ISSN 1001-0742
CN 11-2629/X

2012
Volume 24
Number 4

JOURNAL OF

ENVIRONMENTAL SCIENCES

ELSEVIER
Science Press

Sponsored by
Research Center for Eco-Environmental Sciences
Chinese Academy of Sciences

ISSN 1001–0742 **Journal of Environmental Sciences** Vol. 24 No. 4 2012

CONTENTS

Aquatic environment

Comparison of conventional and inverted A^2/O processes: Phosphorus release and uptake behaviors
Rong Qi, Tao Yu, Zheng Li, Dong Li, Takashi Mino, Tadashi Shoji, Kochi Fujie, Min Yang ····· 571

Distribution of heavy metals in sediments of the Pearl River Estuary, Southern China: Implications for sources and historical changes
Feng Ye, Xiaoping Huang, Dawen Zhang, Lei Tian, Yanyi Zeng ····· 579

Removal of arsenate and arsenite from aqueous solution by waste cast iron
Nag-Choul Choi, Song-Bae Kim, Soon-Oh Kim, Jae-Won Lee, Jun-Boum Park ····· 589

Effect of artificial aeration on the performance of vertical-flow constructed wetland treating heavily polluted river water
Huiyu Dong, Zhimin Qiang, Tinggang Li, Hui Jin, Weidong Chen ····· 596

A 60-year sedimentary record of natural and anthropogenic impacts on Lake Chenghai, China
Fengyu Zan, Shouliang Huo, Beidou Xi, Jingtian Zhang, Haiqing Liao, Yue Wang, Kevin M. Yeager ····· 602

Preparation and application of amino functionalized mesoporous nanofiber membrane via electrospinning for adsorption of Cr^{3+} from aqueous solution
Ahmed A. Taha, Junlian Qiao, Fengting Li, Bingru Zhang ····· 610

Removal of phosphate ions from aqueous solution using Tunisian clays minerals and synthetic zeolite
Noureddine Hamdi, Ezzeddine Srasra ····· 617

Atmospheric environment

Impacts of continuously regenerating trap and particle oxidation catalyst on the NO_2 and particulate matter emissions emitted from diesel engine
Zhihua Liu, Yunshan Ge, Jianwei Tan, Chao He, Asad Naeem Shah, Yan Ding, Linxiao Yu, Wei Zhao ····· 624

Dry deposition velocity of total suspended particles and meteorological influence in four locations in Guangzhou, China
Leifu Chen, Shaolin Peng, Jingang Liu, Qianqian Hou ····· 632

Synthesis, characterization and experimental investigation of Cu-BTC as CO_2 adsorbent from flue gas
Jiangkun Xie, Naiqiang Yan, Zan Qu, Shijian Yang ····· 640

Aerosol effects on ozone concentrations in Beijing: A model sensitivity study
Jun Xu, Yuanhang Zhang, Shaoqing Zheng, Youjiang He ····· 645

Measurement of air exchange rates in different indoor environments using continuous CO_2 sensors
Yan You, Can Niu, Jian Zhou, Yating Liu, Zhipeng Bai, Jiefeng Zhang, Fei He, Nan Zhang ····· 657

Influence of different weather events on concentrations of particulate matter with different sizes in Lanzhou, China
Xinyuan Feng, Shigong Wang ····· 665

Terrestrial environment

Sorption of chlorophenols onto fruit cuticles and potato periderm
Yungui Li, Yingqing Deng, Baoliang Chen ····· 675

Effects of urea and $(NH_4)_2SO_4$ on nitrification and acidification of Ultisols from Southern China
Deli Tong, Renkou Xu ····· 682

Health risk assessment of heavy metals in soils and vegetables from wastewater irrigated area, Beijing-Tianjin city cluster, China
Yanchun Wang, Min Qiao, Yunxia Liu, Yongguan Zhu ····· 690

PCDD/Fs in soil around a hospital waste incinerator: comparison after three years of operation
Xiaodong Li, Mi Yan, Jie Yang, Tong Chen, Shengyong Lu, Jianhua Yan ····· 699

Dissolved organic sulfur in streams draining forested catchments in southern China
Zhanyi Wang, Xiaoshan Zhang, Zhangwei Wang, Yi Zhang, Bingwen Li, Rolf Vogt ····· 704

Environmental biology

Ammonium-dependent regulation of aerobic methane-consuming bacteria in landfill cover soil by leachate irrigation
Fan Lü, Pinjing He, Min Guo, Na Yang, Liming Shao ····· 711

Steady performance of a zero valent iron packed anaerobic reactor for azo dye wastewater treatment under variable influent quality
Yaobin Zhang, Yiwen Liu, Yanwen Jing, Zhiqiang Zhao, Xie Quan ····· 720

Identification of naphthalene metabolism by white rot fungus *Armillaria* sp. F022
Tony Hadibarata, Abdull Rahim Mohd Yusoff, Azmi Aris, Risky Ayu Kristanti ····· 728

Environmental health and toxicology

Inhibition of ROS elevation and damage to mitochondrial function prevents lead-induced neurotoxic effects on structures and functions of AFD neurons in *Caenorhabditis elegans*
Qiuli Wu, Peidang Liu, Yinxia Li, Min Du, Xiaojuan Xing, Dayong Wang ····· 733

Environmental catalysis and materials

Photodegradation of Norfloxacin in aqueous solution containing algae
Junwei Zhang, Dafang Fu, Jilong Wu ····· 743

Synthesis of TiO_2 nanoparticles in different thermal conditions and modeling its photocatalytic activity with artificial neural network
Fatemeh Ghanbary, Nasser Modirshahla, Morteza Khosravi, Mohammad Ali Behnajady ····· 750

Preparation of $Fe_xCe_{1-x}O_y$ solid solution and its application in Pd-only three-way catalysts
Jianqiang Wang, Meiqing Shen, Jun Wang, Mingshan Cui, Jidong Gao, Jie Ma, Shuangxi Liu ····· 757

Dechlorination of chlorophenols by zero valent iron impregnated silica
Praveena Juliya Dorathi, Palanivelu Kandasamy ····· 765

Photocatalytic degradation of perfluorooctanoic acid with β-Ga_2O_3 in anoxic aqueous solution
Baoxiu Zhao, Mou Lv, Li Zhou ····· 774

Serial parameter: CN 11-2629/X*1989*m*210*en*P*27*2012-4

jesc.ac.cn

Available online at www.sciencedirect.com
ScienceDirect
Journal of Environmental Sciences 2012, 24(4) 675–681
JOURNAL OF ENVIRONMENTAL SCIENCES
ISSN 1001-0742
CN 11-2629/X
www.jesc.ac.cn

Sorption of chlorophenols onto fruit cuticles and potato periderm

Yungui Li[1,3], Yingqing Deng[1], Baoliang Chen[1,2,*]

1. Department of Environmental Science, Zhejiang University, Hangzhou 310058, China. E-mail: yungui2008@yahoo.com.cn
2. Zhejiang Provincial Key Laboratory of Organic Pollution Process and Control, Hangzhou 310058, China
3. Department of Environmental Engineering, Southwest University of Science and Technology, Mianyang 621010, China

Received 10 August 2011; revised 27 September 2011; accepted 10 October 2011

Abstract

To better understand the interaction mechanisms of plant surfaces with polar organic compounds, sorption of 4-chlorophenol, 2,4-dichlorophenol, and 2,4,6-trichlorophenol by fruit cuticles (i.e., tomato, apple, and pepper), and potato tuber periderm were investigated. The roles of cuticular components (waxes, cutin, cutan and sugar) on sorption of chlorophenols are quantitatively compared. Cutin and waxes govern the sorption capacity of bulk apple cuticle by hydrophobic interactions. Potato periderm with highest sugar content exhibits the lowest sorption capability for the chlorophenols. With the increase of hydrophobicity (i.e., K_{ow}) of sorbate, the relative contribution of lipophilic components (wax, cutin and cutan) on total sorption increases, however, the ratios of K_{oc} to K_{ow} decreases due to increasing ionization degree of sorbates.

Key words: potato periderm; fruit cuticle; chlorophenol; sorption; waxes; cutin

DOI: 10.1016/S1001-0742(11)60891-7

Introduction

Plant cuticles (above-ground parts) along with periderm (below-ground) covered the outmost of higher plants play a significant role in the physiology and autecology of plant. Plant cuticles serve as the initial contact of plant tissue with agrichemicals and environmental contaminants (Chen et al., 2005; Koch et al., 2008; Wang et al., 2008). Cuticle is mainly made up of the lipid biopolymer, e.g., waxes, cutin and cutan, and non-lipid components, e.g., polysaccharides, polypeptides and phenolic compounds (Müller and Riederer, 2005; Li and Chen, 2009). Waxes are the extractable lipids by organic solvents, whereas cutin (depolymerizable ester-bound lipids) and cutan (non-saponifiable biopolymer) are insoluble polymeric lipids (Li and Chen, 2009). As an initial process of cuticle (periderm) penetration, sorption process dominated the efficiency of agrichemicals plant uptake and the degree of contaminants plant accumulation (Riederer and Schnöherr, 1984; Buchholz, 2006). Several studies were conducted to illustrate the sorption characteristics and mechanisms of nonpolar organic compounds by plant cuticles (Riederer and Schnöherr, 1984; Sabljic et al., 1990; Chefetz, 2003; Chen et al., 2005, 2008; Chen and Li, 2007; Li and Chen, 2009; Li et al., 2010). Plant cuticles were demonstrated to be highly efficient sorbents for nonpolar organic compounds (Riederer and Schnoherr, 1984), and their sorption coefficients were predictable from the octanol/water partition coefficients (K_{ow}) of sorbates (Sabljic et al., 1990). Recently, the relative role of each cuticle composition on total sorption behavior was illustrated (Chefetz, 2003; Chen et al., 2005, 2008; Shechter et al., 2006; Li and Chen, 2009; Li et al., 2010). Wax and cutin were the main sorption contributors of cuticle for nonpolar organic pollutants, whereas polar sugar component played a negative role. The sugar component with poor affinity exhibited restrictive effect on the powerful sorptive regions of cuticle (Chefetz, 2003; Chen et al., 2005; Li and Chen, 2009). Sorption coefficients of nonpolar organic pollutants were sharply decreased after the removal of cutin, but increased with the consumption of sugar component via acid hydrolysis (Chefetz, 2003; Shechter et al., 2006; Chen et al., 2008; Li et al., 2010).

In comparison with nonpolar organic contaminants (NOCs), few studies focused on sorption property and mechanism of polar and ionizable organic pollutants onto plant cuticles. Differently from NOCs, ionizable organic pollutants exist either as non-dissociated (molecular) or as dissociated species (organic ion) in aqueous solution. Sorption properties of the two species may be distinctive. Dissociated species often has low partition coefficients with plant cuticles, because ionic groups are surrounded by water molecules and the hydrated organic molecules are essentially insoluble in cutin and waxes (Schönherr, 2006). Non-dissociated polar organic molecules are expected to affinity with cutin and waxes through hydrophobic interaction, as well as with polar groups of plant cuticle via specific interaction. Thus, the relative role of each com-

* Corresponding author. E-mail: blchen@zju.edu.cn

jesc.ac.cn

ponents of cuticle on sorption of polar organic pollutants would be quite different with that of NOCs. Taking 1-naphthol as an example, sorption coefficient of pepper cuticle did not increase but slightly decreased after sugar removal, suggesting that sugar component seems to play a positive role in uptake of polar organic pollutants (Chen et al., 2005). However, sugar removal resulted in an increase of sorption capacity of 1-naphthol onto tomato cuticle (Chen and Li, 2007). Therefore, more works are needed to well understand sorption of ionizable organic polluants with plant surface since most foliar agrichemicals and many environmental contaminants are ranked to this species.

The main objective of this study is to elucidate relationship between sorption properties of ionizable organic pollutants and compositional characteristics of plant cuticles. Three chlorophenols, i.e., 4-chlorophenol, 2,4-dichlorophenol, and 2,4,6-trichlorophenol, were selected as representatives of ionizable organic pollutants, because they are widely presented in the effluents from pesticides, dyestuffs, pharmaceuticals, petrochemicals industries (Kah and Brown, 2006; Núñez-Gaytán et al., 2010). Three typical fruit cuticles, such as apple, pepper and tomato, as well as potato periderm were chosen as models of plant surfaces.

1 Material and methods

1.1 Isolation of plant cuticle and periderm fractions

Bulk cuticles of tomato (*Solanum lycopersicum*, TC1) and green pepper (*Capsicum annuum*, PC1), as well as potato periderm fraction (*Solanum tuberosum*, PP1) were selected and isolated as described previously (Chen et al., 2005; Li and Chen, 2009). Their composition characteristics have been described (Chen et al., 2005; Li and Chen, 2009), and the yields of the cuticular components were cited as follows: respective waxes content of 6.2%, 6.4% and 13.4% for pepper cuticle, tomato cuticle and potato periderm; cutin/suberin content of 64.8%, 69.5% and 21.5%; cutan/suberan content of 7.9%, 0% and 21.2%; sugar content of 21.5%, 24.0% and 43.9%.

Apple cuticle was isolated from apple fruits (*Malus domestica)* by enzymatic method modified from procedure described by Orgell (1955) and Yamada et al. (1964). Briefly, cuticle sheets were manually peeled from fresh apple fruits, and then were incubated in a mixture of cellulase (2%, *W*/*V*), pectinase (2%, *W*/*V*), and NaN_3 (1 mmol/L) in citric acid buffer (20 mmol/L, pH 3.8) at room temperature. Enzyme solution was refreshed periodically until the cuticle fully separated from the tissue. Subsequently, cuticles were washed extensively in deionized water, oven-dried at 60°C, ground, and sieved (< 0.18 mm) for sorption experiments. This procedure yielded the bulk apple cuticle fraction (AC1). Six apple cuticular fractions, i.e., dewaxed apple cuticle (AC2), nonsaponifiable fraction (AC3), cutan (dewaxed-nonsaponifiable fraction AC4), dewaxed-hydrolyzed cuticle (AC5), desugared residue (AC6) and waxes fraction (AW), were obtained according to the procedure described previously (Chen and Li, 2007; Li and Chen, 2009).

1.2 Characterization of the apple cuticular fractions

Elemental (C, H, N) analyses for the apple cuticular fractions (AC1–AC6, AW) were conducted using an EA 112 CHN elemental analyzer (Thermo Finnigan, USA), while the oxygen content was calculated by the mass difference because the ash content was neglected. The H/C and (O+N)/C atomic ratios were calculated. Because the tomato cuticle, pepper cuticle, potato periderm used in the current study were the same as our previous reports (Chen et al., 2005; Li and Chen, 2009), the CHNO data for these samples were cited from the reference.

1.3 Batch sorption experiment

4-Chlorophenol (CP), 2,4-dichlorophenol (DCP), and 2,4,6-trichlorophenol (TCP) were chosen as representatives of polar organic pollutants, and their selected physicochemical properties are listed in Table 1. Sorption of sorbate onto the isolated cuticular and peridermal fractions (AC1–AC6, AW, TC1, PC1 and PP1) was performed at (25 ± 0.5)°C by a batch equilibrium technique (Chen et al., 2008). Each isotherm consisted of eight or ten concentration points, and each point (including the control and calibration) was run in duplicate. The background solution included 0.01 mol/L $CaCl_2$ (to keep a constant ionic strength) and 200 mg/L NaN_3 (to inhibit incidental biodegradation). The pH of the solution was kept original without any adjustment, i.e., pH 6.9 for 400 mg/L 4-chlorophenol, pH 6.4 for 400 mg/L 2,4-dichlorophenol, and pH 5.5 for 250 mg/L 2,4,6-trichlorophenol. The sorption properties of each compound to plants or plant components were generated in the different pH environment. To compare their sorption properties, the degree of ionization (α) of the sorbates at different pH values were calculated, i.e., α = 0.36% for 4-chlorophenol at pH 6.9, α = 3.23% for 2,4-dichlorophenol at pH 6.4, and α = 20.1% for 2,4,6-trichlorophenol at pH 5.5. The 8-mL vials were filled with sorbate solution to minimize the headspace volumes of the vial and sealed with alu-

Table 1 Selected properties of the tested chlorophenols

Organic pollutant	M (g/mol)	S_w (mg/L)	logK_{ow}	pK_a	π^*	β_m	α_m
4-Chlorophenol (CP)	128.56	26300	2.39	9.38	0.72	0.23	0.67
2,4-Dichlorophenol (DCP)	163.00	4600	3.11	7.90	0.87	0.18	0.78
2,4,6-Trichlorophenol (TCP)	197.45	800	4.02	6.10	1.01	0.08	0.82

M: molecular weight; S_w: water solubility; K_{ow}: octanol-water partition coefficient; pK_a: dissociated constant; π^*: polarity/polarizability parameter; β_m: hydrogen-bonding acceptor parameter; α_m: hydrogen-bonding donor parameter. Data of π^*, β_m, and α_m were obtained from the reference of Kamlet et al., 1988.

jesc.ac.cn

minum foil-lined Teflon screw caps to avoid sorbate's evaporation, and then agitated in the dark for 3 days. The solution was separated by centrifugation at 4000 r/min for 20 min. Supernatant concentrations of the tested sorbate were measured with an Agilent 1200 High Performance Liquid Chromatograph (HPLC, USA) fitted with G1314B variable wavelength detector and Agilent Eclipse XDB-C 18 column. The concentrations in the control groups were also determined, and remained the same during the experimental period. Because of minimal sorption by the vials, and negligible losses from evaporation, biodegradation and photodegradation, the sorbed amount was then determined by difference in aqueous concentration between nominal aqueous concentration without sorbent and with sorbent.

1.4 Data analysis

The Freundlich parameters (K_f and N) were calculated using the logarithmic form of Eq. (1):

$$Q = K_f \times C_e^N \quad (1)$$

where, Q (mg/kg) is the sorbed amount per unit weight of sorbent; C_e (mg/L) is the equilibrium concentration of sorbate; K_f ((mg/kg)/(mg/L)^N) is the Freundlich capacity coefficient, and N (dimensionless) describes the isotherm curvature. Sorption coefficients (K_d) were calculated from the slope of the linear isotherms. The K_{oc} is the carbon-normalized K_d, i.e., $K_{oc} = K_d/f_{oc}$ (f_{oc} is the carbon level of sorbent). K_{owc} is the carbon-normalized K_{ow} ($K_{owc} = K_{ow}/f_{oc}$, f_{oc} is the percentage of carbon content of octanol, i.e., 73.8%). For apple cuticle, the relative contribution (RC) of each component to the total sorption was estimated by the ratio of the $f_i K_{d,i}$ (where i represents wax, cutin, cutan, and sugar) to K_d of bulk apple cuticle (Li and Chen, 2009).

2 Results and discussion

2.1 Characterization of plant cuticles

The mass fractions and elemental compositions of isolated apple cuticular fractions (AC1–AC6, and AW) are listed in Table 2, which is similar to previous report (Li and Chen, 2009). Cutan exhibited the highest aromatic nature.

2.2 Sorption of plant cuticles and periderm

Sorption isotherms of three chlorophenols to bulk fruit cuticles (AC1, PC1 and TC1) and potato periderm (PP1) are presented in Fig. 1. Isotherms fit well to the Freundlich equation, and the regression parameters are listed in Table 3. The sorption isotherms are apparently linear, suggesting that the dominant mechanism is partition (hydrophobic interaction). For 4-chlorophenol, the magnitude of sorption coefficients (K_d) are in the order of pepper cuticle (PC1, 155 L/kg) > apple cuticle (AC1, 124 L/kg)

Table 2 Elemental analysis and atomic ratios of fruit cuticles and potato periderm

Sample	Yield	C (%)	H (%)	N (%)	O (%)[c]	H/C	(N+O)/C
AC1[a]	100	69.84	10.29	0.64	19.24	1.76	0.21
AC2[a]	62.7	61.36	8.80	1.15	28.69	1.71	0.37
AC3[a]	22.4	46.53	6.68	1.73	45.06	1.71	0.76
AC4[a] (cutan)	6.1	56.20	6.36	1.20	36.25	1.35	0.50
AC5[a]	41.7	67.73	9.13	0.45	22.69	1.61	0.26
AC6[a]	78.8	73.95	10.62	0.25	15.18	1.71	0.16
AW[a]	37.3	78.40	11.38	0.24	9.97	1.73	0.10
TC1[b]	–	63.45	8.78	1.45	26.32	1.65	0.33
PC1[b]	–	64.20	9.29	1.06	25.45	1.72	0.31
PP1[b]	–	47.44	6.46	2.92	43.18	1.62	0.74

[a] AC1: bulk cuticle of apple; waxes (AW) were extracted from AC1 by Soxhlet extraction, yielded dewaxed cuticle (AC2); saponification of AC2 produced nonsaponifiable fraction (AC3); AC1, AC2 and AC3 samples were acid hydrolyzed to yield a desugared residue (AC6), dewaxed-hydrolyzed cuticle (AC5) and cutan (AC4), respectively; [b] the CHNO data for tomato and pepper cuticle (TC1 and PC1) as well as potato periderm (PP1) were cited from our previous report (Chen et al., 2005; Li and Chen, 2009); [c]oxygen content was calculated by the mass difference.

Table 3 Sorption regression parameters of 4-chlorophenol, 2,4-dichlorophenol, and 2,4,6-trichlorophenol onto three fruit cuticles and potato periderm

Sorbate	Sorbent[a]	logK_f[b]	N[b]	Freundlich R^2	K_d[c] (L/kg)	Linear R^2	K_{oc}[d]	K_{oc}/K_{owc}[e]	n[f]
4-Chlorophenol	AC1	2.329±0.039	0.913±0.024	0.995	124±4.0	0.992	178	0.536	19
	TC1	2.160±0.052	0.987±0.031	0.993	117±4.9	0.986	184	0.554	20
	PC1	2.296±0.024	0.969±0.014	0.998	155±3.2	0.996	241	0.726	19
	PP1	1.481±0.052	1.030±0.028	0.995	31.9±1.1	0.990	67.2	0.202	20
2,4-Dichlorophenol	AC1	2.804±0.035	0.925±0.025	0.995	400±9.8	0.995	573	0.328	18
	TC1	2.928±0.021	0.891±0.017	0.998	445±11.5	0.994	701	0.402	20
	PC1	3.049±0.025	0.889±0.018	0.997	581±16.3	0.993	905	0.519	20
	PP1	2.302±0.019	0.904±0.011	0.999	111±1.9	0.997	234	0.134	20
2,4,6-Trichlorophenol	AC1	2.923±0.063	0.969±0.045	0.983	787±32.6	0.985	1127	0.079	20
	TC1	2.927±0.072	1.102±0.067	0.975	1449±44.9	0.993	2284	0.161	18
	PC1	3.217±0.031	0.953±0.025	0.995	1404±42.5	0.993	2187	0.154	20
	PP1	2.608±0.016	0.914±0.011	0.999	252±2.37	0.999	531	0.037	19

[a]All sorbents were the bulk plant skins; [b] the Freundlich parameters (K_f and N) were calculated using the logarithmic form of Eq. (1); R^2 is regression coefficient; [c] K_d is the sorption coefficient ($K_d = Q/C_e$), calculated from the slope of linear equation; [d] K_{oc} is the carbon-normalized sorption coefficient ($K_{oc} = K_d/f_{oc}$); [e] K_{owc} is the carbon-normalized octanol-water partition coefficient of chlorophenols (K_{owc} = 332, 1745, 14188 for 4-chlorophenol, 2,4-dichlorophenol, and 2,4,6-ttrichlorophenol, respectively); [f] n is the number of sorption data.

jesc.ac.cn

> tomato cuticle (TC1, 117 L/kg) > potato periderm (PP1, 31.9 L/kg). The K_{oc}/K_{owc} ratios for 4-chlorophenol range 0.20–0.73 (Table 3), much lower than those of phenanthrene (K_{oc}/K_{owc} = 0.90–2.72) with these four plant surfaces (Chen et al., 2005; Li and Chen, 2009). This may be attributed to that the polar function group (–OH) of 4-chlorophenol significantly decreases the affinity for plant cuticles. Magnitude of sorption increases with the increase in sorbate's K_{ow}, e.g., K_d (2,4,6-trichlorophenol) > K_d (2,4-dichlorophenol) > K_d (4-chlorophenol). For the tested polar chemicals, potato periderm shows the poorest affinity due to its highest sugar content. Tomato cuticle exhibits most sensitive to the hydrophobicity of sorbates, and the K_d value for 2,4,6-trichlorophenol is up to 12-times higher than 4-chlorophenol, while for the other plant cuticles the ratio of K_d (2,4,6-trichlorophenol) to K_d (4-chlorophenol) are about 6–9. Considering the strong affinity of cutin with organic compounds via hydrophobic interaction, the highest cutin content of tomato cuticle (69.5%, Table 2) is accounted for its biggest increase in K_d with increasing K_{ow} of the sorbates. In the previous study with the same content of cutin in tomato cuticles, the same trends were observed (Li and Chen, 2009). That could explain that the presence of cutin plays the critical role in strong affinity.

Although the enhancement affinity with plant cuticles during the increase of sorbates' K_{ow} was observed, however, the ratios of K_{oc}/K_{owc} decreased with increasing ionization degree of the sorbates ($\alpha = 1/(1+10^{(pKa-pH)})$), i.e., 2,4,6-trichlorophenol (α= 20.1% at pH 5.5) > 2,4-dichlorophenol (α = 3.23% at pH 6.4) > 4-chlorophenol (α= 0.36% at pH 6.9). These indicate that the affinity of plant cuticle with organic molecular species is much stronger than the ionic species of organic compound.

2.3 Sorption isotherms of apple cuticular fractions

Sorption isotherms of isolated apple cuticular fractions (AC1–AC6 and AW) are presented in Fig. 2. Isotherms fit well to the Freundlich equation, and the regression parameters are listed in Table 4. All apple cuticular fractions (except AC4) presented linear isotherms, suggesting the dominant sorption mechanism was the partitioning process into organic phase.

Because of the heterogeneous nature, sorption of bulk plant cuticle is contributed from a series of interactions of different cuticular components with sorbate. However, few studies dealt with the effects of physicochemical properties of sorbate (e.g., hydrophobic nature and polarity) on the sorption characteristic of different cuticular components (such as waxes, cutin, cutan and sugar). K_d of 4-chlorophenol on AW is 57.8 L/kg, which is much lower than the sorbate's K_{ow} value (K_{oc}/K_{owc} = 0.222). The K_d ratio of waxes (AW) to bulk cuticle (AC1) is 0.47 (Table 4), suggesting that the contribution of waxes to the total sorption of apple bulk cuticle is relatively low (17.4%, Table 6). With increase in K_{ow} value, the respective K_d value of AW increases to 194 L/kg for 2,4-dichlorophenol and 517 L/kg for 2,4,6-trichlorophenol, and their relative contribution of wax to total sorption increases correspondingly to RC = 18.1% and 24.5%. It is also worth noting that the K_{oc}/K_{owc} value for phenanthrene (nonpolar) on AW (2.16) is larger than that of 2,4,6-trichlorophenol (0.046), i.e., 47-fold. Furthermore, the relative contribution of wax to phenanthrene sorption is up to 52.97% (Li and Chen, 2009), which is two-fold higher than that of 2,4,6-trichlorophenol (24.5%). This is a good evidence to demonstrate that polar group of chlorophenols can heavily depress the strong hydrophobic affinity of waxes. Sorption coefficients of chlorophenols all slightly increased after waxes removal, i.e., both $K_{d(AC2)}/K_{d(AC1)}$ and$K_{d(AC5)}/K_{d(AC6)}$ > 1 (Table 5), indicating that waxes were not the major sorption medium for polar organic pollutants to the bulk plant cuticles.

The absence of cutin monomer decreased the K_d value (i.e., $K_{d(AC3)}/K_{d(AC2)}$, $K_{d(AC4)}/K_{d(AC5)}$ < 1, Table 5), demonstrating that cutin component was a powerful sorption medium for polar organic pollutants. Moreover, the drop

Table 4 Sorption regression parameters of 4-chlorophenol, 2,4-dichlorophenol, and 2,4,6-trichlorophenol onto apple cuticular fractions

Sorbate	Sorbent	logK_f	N	Freundlich R^2	K_d (L/kg)	Linear R^2	K_{oc}	K_{oc}/K_{owc}	n
4-Chlorophenol	AC1	2.329±0.039	0.913±0.024	0.995	124±4.0	0.992	178	0.536	19
	AC2	2.334±0.024	0.971±0.014	0.998	169±3.5	0.996	275	0.828	20
	AC3	1.229±0.235	1.107±0.132	0.913	33.7±1.7	0.983	72.4	0.218	20
	AC4	1.692±0.076	1.097±0.041	0.991	72.6±1.7	0.996	129	0.389	18
	AC5	1.833±0.080	1.179±0.047	0.987	142±4.2	0.992	210	0.633	20
	AC6	1.737±0.110	1.154±0.061	0.980	95.1±3.1	0.992	129	0.389	18
	AW	1.647±0.083	1.078±0.044	0.989	57.8±2.4	0.986	73.7	0.222	19
2,4-Dichlorophenol	AC1	2.804±0.035	0.925±0.025	0.995	400±9.8	0.995	573	0.328	18
	AC2	3.048±0.028	0.882±0.020	0.997	578±22.7	0.990	942	0.540	15
	AC3	1.005±0.153	1.203±0.077	0.978	36.5±1.4	0.992	78.4	0.045	14
	AC4	2.706±0.032	0.805±0.020	0.995	177±5.2	0.992	315	0.181	20
	AC5	2.821±0.033	0.949±0.024	0.995	492±13.4	0.993	726	0.416	20
	AC6	2.751±0.019	0.927±0.012	0.998	373±6.2	0.998	504	0.289	20
	AW	2.696±0.022	0.834±0.014	0.998	194±6.1	0.991	247	0.142	20
2,4,6-Trichlorophenol	AC1	2.923±0.063	0.969±0.045	0.983	787±32.6	0.985	1127	0.079	20
	AC2	3.241±0.011	0.962±0.009	0.999	1399±19.7	0.998	2280	0.161	20
	AC3	1.503±0.059	0.958±0.036	0.989	32.7±1.3	0.985	70.3	0.005	20
	AC4	3.020±0.018	0.768±0.012	0.998	287±8.1	0.993	511	0.036	20
	AC5	3.285±0.019	0.979±0.016	0.998	1663±13.1	0.999	2455	0.173	20
	AC6	3.161±0.007	0.959±0.006	1.000	1186±9.6	0.999	1604	0.113	20
	AW	2.684±0.029	1.033±0.022	0.997	517±6.0	0.999	659	0.046	19

jesc.ac.cn

Table 5 Ratios of sorption coefficients (K_d) with different apple cuticular fractions

Different coexisting component	Sample	$K_{d,CP}$ ratio	$K_{d,DCP}$ ratio	$K_{d,TCP}$ ratio	Same coexisting component
Sugar	AC6/AC1	0.77	0.93	1.51	Wax, cutin and cutan
	AC5/AC2	0.84	0.85	1.19	Cutin and cutan
	AC4/AC3	2.15	4.85	8.78	Cutan
Wax	AC2/AC1	1.36	1.45	1.78	Sugar, cutin and cutan
	AC5/AC6	1.49	1.32	1.40	Cutin and cutan
Cutin	AC3/AC2	0.20	0.06	0.02	Sugar and cutan
	AC4/AC5	0.51	0.36	0.17	Cutan

Table 6 Relative contribution of waxes, cutin, and cutan to the sorption of chlorophenols by bulk apple cuticles

Sorbate	K_d (L/kg) [a]	RC^b_{waxes} (%)	RC^b_{cutin} (%)	RC^b_{cutan} (%)	RC^b_{sugar} (%)	Σ^c RC (%)
4-Chlorophenol	124±4.0	17.4	79.3	3.6	4.4	105
2,4-Dichlorophenol	400±9.8	18.1	88.6	2.7	1.5	111
2,4,6-Trichlorophenol	787±32.6	24.5	110.5	2.2	0.7	138

[a] Sorption coefficients ($K_d = Q/C_e$) were calculated from experimental isotherms of bulk apple cuticle; [b] the relative contribution (RC) of each component was calculated by the ratio of the $f_i K_{d,i}$ to K_d of bulk cuticle. The symbol of i represents wax, cutin, cutan and sugar; f_i is the percentage of i component in bulk apple cuticle (Table 2); $K_{d,i}$ is the sorption coefficient of i component; [c] ΣRC is the sum of RC of waxes, cutin, cutan and sugar.

was dependent on the K_{ow} values of sorbates, i.e., the higher K_{ow} the bigger fall with the absence of cutin (Table 5). For example, K_d values of dewaxed apple cuticle (AC2) decreased 5, 17 and 50 times after alkaline saponification, i.e., $K_{d(AC3)}/K_{d(AC2)}$ = 0.20, 0.06 and 0.02 for 4-chlorophenol, 2,4-dichlorophenol and 2,4,6-trichlorophenol, respectively. This was attributed to the hydrophobic rubbery nature of cutin fractions, producing high affinity for lipophilic sorbates (Shechter and Chefetz, 2008). To assess the relative contribution of cutin, sorption coefficients (K_d) of cutin was estimated through mass balance, i.e., $K_{d,AC2} \times f_2 = K_{d,AC3} \times f_3 + K_{d,cutin} \times f_{cutin}$, where f_2, f_3, and f_{cutin} are the corresponding mass contents of AC2, AC3 and cutin in the bulk apple cuticle (Li and Chen, 2009). The respective calculated K_d of cutin were 244, 879 and 2158 L/kg for 4-chlorophenol, 2,4-dichlorophenol and 2,4,6-trichlorophenol. Correspondingly, their relative contribution of cutin was 79.3%, 88.6% and 110.5%, which were much higher than that of the other cuticular components.

Cutan (AC4) showed the most nonlinear isotherms for the stronger π–π bonding interaction (Table 4). With the increase in K_{ow} of sorbates, the nonlinearity raised due to the increasing π* parameter (Table 1) (Li et al., 2010), and the sorption coefficients of cutan (AC4) were also enhanced, i.e., K_{oc} = 129, 315 and 511 L/kg for 4-chlorophenol, 2,4-dichlorophenol and 2,4,6-trichlorophenol, respectively. These values were similar to the sorption coefficients of polar sorbates with K_{ow} values of 257–501 onto pure cutan of *A. americana* leaves, i.e., K_{oc} = 340, 110 and 260 L/kg for atrazine, carbamazepine and chlorotoluron, respectively (Shechter and Chefetz, 2008). The lower sorption capacity of polar sorbates was attributed to the polar adsorptive sites in cutan inaccessible for sorption interactions. In comparison, cutan exhibited powerful sorption capability for nonpolar organic pollutants (i.e., phenanthrene and naphthalene), but the relative role of cutan depended upon whether the sugar component existed or not. With the coexistence of sugar, the sorption of cutan was completely suppressed. Hence, for nonpolar organic pollutants, sorption coefficients of cutan were usually much higher than that of AC3 (e.g., AC4/AC3 = 11 for phenanthrene). However, the enhancement in K_d was smaller for 4-chlorophenol after acid hydrolysis ($K_{d(AC4)}/K_{d(AC3)}$ = 2.15), indicating that the suppression effect of sugar was not so heavily when the sorbates were polar organic pollutant (Table 5). Moreover, such suppression effect became more and more distinctively with sorbate's K_{ow} increasing, supported by the higher enhancement of K_d values after acid hydrolysis, i.e., $K_{d(AC4)}/K_{d(AC3)}$ = 4.85 for 2,4-dichlorophenol and 8.78 for 2,4,6-trichlorophenol. Despite the slighter suppression effect, the relative contribution of cutan to total sorption of bulk cuticle was very small (2.2%–3.6%) for the selected chlorophenols, which was similar to the contribution of cutan to phenanthrene sorption (2.84%).

The affinity of sugar with chlorophenols was the poorest in comparison with other components. Interestingly, the K_d values of 4-chlorophenol, 2,4-dichlorophenol and 2,4,6-trichlorophenol with AC3 were 33.7, 36.5 and 32.7 L/kg, respectively, which were quite similar. According to Table 2, the main composition of AC3 was cutan (27%) and sugar (73%). Since the sorption capacity of cutan was powerful and increased with the increase of sorbate's K_{ow}, sorption capacity of AC3 was expected to correspondingly rise. The almost constant K_d values of AC3 indicated that cutan in AC3 were unavailable to sorbates. Sorption of AC3 mainly was contributed from sugar, and the sorption capacity of sugar was similar for the selected chlorophenols because the sorption process was specific interactions (such as dipole-dipole and ion-dipole interaction) rather than hydrophobic interaction.

The relative roles of sugar to sorption of chlorophenols were sorbate-dependent. K_d value of 2,4,6-trichlorophenol increased after sugar removal, i.e., $K_{d(AC6)}/K_{d(AC1)}$ = 1.51 and $K_{d(AC5)}/K_{d(AC2)}$ = 1.19, consistent with previous reports (Chen et al., 2005). Nevertheless, the K_d values for 4-chlorophenol and 2,4-dichlorophenol decreased after acid hydrolysis ($K_{d(AC6)}/K_{d(AC1)}$ and $K_{d(AC5)}/K_{d(AC2)}$ < 1, Table 6). Chen et al. (2005) observed a similar phenomena,

jesc.ac.cn

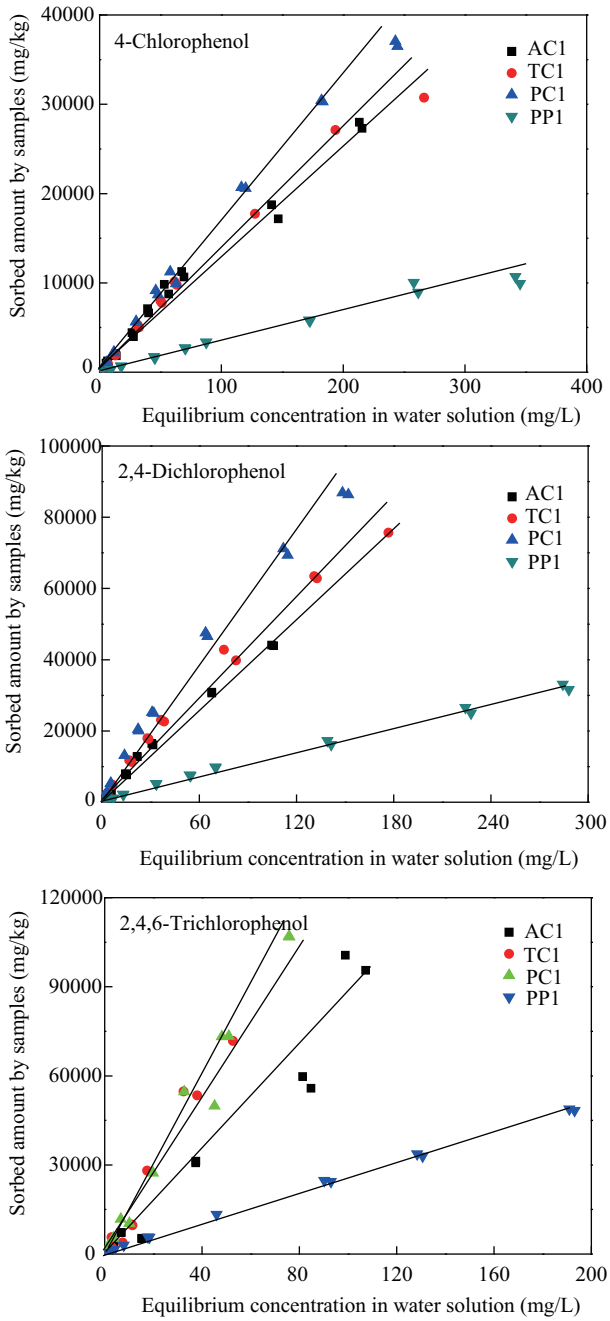

Fig. 1 Sorption isotherms of 4-chlorophenol, 2,4-dichlorophenol, and 2,4,6-trichlorophenol onto fruit cuticles and periderm. AC1: bulk apple cuticle; TC1: bulk tomato cuticle; PC1: bulk pepper cuticle; PP1: bulk potato periderm.

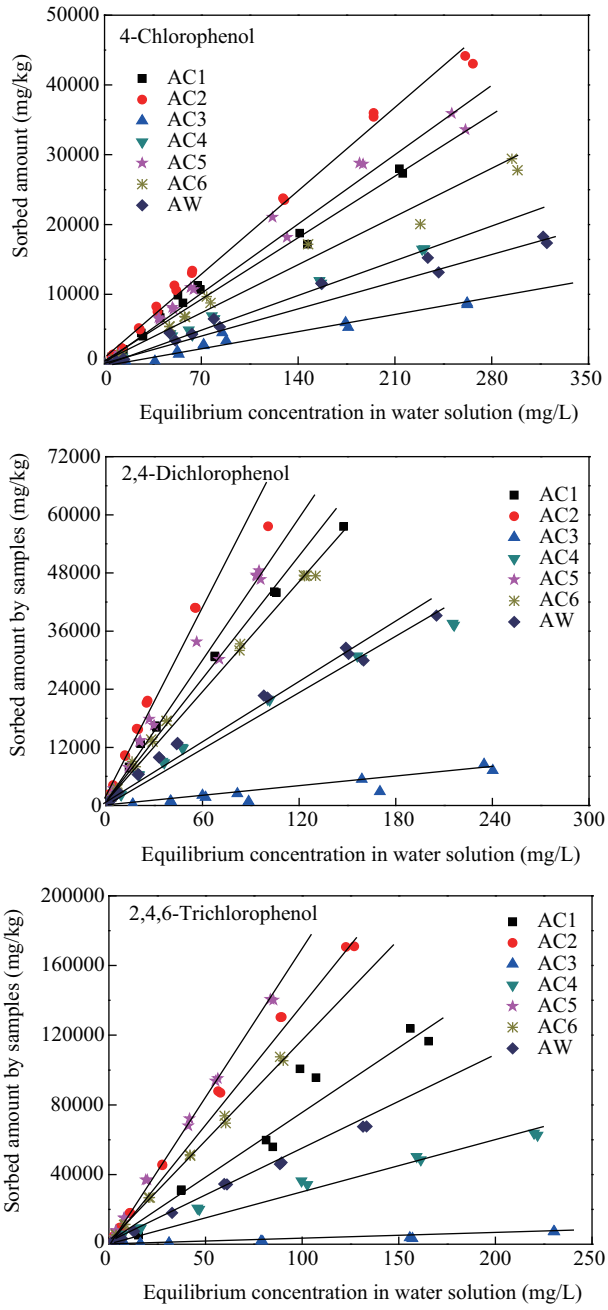

Fig. 2 Sorption isotherms of 4-chlorophenol, 2,4-dichlorophenol, and 2,4,6-trichlorophenol onto apple cuticular fractions.

i.e., sorption affinity of 1-naphthol on pepper cuticle decreased after sugar removal ($K_{d(AC5)}/K_{d(AC2)}$ <1). In these cases, sugar did not play a negative role anymore and presented as an effective sorption medium, with relative contribution of 4.4% and 1.5% for 4-chlorophenol and 2,4-dichlorophenol, respectively (Table 6).

Note that, the sum of relative contribution was up to 100%, meaning that suppression effects between different cuticular components on sorption existed. This effect became stronger with K_{ow} increasing, supported by the increasing total RC of sorption from 105% for 4-chlorophenol to 138% for 2,4,6-trichlorophenol. With the increase of sorbate's K_{ow}, the K_{oc}/K_{owc} ratios for all cuticular fractions decreased. Positive correlation of the decreasing degree of K_{oc}/K_{owc} ratios with the sorbents' polarities is observed. For AC3 with highest polarity (Table 2), the K_{oc}/K_{owc} ratios of 2,4,6-trichlorophenol was 44 times lower than 4-chlorophenol, which may be attributed to the higher suppression effect contributed by the higher polarity of sorbents.

In summary, cutin and waxes are the major sorption medium of apple bulk cuticle with chlorophenols, and the dominant sorption mechanism is hydrophobic interactions. The ratios of K_{oc}/K_{owc} decrease for the increasing degree of ionization of the sorbates. Sorption capacity of plant cuticle/periderm samples increases with increasing sorbate's K_{ow} (except AC3). The polarity rooting from sorbents and sorbates could restrict hydrophobic interactions, and the

jesc.ac.cn

K_{oc}/K_{owc} ratios decrease with the increase of sorbates' K_{ow}. The relative contribution of each cuticular component is in an order of cutin > waxes > sugar (cutan). With the increase of K_{ow} values, the relative contribution of lipophilic components (wax, cutin and cutan) on sorption increases, whereas the contribution of polar sugar decreases.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (No. 20977081), the Foundation for the Author of National Excellent Doctoral Dissertation of China (No. 200765), the Zhejiang Provincial Natural Science Foundation of China (No. R5100105), and the Doctoral Fund of Ministry of Education of China (No. J20091588).

References

Buchholz A, 2006. Characterization of the diffusion of nonelectrolytes across plant cuticles: properties of the lipophilic pathway. *Journal of Experimental Botany*, 57(11): 2501–2513.

Chen B L, Johnson E J, Chefetz B, Zhu L Z, Xing B S, 2005. Sorption of polar and nonpolar aromatic organic contaminants by plant cuticular materials: role of polarity and accessibility. *Environmental Science and Technology*, 39(16): 6138–6146.

Chen B L, Li Y G, 2007. Sorption of 1-naphthol by plant cuticular fractions. *Journal of Environmental Sciences*, 19(10): 1214–1220.

Chen B L, Li Y G, Guo Y T, Zhu L Z, Schnoor J F, 2008. Role of the extractable lipids and polymeric lipids in sorption of organic contaminants onto plant cuticles. *Environmental Science and Technology*, 42(5): 1517–1523.

Chefetz B, 2003. Sorption of phenanthrene and atrazine by plant cuticular fractions. *Environmental Toxicology and Chemistry*, 22(10): 2492–2498.

Kah M, Brown C D, 2006. Adsorption of ionisable pesticides in soils. *Reviews of Environmental Contamination and Toxicology*, 188: 149–217.

Kamlet M J, Doherty R M, Abraham M H, Marcus Y, Taft R W, 1988. Linear solvation energy relationships. 46. An improved equation for correlation and prediction of octanol/water partition coefficients of organic nonelectrolytes (including strong hydrogen bond donor solutes). *The Journal of Physical Chemistry*, 92(18): 5244–5255.

Koch K, Bhushan B, Barthlott W, 2008. Diversity of structure, morphology and wetting of plant surfaces. *Soft Matter*, 4(10): 1943–1963.

Li Y G, Chen B L, 2009. Phenanthrene sorption by fruit cuticles and potato periderm with different compositional characteristics. *Journal of Agricultural and Food Chemistry*, 57(2): 637–644.

Li Y G, Chen B L, Zhu L Z, 2010. Single-solute and bisolute sorption of phenanthrene and pyrene onto pine needle cuticular fractions. *Environmental Pollution*, 158(7): 2478–2484.

Müller C, Riederer M, 2005. Plant surface properties in chemical ecology. *Journal of Chemical Ecology*, 31(11): 2621–2651.

Núñez-Gaytán A M, Vera-Avila L E, De Llasera M G, Covarrubias-Herrera R, 2010. Speciation and transformation pathways of chlorophenols formed from chlorination of phenol at trace level concentration. *Journal of Environmental Science and Health, Part A*, 45(10): 1217–1226.

Orgell W H, 1955. The isolation of plant cuticle with pectic enzymes. *Plant Physiology*, 30(1): 78–80.

Riederer M, Schönherr J, 1984. Accumulation and transport of (2,4-dichlorophenoxy) acetic acid in plant cuticles: I. Sorption in the cuticular membrane and its components. *Ecotoxicology and Environmental Safety*, 8(3): 236–247.

Sabljic A, Gusten H, Schonherr J, Riederer M, 1990. Modeling plant uptake of airborne organic chemicals. 1. Plant cuticle/water partitioning and molecular connectivity. *Environmental Science and Technology*, 24(9): 1321–1326.

Schönherr J, 2006. Characterization of aqueous pores in plant cuticles and permeation of ionic solutes. *Journal of Experimental Botany*, 57(11): 2471–2491.

Shechter M, Chefetz B, 2008. Insights into the sorption properties of cutin and cutan biopolymers. *Environmental Science and Technology*, 42(4): 1165–1171.

Shechter M, Xing B S, Kopinke F D, Chefetz B, 2006. Competitive sorption-desorption behavior of triazine herbicides with plant cuticular fractions. *Journal of Agricultural and Food Chemistry*, 54(20): 7761–7768.

Wang Y Q, Tao S, Jiao X C, Coveney R M, Wu S P, Xing B S, 2008. Polycyclic aromatic hydrocarbons in leaf cuticles and inner tissues of six species of trees in urban Beijing. *Environmental Pollution*, 151(1): 158–164.

Yamada Y, Wittwer S H, Bukovac M J, 1964. Penetration of ions through isolated cuticles. *Plant Physiology*, 39(1): 28–32.

jesc.ac.cn

JOURNAL OF ENVIRONMENTAL SCIENCES

Editors-in-chief
Hongxiao Tang

Associate Editors-in-chief
Nigel Bell Jiuhui Qu Shu Tao Po-Keung Wong Yahui Zhuang

Editorial board

R. M. Atlas
University of Louisville
USA

Alan Baker
The University of Melbourne
Australia

Nigel Bell
Imperial College London
United Kingdom

Tongbin Chen
Chinese Academy of Sciences
China

Maohong Fan
University of Wyoming
Wyoming, USA

Jingyun Fang
Peking University
China

Lam Kin-Che
The Chinese University of
Hong Kong, China

Pinjing He
Tongji University
China

Chihpin Huang
"National" Chiao Tung University
Taiwan, China

Jan Japenga
Alterra Green World Research
The Netherlands

David Jenkins
University of California Berkeley
USA

Guibin Jiang
Chinese Academy of Sciences
China

K. W. Kim
Gwangju Institute of Science and
Technology, Korea

Clark C. K. Liu
University of Hawaii
USA

Anton Moser
Technical University Graz
Austria

Alex L. Murray
University of York
Canada

Yi Qian
Tsinghua University
China

Jiuhui Qu
Chinese Academy of Sciences
China

Sheikh Raisuddin
Hamdard University
India

Ian Singleton
University of Newcastle upon Tyne
United Kingdom

Hongxiao Tang
Chinese Academy of Sciences
China

Shu Tao
Peking University
China

Yasutake Teraoka
Kyushu University
Japan

Chunxia Wang
Chinese Academy of Sciences
China

Rusong Wang
Chinese Academy of Sciences
China

Xuejun Wang
Peking University
China

Brian A. Whitton
University of Durham
United Kingdom

Po-Keung Wong
The Chinese University of
Hong Kong, China

Min Yang
Chinese Academy of Sciences
China

Zhifeng Yang
Beijing Normal University
China

Hanqing Yu
University of Science and
Technology of China

Zhongtang Yu
Ohio State University
USA

Yongping Zeng
Chinese Academy of Sciences
China

Qixing Zhou
Chinese Academy of Sciences
China

Lizhong Zhu
Zhejiang University
China

Yahui Zhuang
Chinese Academy of Sciences
China

Editorial office
Qingcai Feng (Executive Editor) Zixuan Wang (Editor) Suqin Liu (Editor) Zhengang Mao (Editor)
Christine J Watts (English Editor)

Journal of Environmental Sciences (Established in 1989)
Vol. 24 No. 4 2012

Supervised by	Chinese Academy of Sciences	**Published by**	Science Press, Beijing, China
Sponsored by	Research Center for Eco-Environmental		Elsevier Limited, The Netherlands
	Sciences, Chinese Academy of Sciences	**Distributed by**	
Edited by	Editorial Office of Journal of	Domestic	Science Press, 16 Donghuangchenggen
	Environmental Sciences (JES)		North Street, Beijing 100717, China
	P. O. Box 2871, Beijing 100085, China		Local Post Offices through China
	Tel: 86-10-62920553; http://www.jesc.ac.cn	Foreign	Elsevier Limited
	E-mail: jesc@263.net, jesc@rcees.ac.cn		http://www.elsevier.com/locate/jes
Editor-in-chief	Hongxiao Tang	**Printed by**	Beijing Beilin Printing House, 100083, China

CN 11-2629/X **Domestic postcode: 2-580** **Domestic price per issue RMB ¥ 110.00**

ISSN 1001-0742

jesc.ac.cn