Electronic Supplementary Material (ESI) for Environmental Science: Processes & Impacts.

Supplementary Information

Environmental Science: Processes & Impacts

Pharmaceuticals and personal care products (PPCPs) in urban and suburban rivers of Beijing, China: occurrence, source apportionment and potential ecological risk

Guohua Dai[a,b], Bin Wang[*b,c], Chaochen Fu[d], Rui Dong[b,c], Jun Huang[b,c], Shubo Deng[b,c], Yujue Wang[b,c], Gang Yu[b,c]

[a] State Key Laboratory of Vegetation and Environmental Change, Institute of Botany, Chinese Academy of Sciences, Beijing 100093, China;

[b] Beijing Key Laboratory of Emerging Organic Contaminants, State Key Joint Laboratory of Environmental Simulation and Pollution Control, School of Environment, Tsinghua University，Beijing 100084, China. E-mail address: thuwb@tsinghua.edu.cn, Fax: +86-10-62794006, Tel.: +86-10-62795315.

[c] Collaborative Innovation Center for Regional Environmental Quality, Tsinghua University, Beijing 100084, China

[d] Beijing Water Authority, Beijing, Beijing, 100038, China

This file includes:
Supplemental Tables S1-S5
Supplemental Figure S1
Supplemental References

Table S1 Information of the study area and WWTPs investigated

Watershed	Area (km^2)	Population × 10^3	WWTPs	Population serviced × 10^3 [a]	Daily flow (10^3 m^3)	HRT (h)	SRT (d)	Secondary treatment
Qing River	210	3000	QWTP	2000	400	13.5	12-15	A^2/O
			XJWTP	500	80	11	15	A^2/O
Liangshui River	624	4500	XHMWTP	2415	600	11	15	A^2/O
			BWTP	400	80	10.6	12-15	OD
			YJWTP	--	10	--	--	--

QWTP, XJHWTP, XHMWTP and BWTP employ similar conventional treatment process: primary treatment to remove particles coupled with secondary biological treatment. YJWTP only have primary treatment equipment to remove particles without secondary biological treatment. For the secondary biological treatment process, QWTP, XJHWTP and XHMWTP employ anaerobic/anoxic/oxic (A^2/O) activated sludge process, and BWTP employs oxidation ditch (OD). HRT: hydraulic retention time; SRT: solid retention time. [a] Population serviced by QWTP was estimated according to its capacity.

Table S2 Optimized ESI-MS/MS parameters for analysis of the analytes by MRM

Compound	Acronym	ESI	Retention time (min)	Precursor ion ($m z^{-1}$)	Product ion ($m z^{-1}$)	MS/MS parameters				
						DP (V)	EP (V)	CEP (V)	CE (V)	CXP (V)
Sulpiride	SP	+	2.34	342.0	**112.1**	65	5	8	22	2
					214.2	65	5	14.6	28	2
Trimethoprim	TP	+	5.23	291.2	**230.3**	70	8	20	30	2
					123.2	70	7	13	30	3
Propranolol	PPN	+	5.87	259.8	**155.2**	65	5	8	22	2
					127.2	65	5	14.6	28	2
Caffeine	CF	+	5.91	195.1	**138.1**	57	5	11.6	23	2.2
					110.0	55	4	10	32	2.2
Metoprolol	MTP	+	6.75	268.2	**116.0**	50	4	10	24	2.2
					133.2	60	4	10	30	2
^{13}C-phenacetin		+	8.75	181.1	**139**	53	4	10	20	4
					110	63	4	7	30	4
Nalidixic acid	NA	+	10.3	233.2	**215.3**	60	5	10	20	4
					187.2	60	5	10	30	4
Carbamazepine	CBZ	+	11.08	237.1	**194.2**	57	6	14	32	2.5
					192.3	61	8	10	32	2.5
DEET-d_7		+	11.94	199.2	**126.2**	53	4	8	35	2
					98.1	55	4	7	28	2
N,N-diethyl-meta - toluamide	DEET	+	12.06	192.2	**119.1**	60	8	18	20	2
					91.1	60	8	14	40	3
Chloramphenicol-d_5		-	4.37	326	**157.1**	-60	-4	-12	-28	-2
					262.1	-55	-3	-25	-26	-2
Chloramphenicol	CP	-	4.43	320.8	**152.1**	-70	-4.9	-20	-30	-2
					257.0	-70	-4.5	-20	-22	-2
Ketoprofen	KP	-	5.60	252.9	**209.1**	-33	-4	-25	-20	-2
Mecoprop-d_3		-	5.86	215.7	**144**	-35	-3.2	-5	-25	-1
Bezafibrate	BF	-	6.34	360.0	**274.0**	-44.5	-4.5	-20	-25	-2.3
					154.2	-40	-4.1	-20	-25	-1.4
Diclofenac	DF	-	7.12	293.7	**250.0**	-36	-4.5	-24	-25	-2
					214.2	-33	-4	-20	-33	-2
Indomethacin	IM	-	7.45	355.9	**312.1**	-35	-3	-26	-22	-3
					297.1	-35	-3.5	-25	-35	-3.5
Mefenamic acid	MA	-	7.61	239.9	**196.1**	-50	-3	-13	-29	-1.5
					180.1	-50	-4.5	-14	-40	-1.5
Gemfibrozil-d_6		-	8.73	255.1	**121.1**	-40	-2.5	-20	-30	-2.5
					133.2	-40	-2.5	-17	-17	-2
Gemfibrozil	GF	-	8.73	248.9	**121.1**	-65	-4	-17	-30	-2
					127.1	-65	-4	-20	-17	-2

Note: The bold figure of parent ions were used for quantification, other ions were used for confirmation

DP: declustering potential; EP: entrance potential; CEP: collision cell entrance potential; CE: collision energy potential; CXP: collision cell exit potential

Table S3 Concentration (ng L-1) and detection frequency (%) of pharmaceuticals and personal care products (PPCPs) in all samples

Compounds	Concentration (ng L^{-1}) River waters L-H (M)[a]	River waters Frequency (%)	WWTP effluents L-H (M)	WWTP effluents Frequency (%)	Discharged samples L-H (M)	Discharged samples Frequency (%)	Recovery (%) (mean±SD)	Matrix effect (%) (mean±SD)	LOQ[b] (ng L^{-1})
CP	13.4-43.2 (17.0)	100	14.7-48.4 (18.3)	100	nq-73.2 (25.2)	92	90±6.2	35.6±7.1	5.32
NA	nq-231 (89.7)	91	22.7-254 (130)	100	nq-243 (93.1)	75	49±5.3	37.5±6.3	4.98
TP	nq-125 (51.5)	69	33.0-167 (39.2)	100	nq-862 (63.5)	83	71±5.1	4.3±2.2	3.85
GF	8.24-39.5 (15.5)	100	11.1-19.5 (12.0)	100	8.95-63.5 (13.3)	100	111±2.6	26.7±2.7	4.24
BF	14.4-116 (36.3)	100	14.0-297 (40.4)	100	13.7-148 (31.6)	100	99±2.9	25.6±3.1	4.17
DF	17.5-241 (71.5)	100	75.4-214 (135)	100	14.1-159 (88.5)	100	109±3.1	2.3±1.2	7.62
IM	12.2-91.6 (42.3)	100	30.5-148 (73.8)	100	nq-157 (42.8)	92	96±5.0	1.5±4.5	6.40
MA	8.63-27.4 (13.1)	100	11.2-16.4 (15.7)	100	8.62-20.9 (13.5)	100	90±8.2	12.3±6.2	2.98
KP	17.4-326 (77.6)	100	57.0-178 (114)	100	15.0-241 (124)	100	104±6.9	25.2±5.6	8.24
MTP	32.1-332 (115)	100	99.8-880 (296)	100	nq-284 (165)	92	69±4.5	15.6±4.3	3.31
PPN	nq	0	nq	0	nq	0	56±2.6	27.6±3.2	11.0
CBZ	5.25-55.6 (24.7)	100	22.0-58.7 (30.5)	100	3.64-85.0 (39.4)	100	90±4.2	5.7±1.2	2.34
SP	5.91-187 (90.0)	100	52.8-174 (141)	100	nq-193 (173)	83	45±2.8	49.5±2.1	3.44
DEET	16.5-177 (83.4)	100	57.2-217 (110)	100	29.9-881 (127)	100	89±1.9	24.3±1.4	1.78
CF	19.8-4720 (1870)	100	23.9-11700 (285)	100	14.5-11900 (3570)	100	117±2.6	35.9±5.2	4.40
SumPPCP	276-6109 (2780)		685-13560 (1971)		219-13805 (4706)				

nq: not quantified (< LOQ).

[a] L, the lowest concentration; H, the highest concentration; M, median concentration.

[b] Limit of quantification (LOQ).

Table S4 Predicted no-effect concentrations (PNECs, ng L^{-1}) and corresponding risk quotients (RQs) for the detected PPCP compounds in the WWTP effluents, directly discharged wastewaters and river waters. Values between 0.1 and 1 (medium risk) are reported in bold

PPCPs	PNEC [a] (μg L^{-1})			Effluents			Discharged wastewater			Liangshui River			Qing River		
	Fish	Daphnia	Algae	Fish	Daphnia	Algae	Fish	Daphnia	Algae	Fish	Daphnia	Algae	Fish	Daphnia	Algae
TP	100	4.8	2.6	0.002	0.03	0.06	0.01	**0.2**	**0.3**	0.001	0.03	0.05	0.0004	0.01	0.02
GF	0.9	6	4	0.02	0.003	0.005	0.07	0.01	0.02	0.04	0.01	0.01	0.02	0.002	0.004
BF	5.3	25	18	0.06	0.01	0.02	0.03	0.006	0.008	0.02	0.005	0.01	0.01	0.001	0.002
DF	532	22.4	16.3	0.0004	0.01	0.01	0.000	0.007	0.010	0.0005	0.01	0.01	0.000	0.004	0.01
IM	3.9	26	18	0.04	0.006	0.008	0.04	0.006	0.009	0.02	0.004	0.01	0.01	0.002	0.003
KP	32	248	164	0.006	0.001	0.001	0.01	0.002	0.003	0.01	0.001	0.002	0.003	0.0004	0.001
MA		0.43			0.04			0.05			0.06			0.04	
MTP	116	8	14	0.008	**0.1**	0.06	0.002	0.04	0.02	0.003	0.04	0.02	0.001	0.02	0.01
CBZ	35.4	13.8	70	0.002	0.004	0.001	0.002	0.006	0.001	0.002	0.004	0.001	0.001	0.002	0.0003
DEET	71.3	75	388	0.003	0.003	0.001	0.01	0.01	0.002	0.002	0.002	0.0005	0.001	0.001	0.0002
CF	151	46	46	0.08	**0.3**	**0.3**	0.08	**0.3**	**0.3**	0.03	**0.1**	**0.1**	0.01	0.05	0.05

[a] PNEC data is assumed as the lowest toxicological value among those available in literature divided per 1000, for the three trophic levels, algae, daphnia and fish, respectively. Detailed information is shown in Table S3.

Table S5 Ecotoxicity data for the selected compounds available in literature, together with the corresponding species assayed, test endpoint, toxicity concentration, references and the resulting Predicted No-Effect Concentrations (PNECs). This is assumed as the lowest toxicological value among those available and here reported divided per 1000

Compounds	Species Assayed	Test (endpoint)	Toxicity (mg/L)	References	PNEC (μg L^{-1})
TP	*Fish*	EC50 ECOSAR	795	1	
	Daphnia	**EC50 ECOSAR**	**4.8**	**1**	**4.8**
	Algae	**EC50 ECOSAR**	**2.6**	**1**	**2.6**
	Bacteria	EC50 (15min)	177	2	
	Daphnia	EC50 (96h-immobility)	121	2	
	Fish	EC50 (48h)	>100	3	
	Invertebrates	LC50 (96h)	>100	2	
	Invertebrates	EC50	110	4	
	Algae	EC50	90	4	
	Fish	**EC50**	**100**	**4**	**100**
GF	***Fish***	**EC50 ECOSAR**	**0.9**	**1**	**0.9**
	Daphnia	**EC50 ECOSAR**	**6**	**1**	**6**
	Algae	**EC50 ECOSAR**	**4**	**1**	**4**
	Bacteria	EC50 (15 min)	35.3	5	
	Bacteria	EC50(15 min)	18.8	6	
	Invertebrates	EC50 (48 h)	10.4	7	
	Invertebrates	EC50 (96 h)	1.18	3	
BF	***Fish***	**EC50 ECOSAR**	**5.3**	**1**	**5.3**
	Daphnia	**EC50 ECOSAR**	**25**	**1**	**25**
	Algae	**EC50 ECOSAR**	**18**	**1**	**18**
	Invertebrates	EC50	50	4	
DF	***Fish***	**EC50 ECOSAR**	**532**	**1**	**532**
	Daphnia	EC50 ECOSAR	5057	1	
	Algae	EC50 ECOSAR	2911	1	
	Daphnia	**EC50 (48h-mortality)**	**22.4**	**8**	**22.4**
	Algae	**EC50 (96h-growth)**	**16.3**	**8**	**16.3**
	Bacteria	EC50(30min-luminescence)	11.4	8	
	Bacteria	EC50 (15min-inhibition)	9.7	9	
	Microtox	EC50 (30min)	11.45	10	
	Daphnia	EC50 (48h)	22.43	10	

Compounds	Species Assayed	Test (endpoint)	Toxicity (mg/L)	References	PNEC (µg L^{-1})
	C. dubia	EC50 (48h)	22.7	10	
	Algae	EC50 (96h-growth)	14.5	10	
	Invertebrates	EC50	90	4	
	Algae	EC50-inhibition	72	11	
	Daphnia	EC50-immobilization	68	11	
IM	***Fish***	**EC50 ECOSAR**	**3.9**	**1**	**3.9**
	Daphnia	**EC50 ECOSAR**	**26**	**1**	**26**
	Algae	**EC50 ECOSAR**	**18**	**1**	**18**
KP	***Fish***	**EC50 ECOSAR**	**32**	**1**	**32**
	Daphnia	**EC50 ECOSAR**	**248**	**1**	**248**
	Algae	**EC50 ECOSAR**	**164**	**1**	**164**
	Bacteria	EC50 (15min)	15.6	6	
MA	***Daphnia***	**EC50 ECOSAR**	**0.43**	**12**	**0.43**
PPN	*Fish*	EC50 ECOSAR	29.5	1	
	Daphnia	**EC50 ECOSAR**	**2.3**	**1**	**2.3**
	Algae	EC50 ECOSAR	5.5	1	
	Bacteria	EC50(30min-luminescence)	61	8	
	Algae	EC50 (48 h)	0.7	13	
	Diatoms	EC50 (96 h-growth)	0.244	8	
	Invertebrates	LC50(48 h)	0.8	14	
	Fish	LC50 (48 h)	24.3	14	
	Invertebrates	EC50	11	4	
	Algae	**EC50**	**0.8**	**4**	**0.8**
	Fish	**EC50**	**20**	**4**	**20**
MTP	***Fish***	**EC50 ECOSAR**	**116**	**1**	**116**
	Daphnia	**EC50 ECOSAR**	**8**	**1**	**8**
	Algae	**EC50 ECOSAR**	**14**	**1**	**14**
	Invertebrates	LC50 (48h)	>100	14	
	Invertebrates	LC50 (48h)	8.8	14	
	Invertebrates	LC50 (48h)	63.9	14	
	Fish	LC50 (48h)	>100	14	
CBZ	*Fish*	EC50 ECOSAR	101	1	
	Daphnia	EC50 ECOSAR	111	1	
	Algae	**EC50 ECOSAR**	**70**	**1**	**70**

Compounds	Species Assayed	Test (endpoint)	Toxicity (mg/L)	References	PNEC (µg L^{-1})
	Algae	EC50 (3days)	74	15	
	Bacteria	EC50 (15min)	52.2	2	
	Fish	**EC50 (48h)**	**35.4**	**2**	**35.4**
	Daphnia	**EC50 (48h-mortality)**	**13.8**	**8**	**13.8**
	Diatoms	EC50 (96h- growth)	31.6	8	
	C. dubia	EC50 (48h)	77.7	10	
DEET	***Algae***	**EC50 (24 h)**	**388**	**16**	**388**
	Daphnia	**EC50 (48h-immobilisation)**	**75**	**17**	**75**
	Fish	**LC50 (96 h)**	**71.3**	**17**	**71.3**
	Daphnia	LC50 (96 h)	108	18	
CF	*Fish*	EC50 ECOSAR	805	1	
	Daphnia	**EC50 ECOSAR**	**46**	**1**	**46**
	Algae	**EC50 ECOSAR**	**46**	**1**	**46**
	Cladocerans	LC50	182	4	
	Fish	**LC50**	**151**	**19**	**151**

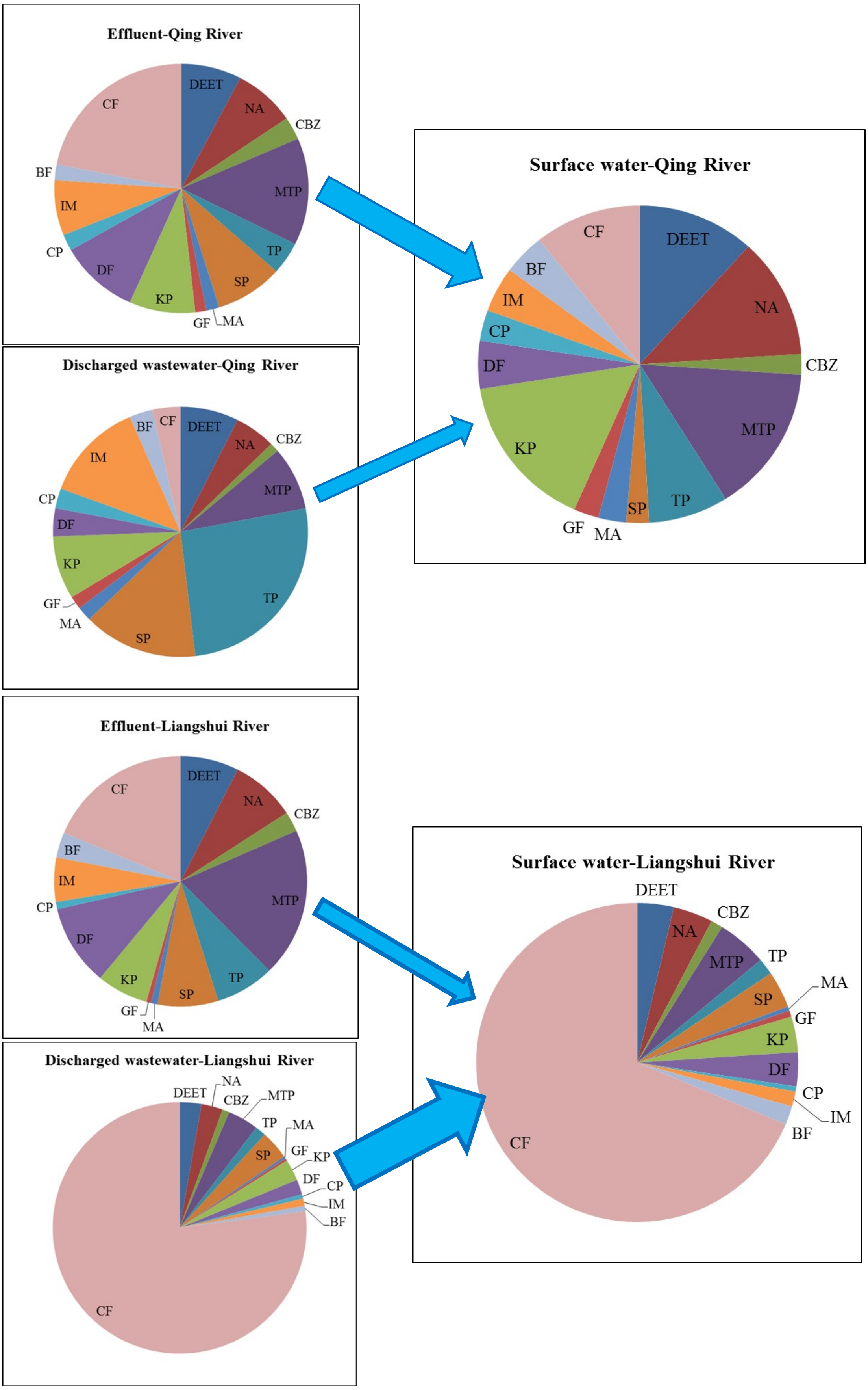

Figure S1: Fraction of PPCPs in effluents, discharged wastewaters and river waters.

Reference

1 H. Sanderson, D. J. Johnson, C. J. Wilson, R. A. Brain, K. R. Solomon, *Toxicol. Lett*., 2003, **144**, 383-395.

2 Y. Kim, K. Choi, J. Jung, S. Park, P. Kim, J. Park, *Environ. Int*., 2007, **33**, 370-375.

3 B. Quinn, F. Gagné, C. Blaise, *Sci. Total Environ*., 2008, **389**, 306-314.

4 C. Boillot, PhD Thesis, 2008, Institut National des Sciences Appliquées de Lyon, France, Nd'ordre ISAL 0021.

5 R. Rosal, M. S. Gonzalo, K. Boltes, P. Letón, J. J. Vaquero, E. García-Calvo, *J. Hazard. Mater*., 2009, **172**, 1061-1068.

6 M. Farré, I. Ferrer, A. Ginebreda, M. Figueras, L. Olivella, L. Tirapu, M. Vilanova, D. Barceló, *J. Chromatogr. A*, 2001, **938**, 187-197.

7 G. H. Han, H. G. Hur, S. D. Kim, *Environ. Toxicol. Chem*., 2006, **25**, 265-71.

8 B. Ferrari, R. Mons, B. Vollat, B. Fraysse, N. Paxeus, R. Lo Giudice, A. Pollio, J. Garric, *Environ. Toxicol. Chem*., 2004, **23**, 1344-1354.

9 J. S. Ra, S. Y. Oh, B. C. Lee, S. D. Kim, *Environ. Int*., 2008, **34**, 184-192.

10 B. Ferrari, N. Paxeus, R. Lo Giudice, A. Pollio, J. Garric, *Environ. Toxicol. Chem.*, 2003, **55**, 359-370.

11 M. Cleuvers, *Ecoto. Environ. Safe*, 2004, **59**, 309-315

12 O. A. H. Jones, N. Voulvoulis, J. N. Lester, *Water Res*., 2002, **36**, 5013-5022.

13 M. Cleuvers, *Chemosphere*, 2005, **59**, 199-205.

14 D. B. Huggett, B. W. Brooks, B. Peterson, C. M. Foran, D. Schlenk, *Bull. Environ. Contam. Toxicol*., 2002, **43**, 229-235.

15 M. Cleuvers,. *Toxicol. Lett*., 2003, **142**, 185-194.

16 S. D. Costanzo, A. J. Watkinson, E. J. Murby, D. W. Kolpin, M. W. Sandstrom, *Sci. Total Environ.*, 2007, **384**, 214-220.

17 Office of Pesticide Programs, Environmental Fate and Effects Division, U.S.EPA, Washington, D.C., 2000.

18 J. Seo, Y. G. Lee, S. D. Kim, C. J. Cha, J. H. Ahn, H. G. Hur, *Arch. Environ. Contam. Toxicol.*, 2005, **48**, 323-328.

19 C. L. Russom, S. P. Bradbury, S. J. Broderius, D. E. Hammermeister, R. A. Drummond, *Environ. Toxicol. Chem*., 1997, **16**, 948-967.