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Sorption and desorption of selected phenyl urea herbicides in laboratory water-sediment systems

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Abstract. Diuron, isoproturon and linuron were phenyl urea herbicides (PUHs) widely used in the world to control annual weeds. The adsorption-desorption behaviors of these PUHs were investigated in lab-scale water-sediment systems set up with water and sediment samples collected from Taihu Lake, China. 12 h was selected as the equilibrium time for the six sediments. Sorption isotherms of these PUHs were well described by the Freundlich model. The sorption of three PUHs in six sediments were all linear or close to it ($0.92 \leq n \leq 1.06$). The logarithms of the normalized distribution coefficient by organic carbon ($\log K_{oc}$) were 2.32 for isoproturon, 2.85 for diuron and 3.02 for linuron. The sorption and desorption potentials of the three PUHs can be arranged in the following order: linuron > diuron > isoproturon. The three PUHs possess moderate to strong sorption affinities to the natural sediments in the drinking water sources in Taihu Lake. Compared to linuron and diuron, the desorption hysteresis of isoproturon is conspicuous with hysteresis indices from 0.657 to 0.872, and the sorption seems to be irreversible.

1. Introduction

Phenyl urea herbicides (PUHs) are herbicides widely used in agriculture [1,2], and they are also some of the most studied potential generators of disinfection by-products (DBPs) [3,4]. Based on previous research, PUHs were found to generate various DBPs in the disinfection process of treatments, such as nitrosodimethylamine, nitrochloroform, trihalomethanes, among others [5,6]. Thus, PUHs present a potential vulnerability for potable supplies [7]. Moreover, PUHs have recently received particular attention because of their possible endocrine disrupting effects, carcinogenic promoting properties and cytogenetic effects [8-10].

PUHs have been detected in different aquatic environments at concentrations up to some hundreds of $\mu\text{g/L}$, either alone or simultaneously [11]. The adsorption-desorption is very important process for the assessment of the fate and distribution of pesticides in water sources because some of the PUHs in the water will be adsorbed and fixed by sediments, which will be released into the environment under suitable conditions and become a secondary pollution source. Due to the polar nature of PUHs, the increased possibility of desorption from the sediments to the water supply and water reserves together with the emergence of potential toxic degradation products and DBPs may constitute a risk for human health [12]. Since sorbed chemicals are unavailable to microorganisms and plants prior to desorption [13], desorption is an important process in the transportation of PUHs in sediments.



This study selected three PUHs (linuron, diuron and isoproturon) to investigate sorption and desorption behaviors with sediments from drinking water sources in Taihu Lake. These results may provide information to evaluate the fates and health risks of PUHs in water sources.

2. Materials and methods

2.1. Sampling sites and chemicals

Taihu Lake is the second largest freshwater lake in China, located in eastern China and adjacent to the Zhejiang and Jiangsu provinces. The sediments were sampled from six drinking water sources in Taihu Lake, namely Xijiu (XJ), Wujiang (WJ), Yuyangshan (YYS), Jinshugang (JSG), Xidong (XD) and Nanquan (NQ).

Diuron, isoproturon, linuron and internal standard isoproturon-d6, of >98% purity, were obtained from Sigma-Aldrich (Flanders, New Jersey, USA). Stock solutions of the test compounds were prepared in methanol and stored at -20°C. Methanol (HPLC grade) was obtained from Merck Serono Co., Ltd. (Darmstadt, Germany). Water was purified by a Milli-Q integral water purification system (Millipore, Milford, MA, USA) and was used in the experiment.

2.2. Laboratory simulation

The sorption and desorption tests of the three PUHs followed OECD guideline 106 [14]. To achieve sterilization, freeze-dried and sieved sediments were autoclaved for 20 min at 121°C and 1.3 bar before use. The stock solutions of PUHs were diluted by 0.01 M CaCl₂ solution to obtain the working solutions for the tests. All batch sorption experiments were performed for 48 h based on the results of preliminary experiments for absorption equilibrium time. To achieve 60–80% sorption, the sediment/solution ratios were set to 1:5 based on pre-test results. 5-g sediment samples (<2 mm size) were added to 100-mL conical flasks containing 25 mL of working solution with PUHs. The reaction mixtures were shaken at 150 rpm for a period of 48 h at 25 ± 1°C in the dark to avoid photodegradation.

Two of the six sampled sediments were selected to carry out the sorption kinetics tests, which were collected from XJ with comparatively high organic carbon and clay content and NQ with low organic carbon and clay content, respectively. The initial concentrations of the three PUHs in the water phase were 100 µg/L. The experiments were performed in two replicates, and two conical flasks were taken out at every sampling time, centrifuged at 5000 rpm for 5 min, and the water and sediment phases were collected for PUH analysis. Control vessels, containing only the CaCl₂ solution spiked with targets to test stability, and blanks prepared only with CaCl₂ solution and sediment as background control during the analysis to detect interfering compounds or contaminated sediments were included in all test series.

Sorption isotherms of PUHs were constructed with the six sediments from Taihu Lake at the same conditions. Six different concentrations (5, 10, 20, 40, 80, 100 µg/L) were used with an equilibration time of 12 h based on the results of the sorption kinetics. The experiments were performed in two replicates. All samples were centrifuged at 5000 rpm for 5 min to separate the sediment and aqueous phases. Subsequently, 25 mL of fresh CaCl₂ solution was added to the sediment and equilibrated for another 12 h as desorption tests. The concentrations of the three PUHs in the water phase at equilibrium were determined for both the sorption and desorption tests. The concentrations of the targets sorbed onto the sediments were calculated from water concentrations on the basis of conservation of mass.

Freundlich model has been widely used to describe the adsorption behavior of pesticides [15,16], therefore, the adsorption-desorption data of the three PUHs were fitted to this model in log format:

$$C_s = K_f C_e^n, \log C_s = \log K_f + n \log C_e. \text{ Then, } K_d = C_s / C_e, \text{ and } K_{oc} = K_d / f_{oc}$$

where C_s (µg/g) is the sorbed concentration of the PUHs at equilibrium; and C_e (µg/L) is the concentration of the PUHs in water phase at equilibrium; K_f is the Freundlich affinity constant related to the capacity of sorption; n is a linearity factor; K_d is the distribution coefficient at the equilibrium state; f_{oc} is the organic carbon fraction in the sediment; and K_{oc} is the normalized distribution coefficient by organic carbon.

2.3. Sample extraction

Surface sediments were taken by a Van Veen grab sampler. Water samples were collected at three different depths from the surface to the bottom, and then mixed together. Freeze-dried sediments were filtered through a sieve with 2 mm openings. A small amount of freeze-dried sediment was used to determine physical-chemical indicators. Particle size distribution was determined using a laser particle analyzer (Mastersizer 2000, Malvern, UK), and the particles were classified as clay (<20 μm), silt (2-20 μm), and sand (20-2000 μm). Cation exchange capacity (CEC) was analyzed using the EDTA- NH_4^+ method, and the organic carbon fraction (f_{oc}) in sediment was analyzed by the potassium dichromate oxidation method.

The water samples were first filtered through 0.45 μm acetate fiber filters, and then filtrated through C18 solid phase extraction (SPE) cartridges (500 mg, 6 mL, Waters, Milford, USA). The cartridges were eluted twice using 3 mL of methanol. The extract was blown to near dry by a gentle nitrogen stream, and then mixed with methanol to 1 mL. Sediment samples were extracted by means of accelerated solvent extraction (ASE 350, Dionex, USA). A known weight of sediments mixed with diatomite were added into a 22-mL stainless steel extraction cell containing glass-fiber filters in the outlet of the cell. The resulting ASE extract was concentrated by a quantitative concentration instrument to approximately 1 mL, and then diluted in 20 mL of ultrapure water and subjected to SPE as mentioned above.

2.4. Quantitative analysis of PUHs

PUHs were chromatographed using an Acquity ultra performance liquid chromatography (Waters Corporation, USA) and detected using a Waters AcquityXevo TQ triple quadrupole mass spectrometer coupled with an electrospray ionization source. A Waters BEH C18 column (2.1 $\times$ 100 mm, 1.7 μm) was used. The injection volume was 5 μL , and the column temperature was 40°C. The two flow phase phases, formic acid 0.1% (v/v) and methanol 0.1% (v/v) aqueous solution (A), formic acid 0.1% (v/v) methanol solution (B), were used for gradient elution at a flow rate of 0.4 mL/min.

Quality Control/Quality Assurance was completed by regular analyses of procedural blanks, spiked blanks, and matrix recoveries. Procedural blanks were consistently analyzed with each batch of samples, and no target PUHs were detected in blank samples. Matrix recovery tests were conducted by adding 10 and 100 ng/L (or ng/g) of target PUHs to water samples (or sediment samples). The recovery tests were carried out in duplicate and the relative standard deviations were less than 20%. The recoveries, limits of detection (LODs) and limits of quantitation (LOQs) of target chemicals in water and sediment are shown in table 1.

Table 1. Recoveries, LODs and LOQs of PUHs in water and sediment.

Name	Recovery, %				LOD		LOQ	
	Water (ng/L)		Sediment (ng/g dw)		Water (ng/L)	Sediment (ng/g dw)	Water (ng/L)	Sediment (ng/g dw)
	10	100	10	100				
Isoproturon	92 $\pm$ 6.2	85 $\pm$ 7.9	108 $\pm$ 17	74 $\pm$ 6.4	0.02	0.06	0.07	0.022
Diuron	82 $\pm$ 13	86 $\pm$ 9.0	101 $\pm$ 16	95 $\pm$ 2.7	0.13	0.40	0.44	1.32
Linuron	80 $\pm$ 12	102 $\pm$ 15	98 $\pm$ 11	90 $\pm$ 3.2	1.72	5.17	5.74	17.2

3. Results and discussion

Prior to adsorption experiments, the target compounds in water, SPM and sediment samples collected from Taihu Lake were determined, and the maximum concentrations were 66.4 ng/L, 19.1 ng/g and 99.2 ng/g for isoproturon, respectively. The background values of the targets are far less than the concentrations of the laboratory design, so they can be neglected in the results analysis. The physical-chemical parameters of the sediments are presented in table 2.

Table 2. Physical-chemical properties of the sediments from different sites in Taihu Lake.

Sediment f_{oc} , %		pH	CEC	Clay, %	Silt, %	Sand, %	Clay, %	Silt, %	Sand, %
				before autoclavation			after autoclavation		
XJ	1.34	7.17	24.45	8.17	46.86	44.97	7.32	46.45	46.23
WJ	0.71	7.26	17.89	5.49	47.28	47.23	5.89	40.25	53.86
YYS	0.75	7.03	12.32	5.96	35.41	58.64	4.38	33.65	61.97
JSG	1.12	8.09	20.78	4.76	46.24	49.00	4.36	37.28	58.36
XD	1.06	7.76	18.67	5.17	43.46	51.38	5.62	37.01	57.37
NQ	0.56	6.23	10.06	4.13	32.07	63.79	3.93	25.39	70.68

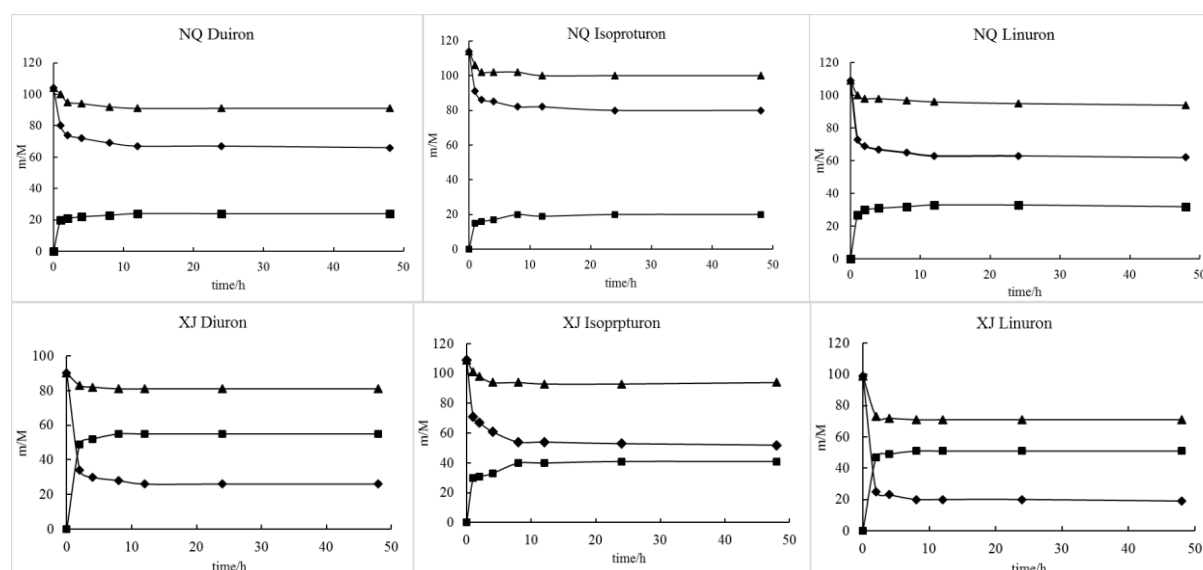


Figure 1. Sorption kinetics of PUHs with autoclaved sediment NQ and XJ. (▲) Total (■) sediment (◆) in water. In axis of ordinates, M means initial mass of the PUHs and m means PUHs remained in the water/sediment phase.

3.1. Sorption kinetics

Sorption kinetics of the three PUHs with the autoclaved sediments from NQ and XJ are presented in figure 1. The loss of the three compounds in the control group was less than 8%, indicating that the hydrolysis and volatility of the compounds and the sorption by test vessels are negligible. The concentrations of PUHs in water and sediment were detected at each sampling, and their sum was total analyte mass (M). According to the material conservation of the whole reaction system, the losses of the three PUHs in treatment groups were between 20%-30%. These losses may mainly result from the biodegradation of the compounds. Despite high pressure sterilization of the system, there is no guarantee that bacteria did not exist in the system. During the reaction cycle over approximately 48 h, bacteria may enter the test vessels alongside dropping targets or sampling, resulting in loss of targets [17,18]. In addition, the loss of the system using XJ sediments was greater than that of NQ, while the clay content of XJ was significantly higher than that of NQ. Wei et al., found that higher clay content promoted the decomposition of organic matter in artificial soils due to increasing substrate availability and greater sustained microbial biomass [19]. As shown in figure 1, the test vessels achieved a balance in response at 12 h, with a total mass loss below 20%. Thus, 12 h was selected as a compromise to reach sorption equilibrium and to avoid significant loss of targets.

3.2. Sorption isotherms

Sorption isotherms of the three PUHs are shown in figure 2. The Freundlich model was used to model the sorption of the three PUHs, and the correlation coefficients (R^2) were obtained from 0.965 to 0.998.

It suggested the sorption isotherms of these PUHs were well described by the Freundlich equation. From figure 2, it is clear that the sorption affinities of the three PUHs differ from each other. Linuron showed the strongest sorption tendency in all six sediments, followed by diuron and isoproturon. Blondel *et al* also obtained the same trend of sorption abilities for PUHs in soils [20].

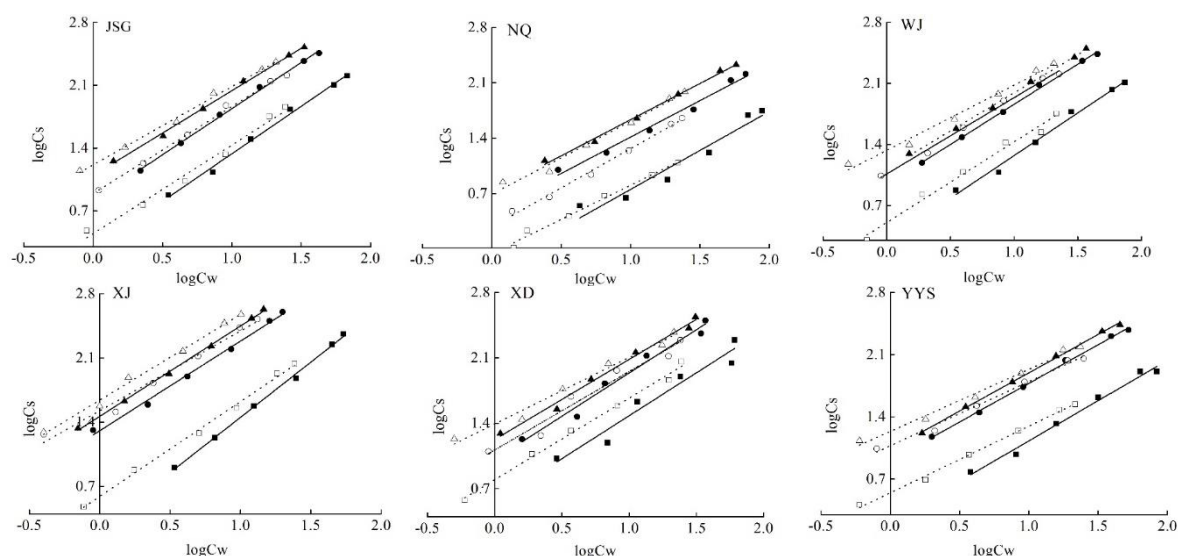


Figure 2. Sorption and desorption isotherms of linuron (▲), diuron (●), and isoproturon (■) in six sediments from Taihu Lake (filled symbols-sorption points, open symbols-desorption points, Cs-PUH concentration in sediment, Cw- PUH concentration in water phase).

The fitted sorption coefficients are shown in table 3. Within the concentration range set by the present study, the sorption of the three selected PUHs to the six sediments was fairly linear, with n values ranging from 0.92 to 1.06, and our results are consistent with previous studies on the adsorption of herbicides in soils [15,16]. Estimated mean $\log K_{oc}$ (K_d normalized to organic carbon) were 2.32 for isoproturon, 2.85 for diuron and 3.02 for linuron by these batch sorption experiments. Diuron and linuron contain Cl atoms that isoproturon lacks, and Cl atoms are electron-withdrawing structures that could enhance H-bonding energy and the ability to promote its adsorption capacity [21]. Blondel *et al* further confirmed that halogen atoms in the molecular structure affect adsorption [18]. Besides, the particle distribution of the sediments also affects the values of K_{oc} . A previous study showed that the higher the sand content, the weaker the adsorption capacity of the sediments [22].

Table 3. Sorption and desorption potential of selected PUHs in six sediments. The K_d and $\log K_{oc}$ values were calculated with all of the measured data points and are shown as the average values.

Sediment	Chemical	Sorption			Desorption			K_d	$\log K_{oc}$	HI
		K_f	n	R^2	K_f	n	R^2			
XJ	Isoproturon	2.86	1.02	0.997	9.77	0.67	0.996	3.19	2.38	0.657
	Diuron	14.5	0.98	0.993	31.62	0.87	0.977	19.6	3.16	0.888
	Linuron	23.1	0.99	0.998	39.8	0.98	0.992	28.5	3.33	0.989
WJ	Isoproturon	1.77	0.98	0.988	3.80	0.78	0.988	1.87	2.42	0.796
	Diuron	8.73	0.92	0.997	11.8	0.87	0.993	7.28	3.01	0.946
	Linuron	11.4	0.92	0.997	17.0	0.85	0.989	9.59	3.13	0.924
YYS	Isoproturon	1.67	0.97	0.986	2.75	0.72	0.987	1.27	2.23	0.742
	Diuron	8.58	0.93	0.998	7.76	0.82	0.988	5.92	2.90	0.882
	Linuron	10.9	0.96	0.998	16.2	0.89	0.988	7.96	3.03	0.927

JSG	Isoproturon	1.89	1.06	0.994	3.89	0.88	0.995	2.26	2.30	0.830
	Diuron	9.47	1.03	0.998	12.8	0.97	0.996	6.94	2.79	0.942
	Linuron	17.4	0.95	0.997	21.3	0.87	0.982	11.1	3.00	0.916
XD	Isoproturon	1.98	1.00	0.965	4.68	0.70	0.981	2.89	2.34	0.700
	Diuron	10.3	0.93	0.974	13.8	0.84	0.954	8.84	2.92	0.903
	Linuron	16.6	0.96	0.988	21.4	0.91	0.979	12.9	3.09	0.947
NQ	Isoproturon	0.30	1.02	0.985	1.47	0.67	0.983	0.82	2.17	0.872
	Diuron	2.03	0.92	0.983	1.91	0.93	0.989	2.52	2.65	1.010
	Linuron	4.06	0.91	0.994	4.90	0.99	0.994	4.23	2.88	1.087

3.3. Desorption

Desorption isotherms were achieved based on the procedure for sorption isotherms. Desorption isotherms describe the equilibrium concentration after one desorption cycle. The results of desorption experiments are shown in figure 2. The desorption isotherms of the three PUHs were more or less deviated from the sorption isotherms, and lay above the sorption isotherms in most cases. The desorption of the PUHs was also well described by the Freundlich equation, and R^2 ranged from 0.954 to 0.995. The fitted desorption coefficients are shown in table 3. The desorption K_f values were consistently higher than those obtained by PUHs sorption on the tested sediments. Regarding different sediments, the order of desorption coefficients for the three PUHs was the same as the sorption. Linuron showed the strongest desorption tendency in all six sediments, followed by diuron and isoproturon. Although isoproturon showed lower desorption rates in all the tested sediments compared to the other two PUHs, the rate of desorption in sediment NQ was much higher than the other five sediments. More sand composition and lower content of organic carbon in the NQ sediments could result in a higher desorption capacity and mobility of isoproturon.

The desorption hysteresis index (HI) was calculated dividing the desorption coefficient by the sorption coefficient [23]. Generally, a value of HI close to 1 means that desorption process happens as quickly as sorption does, meaning that hysteresis is absent. A value of HI lower than 1 indicates that the rate of desorption is lower than that of sorption, thus hysteresis occurs [24]. The HI values of the three PUHs are presented in table 3. The HI values of isoproturon increased from 0.657 for XJ to 0.872 for NQ, while the HI values of diuron and linuron are all close to 1 except for XJ and YYS sediments sorbed to diuron. From this result, significant desorption hysteresis was observed for isoproturon in all the sediments. Desorption hysteresis is a common phenomenon and has been reported in previous studies on herbicides, polycyclic aromatic hydrocarbons, pharmaceutical and personal care products [25-27].

Based on the values of hardness and chemical potential of the three PUHs, linuron is thought of as the most stable substance, while isoproturon is considered the most reactive [28]. Thus, the desorption hysteresis can be explained by the greater ability of the isoproturon molecule to form specific bonds with organic matter. In addition, the organic carbon and clay content were highest in XJ sediment, where the HI value of isoproturon was lowest. For isoproturon, an inverse correlation seemed to exist between the HI values and the clay content ($R^2=0.62$) or f_{oc} ($R^2=0.47$). Sun *et al* found that the HI values of benzene were inversely related to the organic carbon contents and surmised that the organic matter was the major factor for the hysteresis of benzene [23].

4. Conclusion

The present study demonstrated that the sorption behaviors of all three PUHs were well fitted by the Freundlich model. The obtained $\log K_{oc}$ values were 2.32 for isoproturon, 2.85 for diuron and 3.02 for linuron. The PUHs studied exhibited moderate to strong sorption affinities to the natural sediments in the drinking water sources in Taihu Lake. Desorption hysteresis is a common phenomenon for the PUHs tested, and more obvious hysteresis occurred for isoproturon. Considering strong sorption affinities of linuron and diuron, further research on their bioavailability is vital.

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References

- [1] Fenoll J, Sabater P, Navarro G, Pérez-Lucas G and Navarro S 2013 *J. Hazard. Mater.* **244-245** 370-9
- [2] Ge H, Lin Z, Yao Z, Gao Y, Cong Y and Yu H 2014 *Aquat. Toxicol.* **150** 165-74
- [3] Brock T, Roessink I, Belgers J D M, Bransen F and Maund S J 2009 *Environ. Toxicol. Chem.* **28** 2191-205
- [4] Giacomazzi S and Cochet N 2004 *Chemosphere* **56** 1021-32
- [5] Bond T, Templeton M R and Graham N 2012 *J. Hazard. Mater.* **235-236** 1-16
- [6] Tian F X, Xu B, Zhang T Y and Gao N Y 2014 *Chem. Eng. J.* **258** 210-7
- [7] Chusaksri S, Sutthivaiyakit S, Sedlak D L and Sutthivaiyakit P 2012 *J. Hazard. Mater.* **209-210** 484-91
- [8] De Moura N A, Grassi T F, Rodrigues M A M and Barbisan L F 2010 *Arch. Toxicol.* **84** 165-73
- [9] Federico C, Motta S, Palmieri C, Pappalardo M, Librando V and Saccone S 2011 *Mutat. Res.* **721** 89-94
- [10] Marlatt V L and Martyniuk C J 2017 *Comp. Biochem. Physiol. C Toxicol. Pharm.* **194** 9-21
- [11] Gatidou G, Stasinakis A S and Iatrou E I 2015 *Chemosphere* **119** 569-74
- [12] Chicharro M, Bermejo E, Sánchez A, Zapardiel A, Fernandez-Gutierrez A and Arraez D 2005 *Anal. Bioanal. Chem.* **382** 519-26
- [13] Zhou Q and Wang M 2010 *J. Soil Sediment* **10** 1324-34
- [14] Organization for Economic Cooperation and Development 2000 *OECD Guidelines for Testing of Chemicals 106 1* 1-44
- [15] Liu Z, He Y, Xu J, Huang P and Jilani G 2008 *Environ. Pollut.* **152** 163-71
- [16] Sopena F, Semple K, Sohi S and Bending G 2012 *Chemosphere* **88** 77-83
- [17] Ramil M E, Fink G, Scheurer M and Ternes T A 2010 *Environ. Sci. Technol.* **44** 962-70
- [18] Xu B, Mao D, Luo Y and Xu L 2011 *Bioresour. Technol.* **102** 7069-76
- [19] Wei H, Guenet B, Vicca S, Nunan N, Asard H, AbdElgawad H, Shen W and Janssens I A 2014 *Soil Biol. Biochem.* **77** 100-8
- [20] Blondel A, Langeron J, Sayen S, Hénon E, Couderchet M and Guillon E 2013 *Environ. Sci. Pollut. Res.* **20** 6266-81
- [21] Wang D, Mukome F N D, Yan D, Wang H, Scow K M and Parikh S J 2015 *J. Environ. Sci. Health* **50** 544-51
- [22] Palma P, Köck-Schulmeyer M, Alvarenga P, Ledo L, de Alda M L and Barceló D 2015 *Environ. Sci. Pollut. Res.* **22** 7665-75
- [23] Sun K, Ran Y, Yang Y, Xing B and Mao J 2013 *Geoderma* **204-205** 68-74
- [24] Geoderma Geoderma Tang Z, Zhang W and Chen Y 2009 *J. Hazard. Mater.* **166** 1351-6
- [25] Martínez-Hernández V, Meffe R, Herrera S, Arranz E and de Bustamante I 2014 *Sci. Total Environ.* **472** 273-81
- [26] Ren W, Wang M and Zhou Q 2011 *J. Soil Sediment* **11** 552-61
- [27] Yang K and Xing B 2007 *Environ. Pollut.* **145** 529-37
- [28] Mendoza-Huizar L H 2015 *J. Chem.* **2015** 1-9