2.192	0.00 [c]	0.46 [f]	2.04 [c]	7.06 [l]	-5.59 [m]
BghiP	4.073 [e]	13.264 [c]	2.084	0.00 [e]	0.46 [e]	1.90 [e]	6.22 [g]	-5.26 [g]

a) Abraham and McGowan, 1987; b) Torres-Lapasio et al., 2004; c) Abraham, 1993; d) Abraham et al., 1994a; e) Abraham et al., 1994b; f) assumed from homologues; g) De Maagd et al., 1998; h) Yalkowsky and Valvani, 1979; i) Paschke et al., 1999; j) Bamford et al., 1999; k) Tenhulscher et al., 1992; l) Predicted using the Abraham descriptors and the relevant equation in (Goss, 2005); m) Predicted using the Abraham descriptors and the relevant equation in (Mintz et al., 2007)

Table S2 BCFs of vegetable shoot and root

type	PAH	Radish	Cauliflower	Chinese cabbage	Rape	Leek	Leaf lettuce
shoot	Nap	2.43	3.14	3.75	2.94	2.2	4.7
	Any	0.54	0.91	0.81	0.32	0.8	0.5
	Ace	1.11	2.72	1.55	1.24	0.95	1.4
	Fle	2.27	3.69	4.6	2.47	1.62	2.8
	Phe	2.6	3.23	3.87	3.89	2.23	4.1
	Ant	1.51	1.79	2.09	1.17	0.93	1.5
	Flu	0.76	0.96	2.16	0.67	0.62	0.9
	Pyr	0.63	0.64	1.56	2.19	0.74	1.0
	BaA	0.43	0.62	0.47	0.33	0.36	2.0
	Chr	0.46	0.72	0.73	0.51	0.82	1.7

	BbF	0	0.06	0	0	0	0.0
	BkF	0	0.19	0	0	0	0.0
	BaP	0.2	0.19	0.61	0.55	0.15	0.4
	IcdP	0.14	0.11	0.23	0.49	0	0.6
	DahA	0.06	0.18	0.85	0.68	0	1.1
	BghiP	0.82	0.39	0.63	1.08	0.22	0.9
root	Nap	1.21	1.73	2.34	1.09	1.39	4.2
	Any	1.27	1.61	2.02	1.68	1.85	6.6
	Ace	3.66	4.75	4.22	3.84	2.28	5.5
	Fle	3.74	5.63	4.86	3.71	4.75	5.6
	Phe	1.64	2.14	1.18	2.12	2.3	3.1
	Ant	1.88	1.41	1.78	1.89	0.37	4.1
	Flu	0.66	0.98	2.06	1.26	0.35	0.7
	Pyr	0.81	1.13	2.73	2	0.47	0.9
	BaA	0.75	0.72	0.91	1.11	0.46	2.1
	Chr	1.58	2.04	2.1	3.3	2.38	4.0
	BbF	0.23	0	0.25	0.18	0.16	0.1
	BkF	0.12	0	0.09	0.11	0.06	0.3
	BaP	0.53	0.32	0.45	0.41	0.29	0.4
	IcdP	0.2	0.25	0.15	0.15	0.2	0.8
	DahA	0.11	0	0.02	0.1	0.16	0.0
	BghiP	1.05	0.8	0.94	0.92	0.21	0.3

References

Abraham, M. H. (1993). Hydrogen Bonding XXVII. Solvation Parameters for Functionally Substituted Aromatic Compounds and Heterocyclic Compounds, from Gas-Liquid Chromatographic Data. *J. Chromatogr.* **644**, 95-139.

Abraham, M. H., Andonian-Haftvan, J., Whiting, G. S., Leo, A. and Taft, R. S. (1994a). Hydrogen Bonding. Part 34. The Factors that Influence the Solubility of Gases and Vapours in Water at 298 K, and a New Method for its Determination. *J. Chem. Soc. Perkin Trans.* **2**, 1777-1791.

Abraham, M. H., Chadha, H. S., Whiting, G. S. and Mitchell, R. C. (1994b). Hydrogen Bonding. 32. An Analysis of Water-Octanol and Water-Alkane Partitioning and the Dlog P Parameter of Seiler. *J. Pharm. Sci.* **83**, 1085-1100.

Abraham, M. H. and McGowan, J. C. (1987). The Use of Characteristic Volumes to Measure Cavity Terms in Reversed Phase Liquid Chromatography. *Chromatographia*. **23**, 243-246.

Bamford, H. A., Poster, D. L. and Baker, J. E. (1999). Temperature dependence of Henry's law constants of thirteen polycyclic aromatic hydrocarbons between 4 degrees C and 31 degrees C. *Environmental Toxicology and Chemistry*. **18**, 1905-1912.

De Maagd, P. G. J., Ten Hulscher, D., Van den Heuvel, H., Opperhuizen, A. and Sijm, D. (1998). Physicochemical properties of polycyclic aromatic hydrocarbons: Aqueous solubilities, n-octanol/water partition coefficients, and Henry's law constants. *Environmental Toxicology and Chemistry*. **17**, 251-257.

Goss, K. U. (2005). Predicting the equilibrium partitioning of organic compounds using just one linear solvation energy relationship (LSER). *Fluid Phase Equilibria*. **233**, 19-22.

Mintz, C., Clark, M., Acree, W. E. and Abraham, M. H. (2007). Enthalpy of solvation correlations for gaseous solutes dissolved in water and in 1-octanol based on the abraham model. *Journal of Chemical Information and Modeling*. **47**, 115-121.

Paschke, A., Popp, P. and Schuurmann, G. (1999). Solubility and partitioning studies with polycyclic aromatic hydrocarbons using an optimized SPME procedure. *Fresenius Journal of Analytical Chemistry*. **363**, 426-428.

Tenhulscher, T. E. M., Vandervelde, L. E. and Bruggeman, W. A. (1992). Temperature-Dependence of Henry Law Constants for Selected Chlorobenzenes, Polychlorinated-Biphenyls and Polycyclic Aromatic-Hydrocarbons. *Environmental Toxicology and Chemistry*. **11**, 1595-1603.

Torres-Lapasio, J. R., Garcia-Alvarez-Coque, M. C., Roses, M., Bosch, E., Zissimos, A. M. and Abraham, M. H. (2004). Analysis of a solute polarity parameter in reversed-phase liquid chromatography on a linear solvation relationship basis. *Anal. Chim. Acta*. **515**, 209-227.

Yalkowsky, S. H. and Valvani, S. C. (1979). Solubilities and partitioning .2. relationships between aqueous solubilities, partition-coefficients, and molecular-surface areas of rigid aromatic-hydrocarbons. *Journal of Chemical and Engineering Data*. **24**, 127-129.