Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2014.883159

53 (2015) 3691–3703
March

Taylor & Francis
Taylor & Francis Group

Simulation analysis of release kinetic of organochlorine pesticides from hydragric acrisols influenced by low-molecular weight organic acids leaching

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Received 30 January 2013; Accepted 4 December 2013

ABSTRACT

The kinetic release behaviors of organochlorine pesticides (OCPs) from hydragric acrisols with three kinds of low-molecular weight organic acids (LMWOAs) solution and water leaching system were investigated by kinetic device designed by ourselves. Results showed that the release percentage of OCPs from soil by LMWOAs can increase by 15–18% for DDTs and 7–25% for HCHs more than that by water leaching system, especially for the initial 240 mL leaching solution. The release velocity of HCHs is far higher than that of DDTs (about 3–4 times) in the leaching systems studied. When using water as leaching solution, the data of release kinetics of OCPs from soil conformed to the apparent first dynamics equation ($R^2 > 0.99$, $p < 0.0001$), it implied that the surface diffuse of OCPs on soil mineral is primary release mechanism of OCPs from soil in water leaching system. The kinetic release behaviors of OCPs in LMWOAs solution leaching systems can be described by parabola diffuse equation, double constant equation, or Elovich equation. It implied that the introduction of LMWOAs into leaching system induced the complication of release mechanisms of OCPs from soil. It may be related to the dissolution of soil mineral surface and structure change of soil inherent organic matters that coating onto soil mineral surface induced by LMWOAs.

Keywords: Organic acids; DDTs; Kinetic; Release

1. Introduction

Organochlorine pesticides (OCPs) have been widely used throughout the world to control arthropod disease—vectors and agricultural pests. They and their metabolites are of great concern as typical persistent organic pollutants due to their long half-life (half-life of DDT can reach 10 years in the soil) [1], that of DDE is longer than DDT [2], high enrichment capability, amplification capability and potential high toxicity. As a kind of environmental estrogens, it may cause some damage to the health of human body and reproductive system [3,4]. Although they have been banned since the early 1970s in the global scope in succession and China also banned these pesticides

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in 1983, recent studies have shown that DDTs and HCHs can still be detected in certain water body and soils [5].

Dissolved organic matter (DOM) in soil is very similar both structurally and functionally with surfactants. DOM can, therefore, enhance the solubility of poorly water-soluble compounds [6,7]. The predominant low-molecular weight (i.e. <10,000 Da) fraction of DOM is highly mobile in soils [8], and as such, a potential consequence of using organic fertilizers is to enhance chemical transport by DOM. Indeed, DOM can serve as a carrier in soil solutions that could result in the rapid flow of organic chemicals through soil profiles. DOM could obviously change the transference behavior of organic pollutants, such as isoproturon [9], phenanthrene [10], imidacloprid [11], 2,4-D, chlorpyrifos and naphthalene [12], napropamide [13], and polycyclic aromatic hydrocarbons (PAHs) [14–16].

Low-molecular weight organic acids (LMWOAs), which are a kind of typical DOM, are the primary active components of rhizosphere. They occur widely in soils and primarily originate from root exudation [17–19]. Moreover, micro-organisms, animals, and the degradation of organic matters can also produce LMWOA [20]. LMWOAs have been shown to disrupt the sequestering of soil matrix, thereby enhancing desorption of organic pollutants in soil [17,18,21,22]. LMWOAs are abundant in the rhizosphere of many plant species, and are highly reactive with some soil fractions such as metal oxides and clay minerals [23,24]. Consequently, it is expected that LMWOAs, in theory, may affect OCPs availability in soil environment. However, studies on the effect of LMWOAs on the retained behavior of OCPs are scarce. The experiment conducted by White showed that seven kinds of LMWOAs could significantly increase the desorption of p,p´-DDE, the increment could reach at the range of 19–80% [21]. Lei et al. also reported that oxalate enhanced the desorption of p,p´-DDT in several contrasting soils, and increases in the desorption of p,p´-DDT from these soils occurred in the presence of root exudates from maize, wheat, and ryegrass. The effects of oxalate and root exudates on the desorption of p,p´-DDT were affected by soil organic carbon (SOC) and DOC contents of soils. Oxalate and root exudates increased the desorption of p,p´-DDT through a partial dissolution of the soil structure, including desorption of organic carbon from soils, and the formation of dissolved complexes with inorganic metal ions. Since oxalate and root exudates are ubiquitous composition of rhizosphere soils, the presence of these dissolved carbon sources will clearly have a profound effect on the mobility and fate of DDT in soils [25].

The aim of this article is to discuss the dynamic release behavior of several OCPs like DDT isomer (DDTs) and HCH isomer (HCHs) with LMWOAs from variable charge soil (red soil) with self-designed dynamics device, and provide some reference for understanding the migration and fate of these kinds of substances in soil and also the phytoremediation and ecological risk assessment of organic pollutants in the environment.

2. Materials and methods

2.1. Instruments and reagents

Several reagents were used in the analysis: n-hexane (chromatographically pure, Tedia Company, USA); petroleum ether with boiling range from 60 to 90°C (analytical reagent, Hangzhou Refinery, Zhejiang province, China); methylene chloride, acetone and concentrated sulfuric acid (analytical reagent, Nanjing Chemical Reagent Plant, China); anhydrous sodium sulfate (analytical reagent, 200 mesh, treated at 225°C for 4 h and stored in sealed container before use); Celite 545 (chromatographic grade, 0.020–0.045 mm, Serva Company) were baked for 4 h at 550°C in muffle furnace, then treated for 2 h at 200°C in oven before addition of 3% of deionized water to deactivate it, and stored in a sealed container before use. Purified SPE column was prepared by packing with a Teflon filter disc, 1 g Celite 545, 1 g anhydrous sodium sulfate and a Teflon filter disc. OCPs standard (o,p´-DDT, o,p´-DDE, p,p´-DDT, p,p´-DDD, p,p´-DDE, α-, β-, γ-, and δ-HCH) were obtained from Dr Ehrenstorfer Company, Germany, some properties of OCPs are shown in Table 1.

Several instruments were used in the analysis: Sigma 2–16 K high speed freezing centrifuge (Sigma, Germany); water bath rotary vacuum evaporator (Yarong Biochemical Instrument Plant, Shanghai, P.R. China); HS-10360D ultrasonic cleaning machine (Heng'ao Science and Technology Company, Tianjin, P.R. China); BS200S-WE1 electronic balance (1/10000, Sartorius Company, Germany); and SPP cartridge and filter disc (Chemical and Physical Institute of National Chromatogram Center in Dalian, China).

The concentrations of OCPs in extracts were analyzed using an Agilent-6890 GC/ECD gas chromatography equipped with HP7683 automatic sampler, HP chemical workstation (Hewlet-Packard, USA) and HP-5-fused capillary column (30 m × 320 μm × 0.25 μm). Separation was achieved according to the following program: initial oven temperature was kept at 60°C

Table 1
Some properties of the OCPs

DDTs	Solubility	log *Kow*	HCHs	Solubility	log *Kow*
p,p´-DDT	1.2–5.5[a]	6.2–6.91	α-HCH	10	3.8
o,p´-DDT	1.2–5.5	6.76	β-HCH	5	3.78
p,p´-DDE	65	5.69–6.96	γ-HCH	7.3–17	3.61, 3.72
o,p´-DDE	65	6.94	δ-HCH	1	4.14

[a] Solubility in water at 24–25℃, μg/L [43,44].

for 1 min, then the temperature was increased to 140℃ at a speed of 20℃ min^{-1}, subsequently increased to 280℃ at a speed of 12℃ min^{-1} and held for 4 min. The injector temperature was set as 220℃, while the detector temperature was set as 280℃. High purity N_2 (99.999%) was used as carrier gas (2 mL min^{-1}) and make-up gas (60 mL min^{-1}). Two microliters of sample was injected in a splitless mode. Quantitative calculation was conducted with external standard method.

2.2. Dynamic experiment methods

2.2.1. Soil sample

The red soil, hydragric acrisols—according to World Reference Base for soil resources [26], was sampled at the depths of 5–20 cm from the Red Soil Ecologic Experimental Station of the Chinese Academy of Science in Yingtan, Jiangxi province, China (28°12´34.1´´N, 116°55´32.3´´E), and was lyophilized and sieved (≤1 mm) for further analysis. The clay minerals of soil sample were mainly composed of kaolinite and hydroxy-aluminum vermiculite, and contained a spot of hydromica and a trace amount of gibbsite. The main physical and chemical characteristics of the soil were as follows: pH 5.07, clay content 32.3%, organic matter content 1.14%, and cation exchange capacity 10.10 Cmol (+) kg^{-1}.

2.2.2. Spiked soil

Soil samples were sieved to <2 mm and stored at room temperature until spiking procedure. Spiked soil samples were prepared by adding 500 μL of standard mixture of eight kinds of OCPs (the concentration is 10 ng μL^{-1} for each compound dissolved in n-hexane) to 20 g of soil according to the reference [27]. This spike level corresponds to 250 μg kg^{-1}. Then, 20 mL of acetone was added and suspension was mixed for 30 min with a mechanical shaker. After the bulk of the solvent was evaporated at room temperature, samples were stored at 4℃ in stoppered glass bottles for six months in the dark. Then, the extractions were carried out.

2.2.3. Preparation of eluent

Three kinds of LMWOAs eluent solutions (oxalic acid, tartaric acid, and citric acid) were all prepared as 10 mmol/L solutions by the analytical reagents, and their pH were adjusted to 5.5 by NaOH or HNO_3.

2.2.4. The dynamic devices are as follows

(1) Storage Bottles; (2) 200Ⅱtype HPLC pump (Scientific Instruments Co., Ltd, YiLite, Dalian, China); (3) dynamic reaction cell made of PTFE to provide reaction space; and (4) SBS-100 automatic fraction collector (Huxi Analytical Instrument Factory Co., Ltd, Shanghai, China).

2.2.5. Dynamics experiment methods

Weigh 7 g of spiked soil, put it into the dynamic reaction cell, and seal the cell tightly after wetting the sample with distilled water. The upper and lower ends of dynamic reaction cell, respectively, were connected with the automatic fraction collector and HPLC pump. The leaching velocity was set up for 1 mL/min; the collection time of each glass tube was 10 min and continuously 100 glass tubes of leacheate were collected. The experimental temperature of the dynamic reaction cell was controlled at 298 ± 0.5 K using thermostatic waterbath. When the samples were determined, two adjacent glass tubes were mixed as one test sample point. The collected liquid was transferred into separating funnel, and 10 μL of internal standard (pentachloronitrobenzene in methanol solution, 5 ng/μL) was added into it. After homogeneous mixing, 10 mL of petroleum ether and 0.5 g of NaCl were added in the separating funnel, and was oscillated for liquid–liquid extraction. After adding 0.5 mL of acetone to eliminate stubborn emulsification phenomenon, organic extraction phase was transferred into pear-shaped bottle, and then 10 mL of petroleum ether was added to repeat the extraction step. These two extracts were combined in pear-shaped bottle, concentrated to about 1 mL by rotary evaporators, and transferred into purifying SPE column. The SPE-purifying column was eluted with 10 mL of 10% dichloromethane/petroleum ether (V:V), and the leacheate was concentrated to about 1 mL by rotary evaporators again and blown by nitrogen, and was adjusted to 1 mL by n-hexane. Determined by GC-ECD, and quantified by external standard method, the results showed that the recovery rate of this liquid–liquid extraction method was 80–105% to different pesticides, and the relative standard deviation was 3–8%, which meet the demands of the analysis of trace organic compounds.

2.3. Quality control and data analysis

Laboratory blank values for all the compounds were generally low and posed no problem to the analytical quantification. The overall reproducibility was evaluated using the replicate analyses ($n = 3$). The coefficient of variation was between 0.01 and 0.35 for the various compounds, and it was less than 0.3 in 90% of the cases. Therefore, the reproducibility of the measurements was considered to be satisfactory.

3. Results

3.1. Effects of LMWOAs on the release rate of OCPs

Average releasing rates of OCPs are calculated by each pesticides quantity contained in leaching solution (20 mL) divided by elution volume. From Fig. 1, the release rates of HCHs eluted by water and organic acids are much higher than that of DDTs, the difference is up to about three times. The release ability of water to DDTs is very low. This kind of pesticides is released by water at a certain concentration, which is practically lower than their solubility, and elution volume does not have evident effects to their release rate. The release patterns of HCHs with high solubility by water and oxalic acid leaching follow a quick release at first, and then a slow release after an elution inflection point, at which the elution volume is about 300 mL.

The release patterns of DDTs with lower solubility by oxalic acid are single-peak type curve. That means the release rates of DDTs increased along with the increase of elution volume, and they reached the maximum elution rate when the elution volume is about 40 mL, after that the rates gradually decreased, and they were not stable until the elution volume reached 120 mL.

The release patterns of DDTs and HCHs by tartaric acid belong to bimodal curve. When the volume of leacheate increased to 40 mL, the release rate of the two kinds of pesticides reached maximum, then the release rate slightly decreased. When the volume of leacheate increased to about 100 mL, the rate reached another maximum and it became stable till the volume reached 240 mL. The release patterns of DDTs and HCHs by citric acid solution were also single-peak type curve, and their inflection point appeared at about 140 mL.

The existence form of OCPs in soil includes free form, loose bound form, and tight bound form (e.g. aging residual form). The researches on sorption and mobility of pesticide suggest that the soluble organic matter in the soil solution had no effect on the sorption characteristics of atrazine, isoproturon, and paraquat, but promoted their desorption in the presence of DOM and LMWOAs; and the soil type affected predominantly the physiochemical process, and the desorption and mobility of these pesticides were promoted [9,28]. In this present study, when the leaching solution flowed through the soil, the free form and loose-bound form would be released firstly, after loose-bound form was eluted completely, the OCPs of tight-bound form were slowly dissolved out soil with approximately constant speed. The leaching pattern of OCPs by tartaric acid displayed the bimodal curve, it may relate to the comparatively weak elution ability of tartaric acid to loose-bound form pesticides. The first peak represents the release of free-form pesticides, the second peak represents the release of loose-bound form pesticides, then the slow release of tight-bound form pesticides. This indicates that the release ability of tartaric acid to loose-bound form pesticides is smaller than that of citric acid. As the citric acid has stronger desorption ability to the free form and loose-bound form pesticides, these two forms of pesticides would be leached out of the soil together and form a single peak.

3.2. The cumulative release of OCPs from soil by LMWOA

Fig. 2 shows the cumulative release of OCPs by several LMWOAs from red soil. Table 2 lists the fitting results of dynamic release data of OCPs according to several common kinetic equations, where t is the time, Q_t is the cumulative release amount of pesticides, a and b are the parameters of the kinetic equation (with different meaning in different equations), k is the apparent speed constant in the first-level dynamic equation, and $q_{\max}$ is the apparent equilibrium desorption amount. The multiple correla-

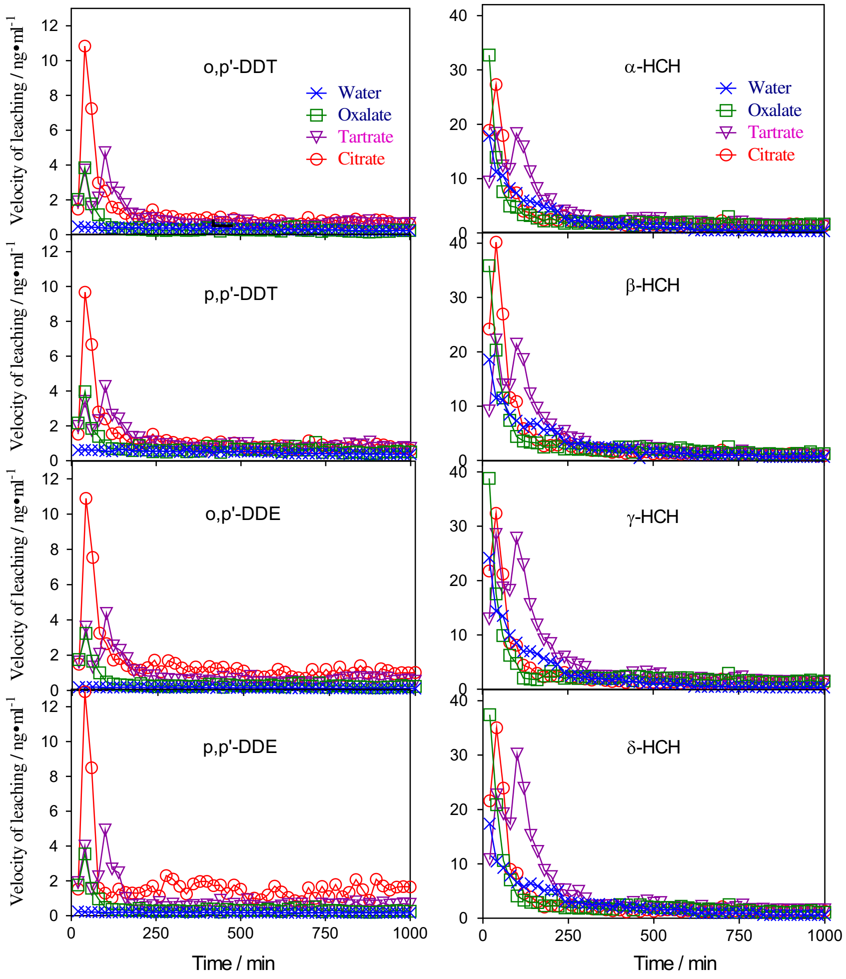

Fig. 1. Release velocity of OCPs from red soil with LMWOAs.

tion coefficient (R^2) and standard error (S_e) can be used to judge the degree of fitting. That is to say the larger R^2 and the smaller S_e contribute to a better fitting degree.

$$S_e = \sqrt{\frac{\sum(s_t - \hat{s}_t)^2}{n-2}},\ R^2 = 1 - \frac{\sum(s_t - \hat{s}_t)^2}{\sum(s_t - \bar{s}_t)^2}$$

where s_t, $\hat{s}_t$, $\bar{s}_t$ and n are the measured value, the predictive value, the average value, and sample number, respectively. Fig. 2 shows that the introduction of LMWOAs strengthens the release of OCPs to a certain extent. Comparing with water leaching system, the release amount of DDTs in LMWOAs leaching systems increased by 15–18%, while that of HCHs increased by 7–25%. The release ability of LMWOA for DDTs are: citric acid (18–26%) > tartaric acid (14–20%) > oxalic acid (6–10%) > water (3–8%). On the other hand, the release ability of LMWOA for HCHs are: tartaric acid (60%) > citric acid (49–55%) > oxalic acid (41–48%) > water (35–41%). The results match the experiment results conducted by White, who used batch method and pot experiment to study the effects of seven kinds of LMWOA to p,p´-DDE [21].

Tables 2 and 3 show that the kinetic release of OCPs in water leaching system is basically in accord with the first-order kinetic equation (R^2: 0.99−0.9999, $p < 0.0001$), while that of p,p´-DDE appears to be more consistent with double constant equation because its S_e is lower than that of the first-order equation, it implies that the release kinetics of the OCPs studied from soil with water leaching is still a kind of surface diffusion on soil particles. In oxalic acid leaching system, the kinetic release behaviours of o,p´- and p,p´-DDE, o,p´-DDT, and HCHs seem to be more consistent with parabolic diffusion equation, and it

Table 2
Fit value of parameters for different kinetic equations

		First-order kinetic				Parabolic diffusion				Elovich equation				Double constant			
		$\ln(1-q_t/q_{\max})=-k_t$				$Q_t=a+bt^{1/2}$				$Q_t=a+b\ln t$				$Q=at^b$			
	Pesticides	$q_{\max}$	k	R^2	S_e	a	b	R^2	S_e	a	b	R^2	S_e	A	b	R^2	S_e
Water	o,p´-DDE	64.3	0.0005	*0.9998*	*0.11*	−7.1	0.97	0.9834	0.93	−31.06	7.47	0.8635	2.67	0.06	0.126	0.9986	0.27
	p,p´-DDE	116.6	0.0003	*0.9999*	*0.09*	−8.6	1.12	0.9753	1.33	36.06	8.63	0.8449	3.32	0.06	0.132	*0.9999*	*0.07*
	o,p´-DDT	123.9	0.0006	*0.9995*	*0.36*	−15.3	2.13	0.9851	1.95	−68.5	16.56	0.8686	5.79	0.14	0.123	0.9977	0.77
	p,p´-DDT	189.6	0.0005	*0.9997*	*0.39*	−22.6	3.10	0.9851	2.83	−99.79	24.06	0.8680	8.43	0.2	0.124	0.9982	0.98
Oxalate	o,p´-DDE	54.9	0.0028	0.8852	4.14	3.1	1.63	*0.9791*	*1.77*	−39.4	12.95	0.9078	3.71	2.29	0.066	0.9769	1.86
	p,p´-DDE	61.84	0.0025	0.8978	4.36	1.5	1.82	*0.9776*	*2.04*	45.36	14.36	0.8943	4.43	1.99	0.070	0.9765	2.09
	o,p´-DDT	59.19	0.0032	0.8802	4.56	5.1	1.76	*0.9813*	*1.80*	−41.33	14.08	0.9220	3.68	3.04	0.062	0.9792	1.90
	p,p´-DDT	141.9	0.0013	0.9684	4.79	−13.1	3.59	0.9767	4.12	−102.6	27.86	0.8631	9.97	1.03	0.096	*0.9894*	*2.77*
Tartrate	o,p´-DDE	124.4	0.0028	0.9583	6.23	−2.8	4.06	*0.9783*	*4.49*	−114.44	33.29	0.9615	5.98	3.86	0.072	0.9774	4.58
	p,p´-DDE	130.8	0.0026	0.9447	7.33	−2.8	4.16	*0.9804*	*4.36*	115.31	33.79	0.9465	7.22	3.77	0.073	0.9799	4.42
	o,p´-DDT	137.4	0.0027	0.9587	6.80	−4.2	4.46	*0.9811*	*4.60*	−126.16	36.44	0.9573	6.91	3.91	0.074	0.9798	4.76
	p,p´-DDT	172.1	0.0020	0.9705	6.83	−14.8	5.33	*0.9903*	*3.91*	−156.29	42.81	0.9360	10.06	2.69	0.084	0.9887	4.23
Citrate	o,p´-DDE	218.1	0.0025	0.9555	10.74	−3.1	6.83	*0.9919*	*4.60*	−186.14	55.19	0.9477	11.7	6.34	0.073	*0.9916*	*4.66*
	p,p´-DDE	299.7	0.0017	0.9655	12.2	−24.0	8.54	0.9862	7.96	243.14	67.34	0.8988	20.8	3.69	0.087	*0.9908*	*6.48*
	o,p´-DDT	172.6	0.0033	0.9330	10.43	9.9	5.38	0.9829	5.27	−137.71	44.06	0.9641	7.64	8.33	0.063	*0.9856*	*4.83*
	p,p´-DDT	182	0.0027	0.9464	9.84	1.4	5.70	0.9898	4.29	−152.14	46.16	0.9510	9.41	6.21	0.069	*0.9900*	*4.25*
Water	α-HCH	346.1	0.006	*0.9908*	*7.38*	77.5	9.8	0.9026	24	−219.6	85.1	0.9874	8.63	39.0	0.329	0.9408	18.7
	β-HCH	414.9	0.005	*0.9905*	*9.45*	56.5	12.7	0.9445	22.9	−313.3	247.6	0.9906	9.40	32.4	0.381	0.9641	18.4
	γ-HCH	404.6	0.006	*0.9901*	*9.37*	114.4	10.8	0.8777	29.9	−218.1	94.5	0.9818	11.6	56.4	0.299	0.9286	22. 9
	δ-HCH	399.7	0.004	*0.9907*	*9.15*	40.2	12.5	0.9598	19.0	−317.7	241.4	0.9877	10.5	26.3	0.404	0.9729	15.6
Oxalate	α-HCH	392	0.004	0.86	31.4	59.7	11.3	*0.9954*	*5.66*	−236.4	90.0	0.9305	22.1	28.6	0.386	0.9909	7.99
	β-HCH	438.6	0.005	0.8536	34.9	92.8	12.2	*0.9923*	*8.01*	−238.3	228.9	0.9578	18.7	43.3	0.346	0.994	7.05
	γ-HCH	427.4	0.004	0.8261	37.1	83.3	11.9	*0.9938*	*7.02*	−231.1	95.5	0.9315	23.3	38.3	0.358	0.988	9.76
	δ-HCH	425	0.005	0.827	36.1	99.4	11.6	*0.9914*	*8.03*	−214.4	217.1	0.9536	18.7	45.9	0.333	0.9916	7.94
Tartrate	α-HCH	541.4	0.004	0.9733	21.6	48.3	17.3	0.9441	31.3	−456.7	146.9	*0.9912*	12.4	34.8	0.409	0.958	27.1
	β-HCH	575.1	0.005	0.9834	17.9	86.3	17.7	0.8956	45.0	−451.9	354.1	*0.9855*	16.8	49.9	0.368	0.9247	38.2
	γ-HCH	726.6	0.005	0.9783	20.4	116.5	22.2	0.8984	45.9	−555.7	192.3	*0.9863*	16.9	65.3	0.363	0.9283	38.6
	δ-HCH	466.3	0.005	0.9737	18.4	67.4	14.5	0.897	36.4	−370.3	288.4	*0.9833*	14. 7	39.5	0.371	0.9242	31.2
Citrate	α-HCH	419	0.005	0.8814	30.9	88.9	11.9	0.9697	15.7	−246.4	98.9	0.9779	13.4	42.8	0.343	*0.9825*	*11.9*
	β-HCH	506.9	0.008	0.8968	31.7	179.6	12.6	0.8978	31.5	−201.4	251.0	*0.9855*	11.9	88.9	0.267	0.9464	22.8
	γ-HCH	426.9	0.007	0.8717	30.6	133.5	11.1	0.9341	21.9	−191.9	94.4	*0.9868*	9.8	64.7	0.288	0.966	15.8
	δ-HCH	447.9	0.007	0.8614	33.4	140.7	11.7	0.931	23.6	−200.3	227.9	*0.9826*	11.8	68.2	0.288	0.9621	17.5

Table 3
Coefficients of determination (R^2) and standard errors (S_e) of four kinetics equations

		First-order kinetic		Parabolic diffusion		Elovich equation		Double constant	
	LMWOA	R^2	S_e	R^2	S_e	R^2	S_e	R^2	S_e
HCHs	Water	*0.9900*	*8.84*	0.9212	23.96	0.9869	10.03	0.9516	18.90
	Oxalate	0.8417	34.87	*0.9933*	*7.18*	0.9434	20.7	0.9911	8.19
	Tartrate	0.9775	19.61	0.9083	39.66	*0.9865*	*15.18*	0.9334	33.79
	Citrate	0.8778	31.65	0.9333	23.16	*0.9832*	*11.72*	0.9643	16.99
DDTs	Water	*0.9997*	*0.24*	0.9822	1.76	0.8613	5.05	0.9986	0.52
	Oxalate	0.9079	4.46	*0.9787*	*2.43*	0.8968	5.45	*0.9805*	*2.16*
	Tartrate	0.9581	6.80	*0.9825*	*4.34*	0.9503	7.54	0.9815	4.50
	Citrate	0.9501	10.80	0.9877	5.53	0.9404	12.39	*0.9895*	*5.06*

indicates that their release behaviours from soil are controlled by a number of diffusion mechanisms, and the outward diffusion process of the pesticides from soil particle interior is the limit step of whole release process; but that of p,p´-DDT more conforms to double constant equation, it may be related to its molecules structure, mineral dissolution and the heterogeneity of energy on soil particles surface induced by oxalic acid (activation and inactivation function of granular surface) for p,p´-DDT.

In tartaric acid leaching system and citric acid leaching system, parabola diffusion equation (tartaric acid system) and double constant equation (citric acid system) may be better to describe the kinetic release behaviours of DDE and DDT; besides α-HCH conforms to double constant equation, the kinetic release behaviours of β-, γ- and δ-HCH seem to be more consistent with the Elovich equation. So, the release behaviours of DDTs in the tartaric acid leaching system are mainly characterized by several diffusion mechanisms, while the release of DDTs in citric acid leaching system is characterized by the release mechanism of different energy position. For the release behaviors of HCHs, which own a larger solubility in water, it may involve some more complex release mechanisms.

Overall, the release behaviours of OCPs in water leaching system are consistent with first-order kinetic equation, which is good at describing a simple surface diffusion mechanism. The release behaviours of DDTs by citric acid leaching system can be well described by double constant equation, which is good at describing a uniform energy distribution; that of DDTs in the oxalic acid and tartaric acid systems can be described by parabolic diffusion equation, which is controlled by a number of diffusion mechanisms. For HCHs, their release behaviours in oxalic acid leaching system conforms to parabolic diffusion equation, and those in tartaric acid and citric acid leaching systems are more consistent with Elovich equation (see Tables 2 and 3), which is good at describing some more complex release mechanisms.

4. Discussion

4.1. Release mechanisms of OCPs from soil in LMWOAs leaching systems

The slow desorption of toxic hydrophobic organic compounds (HOCs) in soil has been a major impediment to successful remediation of many contaminated sites [29]. Much effort has been expended on the optimization of the physical chemistry of the solution in order to maximize desorption [30]. Very little attention has been devoted in changing the properties of the geosorbent itself to enhance the rate of mass transfer of HOCs into the solution phase.

SOC played a predominant role in the retention of HOCs [28,31], sequestration in soil organic matter (SOM) was critical for HOCs distribution in soils [14]. SOM or humic macromolecules may complex with inorganic particles via metal ion bridges or by direct coordination with lattice metals [32,33]. Complexed in this way, they are most likely constrained, restricting the diffusion of bound HOCs [34]. Chelating agents, including DOM, root excudes, LMWOAs and so on, are commonly used to determine activities of heavy metals [35] and organic pollutants [9–14,25,28,30,31,34,36–39] in soils. Chelating agents can also enhance release of SOM, and alter the association between SOM and the inorganic matrix or affect the structure of SOM itself. In addition, polyvalent metal ions can act as cross-linking agents of the SOM "polymer" phase by coordinating to carboxyl or phenolate groups on different strands, increasing the rigidity of the matrix, and hence the diffusional resistance of partitioned molecules.

The ability of carboxylic acids and oxy acids to cause dispersion of humic aggregates into smaller colloids might then be due to their multi-ligand potential. SOM desorption and restructuring due to metal chelation can also improve the availability of HOCs because changes in the binding chemistry and transport characteristics of HOCs are likely [30,40].

For example, the desorption rate and extent of soil dissolved natural organic carbon (DNOC) and PAH from a contaminated soil can be significantly enhanced with the aid of complexing agents, which reduced the degree of cross-linking in the SOM phase and accelerated PAH diffusion [30]. The desorption and mobility of isoproturon were promoted in the presence of DOM and LMWOAs in Eutric gleysols [9]. Dissolved organic carbon reduced imidacloprid sorption by competing with the pesticide molecules for sorption sites on the soil surface [11]. The initial rapid leaching of a small fraction of napropamide was not a result of preferential flow, but is due to DOM-facilitated transport [13]. Gao et al. reported that the presence of inherent DOM in soils was found to impede phenanthrene sorption, and the influence of exotic DOM on phenanthrene sorption was related to DOM concentrations, higher concentrations (>=52 mg DOC/L) of added exotic DOM clearly impeded the distribution of phenanthrene between soil and water [10]. Similarly, LMWOAs could inhibit (4-chloro-2-methylphenoxy)acetic acid sorption in soils through direct competition for sorption sites [37]. Moreover, Ling et al. observed that oxalic and citric acids significantly reduced the sorption of phenanthrene in soils, and organic matter colloids bound to the soil mineral surfaces via polyvalent metal ions might be released into the aqueous phase, resulting in the decreased content of solid organic matter, which was the predominant pool for hydrophobic organic pollutants in soils [17]. Chen et al. showed that the decrease of pentachlorophenol adsorption was induced mainly by the low-molecular weight root exudates promoting the organic matter release from the soil samples, and the higher the content of organic matter, the more was its release amount [39].

LMWOAs, which is a kind of typical DOM and could be retained on soil particle surfaces through ligand exchange [23,41], is the primary active components of rhizosphere and has been shown to disrupt the sequestering of soil matrix and enhancing desorption of OCPs in soil. For example, White et al. found that the presence of organic acids induced the increased solubility of inorganic soil constituents and concomitant increase in the desorption of p,p´-DDE [21]. Gonzalez et al. showed that sodium citrate and oxalate, at levels usually exuded by plant roots, effectively enhanced the desorption of p,p´-DDT, p,p´-DDE, and α-cypermethrin, while no effects were observed for α-endosulfan and endosulfan sulfate [42]. Luo et al. reported that the addition of oxalate resulted in the increased release of dissolved organic carbon and inorganic ions from soils, also significantly increased the desorption of p,p´-DDT for different soils (11–54%).

From the discussion abovementioned, we can put forward some mechanisms about OCPs desorption from soil induced by LMWOAs or root exudates: (1) Mechanism of minerals dissolution. LMWOAs induced the dissolution of soil minerals and resulted in desorption of OCPs adsorbed on soil minerals; (2) Indirect release mechanism. Soil inherent organic matter is dissolved and released by LMWOAs, or SOM matrix is restructured due to LMWOA's multi-ligand potential with polyvalent metal ions acting as cross-linking agents of the SOM matrix, and resulted in desorption of OCPs adsorbed by soil inherent organic matter; (3) Direct release mechanism. The LMWOAs directly competed with OCPs for sorption site on soil surface and released them; and (4) Mechanism of locking and unlocking. LMWOAs interacted with soil inherent organic matter like a key and induced the change in its conformation and properties, which resulted in the locking or unlocking of the OCPs by soil inherent organic matter.

4.2. OCPs-specificity and LMWOAs-specificity of release mechanisms

From Figs. 1–3 and Tables 2–4, one can find that the release behaviours of OCPs in different LMWOAs leaching systems had obvious difference. The results of cluster analysis showed that desorption behaviours of HCHs and DDTs can be divided into two groups, it may relate to their larger difference of dissolvability and n-octanol/water partition coefficient (*Kow*). In order to explore the relationship between the dissolvability and *Kow* of OCPs and their release behaviour, we carried out linear correlation analysis among the cumulative release amount (log Q), dissolvability (log S) and log Kow of OCPs (Fig. 4). Results suggested that the linear correlation degree between log Q and log Kow ($R^2 = 0.9034 - 0.9862$) exceeded that between log Q and log S ($R^2 = 0.9034 - 0.9862$), it implied that their release mechanisms from soil in LMWOAs leaching systems still dominated by partition mechanism.

The release behaviours of OCPs in different LMWOAs leaching systems can be divided into two groups, which include the group of water and oxalate leaching systems and the group of tartrate and citrate

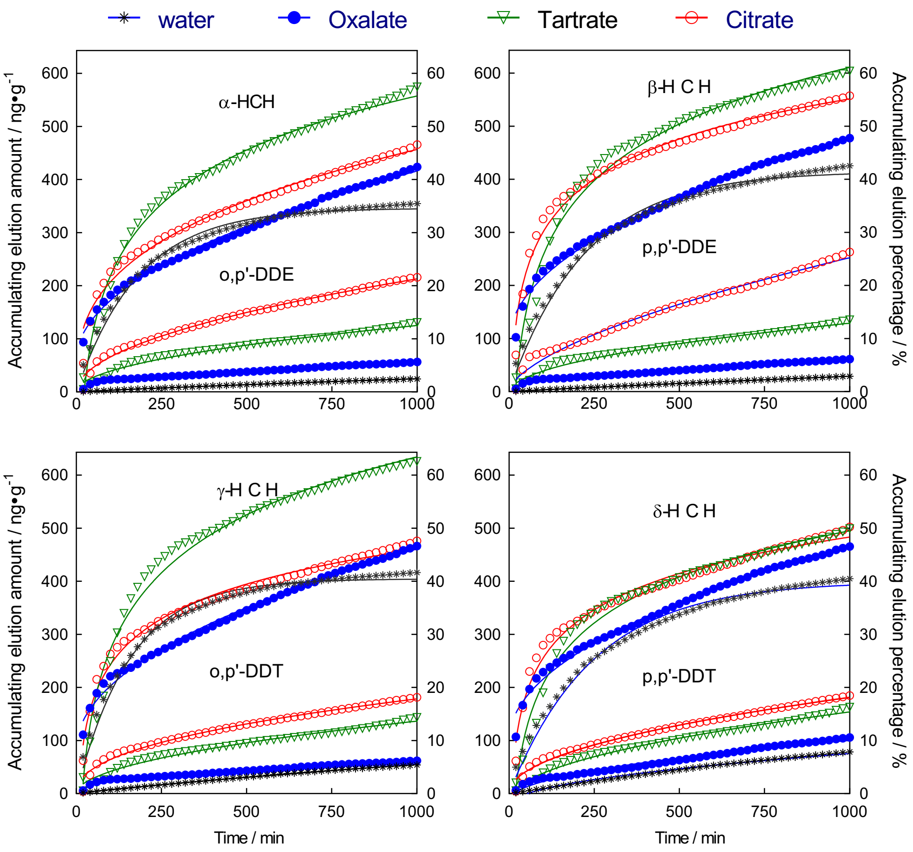

Fig. 2. Accumulative release kinetic of OCPs from red soil with LMWOAs leaching.

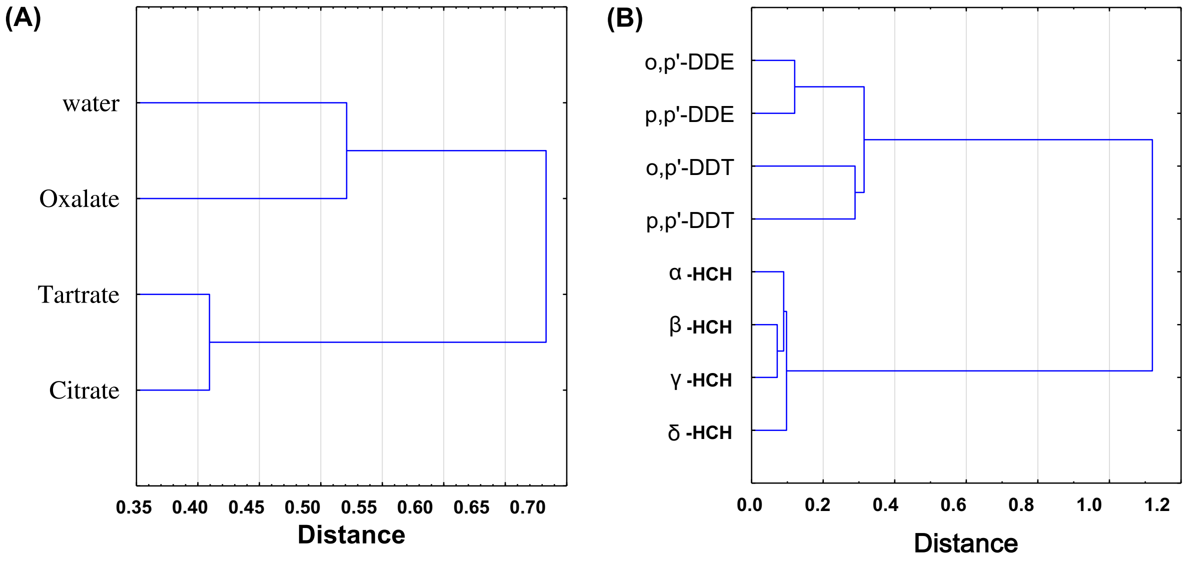

Fig. 3. Cluster analysis about the release kinetics behavior of OCPs from soil in LMWOAs leaching systems.

Table 4
Dunn's multiple comparisons test of release kinetics in different LMWOA systems

		α-HCH				β-HCH				γ-HCH				δ-HCH			
		W1	O1	T1	C1	W2	O2	T2	C2	W3	O3	T3	C3	W4	O4	T4	C4
α-HCH	W1	ns															
	O1	ns	ns														
	T1	****	****	ns													
	C1	*	*	***	ns												
β-HCH	W2					ns											
	O2					**	ns										
	T2					****	****	ns									
	C2					****	****	ns	ns								
γ-HCH	W3									ns							
	O3									ns	ns						
	T3									****	****	ns					
	C3									****	****	*	ns				
δ-HCH	W4													ns			
	O4													ns	ns		
	T4													**	ns	ns	
	C4													**	ns	ns	ns

		o,p´-DDE				p,p´-DDE				o,p´-DDT				p,p´-DDT			
		W5	O5	T5	C5	W6	O6	T6	C6	W7	O7	T7	C7	W8	O8	T8	C8
o,p´-DDE	W5	ns															
	O5	***	ns														
	T5	****	****	ns													
	C5	****	****	****	ns												
p,p´-DDE	W6					ns											
	O6					***	ns										
	T6					****	***	ns									
	C6					****	****	**	ns								
o,p´-DDT	W7									ns							
	O7									***	ns						
	T7									****	**	ns					
	C7									****	****	***	ns				
p,p´-DDT	W8													ns			
	O8													**	ns		
	T8													****	****	ns	
	C8													****	****	***	ns

Notes: W = water, O = oxalate, T = tartrate, C = citrate; ns = no significant.

*represents different significant level.

The "*, **, ***, ****" represent different significant level with p value of ≥ 0.05, 0.01 to 0.05, 0.001 to 0.01, 0.0001 to 0.001 and < 0.0001, respectively.

leaching systems, by cluster analysis according to their cumulative release amount. But viewing from the fitting results of kinetic equation (Tables 3 and 4), there are different classifications results. The introduction of LMWOAs resulted in the complication of release mechanism from simple surface diffusion mechanism in water leaching system to more complication diffusion mechanisms in LMWOAs leaching systems. The difference of OCPs release pattern studied in different LMWOAs leaching systems may be related to the differences of OCPs' three-dimensional structure, the number and position of carboxyl and hydroxyl in LMWOAs molecule, and the influence on their coordination, mineral dissolution, and restructuring ability on soil inherent organic matter structure, and different action mechanisms between LMWOAs

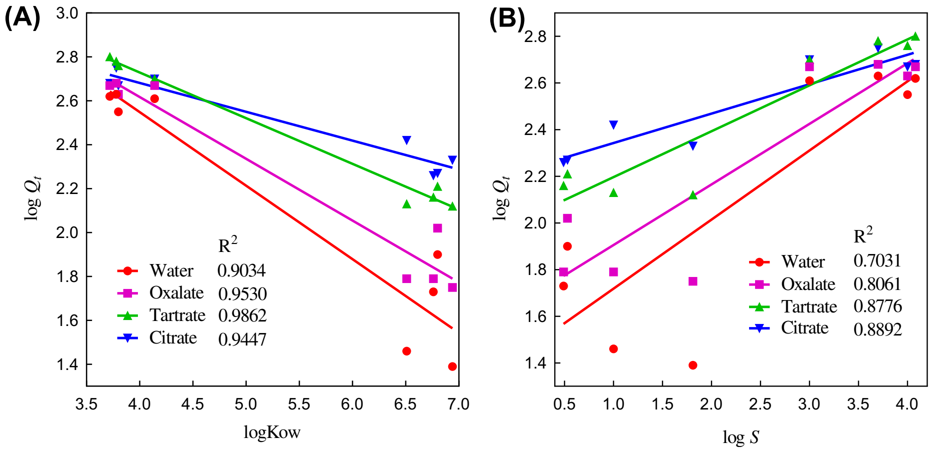

Fig. 4. Linear regressions between the logarithm of accumulation release amount (log Q_t) and log *Kow* (3A) and the logarithm of solubility (log *S*) (3B) for OCPs in water.

and different bound OCPs on the soil surface. In this study, LMWOAs may cause partial dissolution of soil mineral structure and partial destruction of the soil matrix, such as the organo-mineral linkages, resulting in decrease of available sorption sites and the release of organic carbon and metal ions, and thus the subsequent enhanced desorption of OCPs from the soils [25].

5. Conclusion

Results showed that the introduction of LMWOAs could accelerate the release of the tested OCPs (relative to the water, increased 15–18% for DDTs, 7–25% for HCHs). It implied that the LMWOAs induced the complication of the kinetics release mechanisms of OCPs (the best kinetics equation describing the release of pesticide changed from the first-order kinetic equation in water system to parabola diffuse equation, double constant equation, or Elovich equation in LMWOAs systems). It also indicated that the kinetics release mechanisms of OCPs by LMWOAs involved not only the simple granular surface diffusion mechanism in water system, but also the outward diffusion mechanism of soil particles internal, activation and inactivation function of granular surface, the non-uniform mechanism of surface energy distribution induced by the solution of soil mineral, and structure change of soil inherent organic matter coating onto the soil mineral surface by LMWOAs.

The release velocity of HCHs was far higher than that of DDTs by water and LMWOA. Their difference was nearly three times. The variation amplitude of the release velocity and the influence of elution volume on release velocity for DDTs by water were all small and not obvious. The release velocity curves of OCPs from soil by LMWOAs were all peak-type curve, and it included two stages which are rapid release and low release.

Acknowledgments

Thanks for the financial aid of National Natural Science Foundation of China (41371307 41230640), Foundation of Nanjing Institute of Industry Technology (YK11-02-07), Professional education teaching reform research subject of Jiangsu (GYC57), Foundation of modern education technology research in Jiangsu province (2011-R-19984), State Key Laboratory of Soil and Sustainable Agriculture (Institute of Soil Science, Chinese Academy of Sciences) foundation (0812201228), Research subject of the Higher Vocational Education of China (2012-2013, GZYLX1213154); The Opening Funding of Intelligent Sensor Network Engineering Technology Research and Development Center in Jiangsu province (2013) and the Opening Funding of State Key Laboratory of Pollution Control and Resource Reuse (PCRRF12010).

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