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Use of Fe/Al drinking water treatment residuals as amendments for enhancing the retention capacity of glyphosate in agricultural soils

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ABSTRACT

Fe/Al drinking water treatment residuals (WTRs), ubiquitous and non-hazardous by-products of drinking water purification, are cost-effective adsorbents for glyphosate. Given that repeated glyphosate applications could significantly decrease glyphosate retention by soils and that the adsorbed glyphosate is potentially mobile, high sorption capacity and stability of glyphosate in agricultural soils are needed to prevent pollution of water by glyphosate. Therefore, we investigated the feasibility of reusing Fe/Al WTR as a soil amendment to enhance the retention capacity of glyphosate in two agricultural soils. The results of batch experiments showed that the Fe/Al WTR amendment significantly enhanced the glyphosate sorption capacity of both soils ($p < 0.001$). Up to 30% of the previously adsorbed glyphosate desorbed from the non-amended soils, and the Fe/Al WTR amendment effectively decreased the proportion of glyphosate desorbed. Fractionation analyses further demonstrated that glyphosate adsorbed to non-amended soils was primarily retained in the readily labile fraction (NaHCO_3 -glyphosate). The WTR amendment significantly increased the relative proportion of the moderately labile fraction (HCl -glyphosate) and concomitantly reduced that of the NaHCO_3 -glyphosate, hence reducing the potential for the release of soil-adsorbed glyphosate into the aqueous phase. Furthermore, Fe/Al WTR amendment minimized the inhibitory effect of increasing solution pH on glyphosate sorption by soils and mitigated the effects of increasing solution ionic strength. The present results indicate that Fe/Al WTR is suitable for use as a soil amendment to prevent glyphosate pollution of aquatic ecosystems by enhancing the glyphosate retention capacity in soils.

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Introduction

Glyphosate (N-[phosphonomethyl] glycine) is the world's highest-selling herbicide due in part to the introduction of

glyphosate-tolerant crops (Cuhra et al., 2013; Dill et al., 2008). In recent years, glyphosate has been widely detected in surface and ground waters (e.g. Abrantes et al., 2010; Aparicio et al., 2013; Glozier et al., 2012; Sanchís et al., 2012; Van Stempvoort

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et al., 2014). Detailed investigations of the toxic effects of glyphosate on non-target organisms, with particular focus on chronic exposure to sub-lethal concentrations of glyphosate and interactions between glyphosate and abiotic stressors, suggest that glyphosate toxicity to non-target organisms such as aquatic invertebrates may have previously been underestimated (Avigliano et al., 2014; Cuhra et al., 2013; Jones et al., 2011; Soso et al., 2007). Given its widespread use, frequent detection in natural waters, and the documented toxic effects of sub-lethal glyphosate concentrations on chronically-exposed non-target aquatic organisms, it is essential to effectively mitigate environmental pollution by glyphosate.

Although glyphosate is typically regarded as having low mobility in soils due to sorption, repeated glyphosate applications (e.g. 4 times), which are often necessary for acceptable weed control (Askew and Wilcut, 1999), may significantly decrease glyphosate retention by soils owing to the reduction of binding sites (Barrett and McBride, 2007; Shushkova et al., 2010). Repeated applications may also prolong glyphosate persistence due to decreased rates of biodegradation (Andréa et al., 2003), resulting in glyphosate accumulation in soils and thereby increasing the risk of soil-adsorbed glyphosate release to ground or surface waters. In addition, the glyphosate adsorbed by soil particles could be remobilized due to the decomposition of mulch (Aslam et al., 2013), the application of phosphate (Bott et al., 2011), the disruption of the soil-glyphosate sorption equilibrium conditions by rainstorms (Gjettermann et al., 2011), etc. Thus, a high glyphosate retention capacity for soils is in order to prevent glyphosate contamination of aquatic systems adjacent to intensive agricultural production systems. Using agricultural and agro-industrial wastes as soil amendments can significantly enhance the pesticide retention capacity of agricultural soils (Li et al., 2009; López-Piñeiro et al., 2013; Yu et al., 2010; Zhang et al., 2014).

Drinking water treatment residuals (WTRs) are a non-hazardous byproduct of drinking water purification (Babatunde and Zhao, 2007). Several million tons of WTR are annually generated from drinking water treatment facilities in most countries (Verlicchi and Masotti, 2001; Babatunde and Zhao, 2007). Iron and Al coagulants are widely used in drinking water treatment facilities. Hence, many WTR are enriched in Fe/Al hydroxides, as well as the humic materials and sediments precipitated from the water supplies during treatment (Ippolito et al., 2011). The high proportion of Fe/Al hydroxides within WTR confers high sorption capacity for P (Makris et al., 2005), hydrogen sulfide (Wang et al., 2013a), perchlorate (Makris et al., 2006), As (Nagar et al., 2010) and metals such as Cr, Pb, Hg and Se (Babatunde and Zhao, 2007; Hovsepyan and Bonzongo, 2009; Ippolito et al., 2009; Zhou and Haynes, 2011). Due to the strong sorption capacities of Fe/Al WTR, they have been used to mitigate environmental pollution in numerous applications. Notably, Fe/Al WTR have been incorporated into sediments, soils and substrates of constructed wetlands to effectively manage P release from aquatic sediments and off-site transport of P to surrounding aquatic systems, and to adsorb and immobilize metals in polluted soils (Agyin-Birikorang et al., 2009; Elkhatib et al., 2013; Sarkar et al., 2007; Wang et al., 2012, 2013b).

As for land application, Fe/Al WTR may be suitable as soil amendments to buffer pH due to their high content of Fe/Al

hydroxides and humic substances, or as soil conditioners for structural improvement mainly because of their alkaline properties, or even as a soil substitute (Babatunde and Zhao, 2007; Dayton and Basta, 2001; Owen, 2002). Hu et al. (2011) recently reported glyphosate sorption from aqueous solution by Al-based WTR. Given the beneficial reuse of WTR as soil amendments and their sorption capacity for glyphosate, Fe/Al WTRs have great potential for use as soil amendments to enhance the glyphosate retention capacity of agricultural soils.

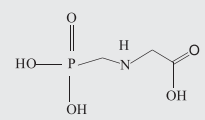
Therefore, the objective of this study was to investigate the feasibility of using Fe/Al WTR as soil amendments to enhance the glyphosate retention capacity in agricultural soils. We hypothesized that: (1) soil amendment by Fe/Al WTR would enhance the glyphosate sorption capacity of agricultural soils; (2) amendment by Fe/Al WTR would stabilize soil-adsorbed glyphosate, reducing the potential for release of soil-adsorbed glyphosate into the aqueous phase; and (3) amendment by Fe/Al WTR would minimize the effects of solution chemistry (pH, ionic strength and composition of background electrolytes) on glyphosate sorption by soils. Results of the present study are anticipated to provide useful information related to the productive re-use of WTR (e.g. as soil amendments in buffer zones including agricultural drainage ditches and buffer strips) to prevent the off-site transport of applied glyphosate to surrounding aquatic systems.

1. Materials and methods

1.1. Sample collection and preparation

Glyphosate of 99.9% (v/v) purity was purchased from Sigma-Aldrich (Taufkirchen, Germany). The physico-chemical properties of glyphosate are summarized in Table 1. The Fe/Al-based WTRs were collected from the Beijing City No. 9 Waterworks in Beijing, China, which primarily treats surface waters from the Miyun Reservoir. Iron and Al salts are the primary coagulants using in the water treatment process. Two agricultural soils with different Fe and Al contents were selected for this study. The first soil, denoted as TJ, was collected from a cornfield in Qixing

Table 1 – Structure and chemical properties of glyphosate.^a

Property	Glyphosate
Structure	
Molecular weight	169
logK _{ow} ^b	−2.8
S _w ^c	12 g/L
pK _a	2, 2.6, 5.6, 10
Half life in water	3.5–32 days
Half life in soil average	40 days (an average)
48 hr EC50	1.4–10.6 mg/L (<i>Daphnia magna</i>)

^a Data obtained from Cuhra et al. (2013), Giesy et al. (2000), Goldsborough and Brown (1993), Mallat and Barceló (1998).

^b Octanol/water partition coefficient.

^c Solubility in distilled water at 25°C.

district, Tianjin City (39°06'42.3"N, 116°59'20.9"E). The second soil, denoted as SD, was collected from a vegetable production base in Shouguang City, Shangdong Province (36°55'15.31"N, 117°44'10.9"E). Both soil samples were collected from the surface (0–20 cm) layer.

Fresh Fe/Al WTR and soil samples were air-dried to a constant mass, gently crumbled and sieved through a 0.15 mm mesh screen. Sub-samples of each soil and the Fe/Al WTR were digested using HNO_3 , HCl and H_2O_2 (US EPA method 3050B), and the resultant solutions were analyzed using an inductively coupled plasma-atomic emission spectrometer (ICP-AES, Ultima-2, Jobin Yvon, Paris, France) to determine the elemental composition of the solid materials. Amorphous Fe and Al (Fe-ox and Al-ox) were quantified by ICP-AES after extraction of soil and WTR sub-samples in the dark with 0.2 mol oxalate and ammonium oxalate (pH 3.0) for 4 hr at a 1:60 solid: solution ratio (g/mL) (Shang and Zelazny, 2008). The organic matter contents of the WTR and soil sub-samples were determined using the dichromate heat-of-dilution method (Nelson and Sommers, 1996) and the organic matter fractions (fulvic acid, humic acid and humin) were extracted according to Zbytyniewski and Buszewski (2005). The cation exchange capacity (CEC) of each solid material was determined using the barium chloride-triethanolamine method (Thomas, 1982). The particle size distribution of each of the soils was measured using a particle size analyzer (Microtrac S3500, Microtrac, Inc., Montgomeryville, Pennsylvania, USA). The respective Brunauer–Emmett–Teller (BET) surface area and porosity of the Fe/Al WTR and each soil were measured by N_2 sorption and desorption using a porosimeter (ASIQM0000-3, Quantachrome Instruments, Florida, USA).

1.2. Glyphosate sorption and desorption

Duplicate 1 ± 0.01 g samples of each soil amended with 0, 2%, 5%, or 10% (w/w) Fe/Al WTR were weighed into 40 mL glass vials with PTFE-lined screw caps containing 20 ± 0.5 mL of glyphosate solution at initial concentrations ranging from 7.5 to 250 mg/L. The maximum concentration of glyphosate (250 mg/L) used in this study was 100 times greater than the field rate application (50 mg active ingredient kg^{-1} soil) (Ratcliff et al., 2006), representing accidental glyphosate spillage or application equipment malfunction. Sodium azide (100 mg/L) and KCl (0.005 mol/L) were added to the glyphosate solutions to prevent microbial degradation and maintain constant solution ionic strength, respectively. The initial pH of each glyphosate solution was adjusted to approximately pH 7 prior to the experiment using 0.1 mol/L HCl or 0.1 mol/L NaOH solutions. Glass vials were agitated at 150 r/min and 25°C for 36 hr. The 36-hr equilibration time was selected based upon the results of a preliminary sorption kinetics experiment (Fig. S1, Supporting Information). Following equilibration, duplicate samples (10 mL) of the suspensions were centrifuged at 5200 g (15 min). The initial and equilibrium concentrations of glyphosate in each solution were determined by high-performance liquid chromatography (HPLC). The adsorbed quantities of glyphosate were calculated as the difference between glyphosate concentrations in the initial solution and in the supernatant after centrifugation.

After equilibration and removal of 10 mL of each suspension for HPLC analysis, the remaining soil suspensions in the vials

were immediately filtered through a qualitative cellulose filter (10–15 μm) and the residual solids were freeze-dried. Duplicate freeze-dried solid samples of 0.75 ± 0.01 g were weighed into the glass vials with 15 ± 0.5 mL solution containing 0.005 mol/L KCl and 100 mg/L NaN_3 . The glass vials were then agitated at 150 r/min and 25°C for 36 hr. After equilibration, 10 mL of the suspensions was withdrawn from each sample and centrifuged at 5200 g (15 min). The quantity of desorbed glyphosate in each solution was determined using HPLC.

1.3. Glyphosate fractionation

Glyphosate was sequentially extracted from Fe/Al WTR and Fe/Al WTR-amended soils using the technique for organic P fractionation in soils (Ivanoff et al., 1998; Zhang et al., 2008). Triplicate glyphosate-loaded solid samples were prepared according to the sorption and desorption steps in Section 2.2 using Fe/Al WTR and soils amended with 0 or 10% (w/w) Fe/Al WTR. The quantities of glyphosate adsorbed are shown in Table S1. The glyphosate-loaded (1.0 ± 0.01 g) and blank samples were sequentially extracted by the following series of reagents (50 mL): (1) shaking for 16 hr in 0.5 mol/L NaHCO_3 at pH 8.5 (NaHCO_3 -glyphosate); (2) shaking for 3 hr in 1.0 mol/L HCl (HCl -glyphosate); (3) shaking for 16 hr in 0.5 mol/L NaOH ; then (iv) 16 hr shaking in 1 mol/L H_2SO_4 (residual glyphosate). Prior to extraction of the residual glyphosate via dissolution in H_2SO_4 , the residue from the NaOH extraction was rinsed with deionized water and ashed at 550°C for 1 hr. The quantity of organic P in sample solutions was calculated by subtracting inorganic P from total P. The quantity of glyphosate was calculated as the difference between organic P quantities in the extracts of the glyphosate-loaded solid samples and the blank samples. The inorganic P and total P were measured for all extracts using the ammonium molybdate spectrophotometric method (Murphy and Riley, 1962) and ICP-AES, respectively.

1.4. Effects of soil solution chemistry on glyphosate sorption

The effects of solution pH, ionic strength and dominant cations on glyphosate sorption to Fe/Al WTR-amended soils were investigated. The solution pH was adjusted within the range of 4–10 using 0.1 mol/L HCl or 0.1 mol/L NaOH solutions. Calcium chloride or KCl was added as the background electrolyte at concentrations between 0.005 and 0.1 mol/L. Air-dried 1.0 ± 0.01 g sub-samples of soil amended with 0, 5% or 10% (w/w) Fe/Al WTR were placed in glass vials with 20 ± 0.5 mL of glyphosate solution containing 0.005–0.1 mol/L KCl or CaCl_2 and 100 mg/L NaN_3 . In order to maintain the glyphosate concentration in a range amenable to accurate quantitation and the percentage adsorbed above 20% (EPA, 2010), the initial glyphosate concentration was 150 mg/L for Fe/Al WTR-amended soils (5% and 10%) and 30 mg/L for soils without WTR (0%). Similar or greater glyphosate solution concentrations have been used in other research examining glyphosate sorption to soil (e.g. Morillo et al., 2000, 2002). The glass vials containing the sorbent mixtures were agitated in the dark in a constant temperature mixer at 150 r/min and 25°C for 36 hr. The suspensions were centrifuged at 5200 g (15 min). The glyphosate concentrations in each supernatant were determined using HPLC. The solution pH before and after glyphosate sorption by

the soil samples in different background electrolyte solutions is shown in Table S2 (Supporting information).

1.5. Glyphosate determination and data analysis

Glyphosate in solution was quantified by HPLC following derivatization (Le Bot et al., 2002; Waiman et al., 2012). For each sample, 2.5 mL solution was derivatized by adding 0.5 mL sodium borate buffer (0.05 mol/L, pH = 9) and 0.5 mL 9-fluorenylmethyl chloroformate (FMOC-C1) solution (1 g/L) to a 10-mL glass centrifuge tube. The mixture was homogenized by manual shaking and then placed in a 35°C thermostatic water bath for 2 hr. Each solution was then mixed with 2.5 mL dichloromethane using a vortex mixer (SI Vortex Genie 2, Scientific Industries, Bohemia, New York, USA) to remove excess derivatization reagent, followed by centrifugation at 3000 g for 15 min to separate the dichloromethane from the aqueous solution. Approximately 1.5 mL of each aqueous phase was recovered for direct HPLC injection. The derivatized glyphosate was analyzed at a wavelength of 270 nm using an HPLC (Waters 2695, Waters Corp., Milford, Massachusetts, USA) equipped with a UV detector (Waters 2489, Waters Corp., Milford, Massachusetts, USA) and a Hypersil ODS column (250 mm × 4.6 mm × 5 µm, Thermo, USA). Sodium phosphate buffer (0.05 mol/L, pH = 6.0) and acetonitrile (80:20, v/v) comprised the mobile phase at a flow rate of 0.8 mL/min. The injected sample volume was 20 µL and the detection limit for glyphosate (with a signal to noise ratio of 3:1) was 20 µg/L. The recovery efficiency of total glyphosate obtained by sequential extraction in WTR and WTR-amended soils ranged from 95.4% to 113% (Table S1).

Glyphosate data shown in the figures herein are averages. The kinetic and isothermal curves were obtained using Sigma Plot 12.0 (Systat Software Inc, San Jose, California, USA). Analysis of variance was performed by one-way ANOVA and two-tailed paired t test using the PASW statistics software package version 18 (SPSS, Inc., Chicago, IL). Differences were considered significant when the significance level was <0.05 (e.g. $\alpha = 0.05$).

2. Results

2.1. Characteristics of Fe/Al WTR and soils

The physico-chemical characteristics of the Fe/Al WTR and the TJ and SD agricultural soils are summarized in Table 2. With respect to the particle size distribution, the TJ soil is classified as silt loam whereas the SD soil is classified as a loam. The BET surface areas and total pore volumes of the TJ and SD soils are similar. The micropore distributions of the Fe/Al WTR and the TJ and SD soils are shown in Fig. S2. The Fe and Al amorphous hydroxide contents of solid materials are the key to glyphosate sorption (Piccolo et al., 1994). Glyphosate sorption may be inhibited by increasing soil pH, P concentration, and organic matter (OM) content (Borggaard and Gimsing, 2008; De Jonge et al., 2001). In comparison to the SD soil, the TJ soil has greater total Fe and Al, P and OM content. Both the TJ and SD soils exhibit low Fe-ox and Al-ox contents, and hydrophobic organic compounds (humins) are the predominant organic component of both soils. The total contents of Fe and Al in the Fe/Al WTR were 133 and 98 mg/g, respectively, of

Table 2 – Characteristics of the soils and Fe/Al WTR.

Samples	TJ soil	SD soil	WTR ^a
pH ^b	7.43	7.40	6.80
Cation exchange capacity (cmol/kg)	7.34	9.00	76.13
Total Fe (mg/g)	35.02	24.87	133
Total Al (mg/g)	80.89	50.80	98
Total Ca (mg/g)	12.91	6.87	21.0
Total Mg (mg/g)	36.72	7.11	1.80
Total Mn (mg/g)	0.63	0.48	2.60
Fe-ox (mg/g)	2.31	1.54	114.52
Al-ox (mg/g)	1.71	1.17	91.45
Total P (mg/g)	1.32	0.86	1.05
Oxalate-extractable P (mg/g)	0.85	0.55	0.89
NaHCO ₃ -P (mg/g)	0.24	0.16	0.05
Total organic matter (mg/g)	36.38	13.10	107
Humic acid (mg/g)	4.72	2.48	1.13
Fulvic acid (mg/g)	2.06	2.01	15.87
Humins (mg/g)	29.60	8.61	90
BET surface area (m ² /g)	18.15	19.84	78.50
Total pore volume (cm ³ /g)	0.035	0.023	0.071
Average pore diameter (nm)	3.84	3.82	3.62
Sand (%)	37.55	47.07	–
Slit (%)	51.73	42.79	–
Clay (%)	10.72	10.14	–

^a Additional characteristics of the Fe/Al WTR listed in the table are detailed in Zhao et al. (2013).

^b pH determined in aqueous slurry with soil/water ratio of 1:2.5.

which amorphous Fe and Al accounted for 114.5 and 91.5 mg/g, respectively.

2.2. Glyphosate sorption by WTR-amended soils

Glyphosate sorption to TJ and SD soils amended with Fe/Al WTR at rates of 0, 2%, 5% and 10% (w/w) is shown in Fig. 1. The sorption kinetics and isotherm of glyphosate on Fe/Al WTR are provided in Fig. S3 and S4. The Fe/Al WTR showed high sorption capacity for glyphosate. Both the SD and TJ soils exhibited relatively low capacity for glyphosate sorption. As the Fe/Al WTR amendment rate increased from 2% to 10% (w/w), the glyphosate sorption capacities of both the TJ and SD soils were significantly enhanced, reaching sorption maxima of nearly 3000 and 3200 mg/kg, respectively. In the absence of WTR amendment, the SD soil exhibited significantly greater glyphosate sorption capacity compared to the TJ soil ($p < 0.05$). No significant difference ($p > 0.05$) was observed between the glyphosate sorption capacity of TJ and SD soils following amendment with equal quantities of the Fe/Al WTR (2%–10%). These results indicate that the glyphosate sorption capacity of the WTR-amended soil was strongly associated with the WTR amendment rate and the physico-chemical characteristics of the two soils examined herein exerted substantially less influence on glyphosate sorption.

Langmuir and Freundlich models were tested to further analyze glyphosate sorption equilibria, and isotherm parameters are given in Table 3. Both the Langmuir and Freundlich models fit the experimental data well. The obtained correlation coefficients (R^2) were within the range of 0.91–0.99. Glyphosate sorption isotherms for TJ and SD soils with and without Fe/Al WTR amendment are of type L ($n < 1$), implying that glyphosate sorption sites will decrease with increasing glyphosate sorption

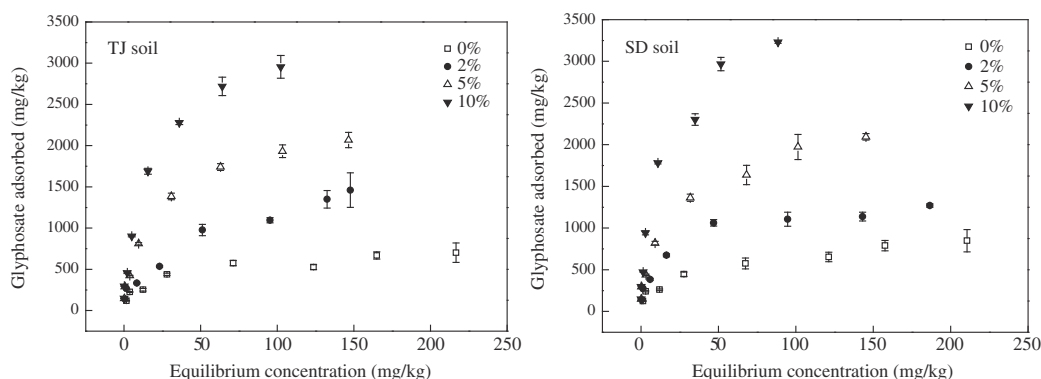


Fig. 1 – Glyphosate sorption to TJ and SD soils amended with Fe/Al WTR at rates of 0, 2%, 5% and 10% (w/w). The initial glyphosate concentration ranged from 7.5 to 250 mg/L (pH = 7.00).

and the gradual saturation of potential sorption sites (Giles et al., 1960). Similar trends for glyphosate sorption have been observed in other soils (Yu and Zhou, 2005). As shown in Table 3, the maximum respective quantities of glyphosate adsorbed (Q_{\max}) by non-amended TJ and SD soils were 690 and 870 mg/kg, respectively. Increasing the rate of Fe/Al WTR amendment resulted in a significant increase in the Q_{\max} for both soils ($p < 0.001$). At the 10% (w/w) WTR amendment rate, the Q_{\max} for both the TJ and SD soils was >3300 mg/kg.

2.3. Glyphosate desorption from WTR-amended soils

Fig. 2 shows the desorption of previously adsorbed glyphosate from TJ and SD soils amended with 0, 2%, 5% and 10% Fe/Al WTR (w/w). The TJ and SD soils exhibited similar glyphosate desorption characteristics, with the quantities of glyphosate desorbed from each soil with equal WTR content proportional to the respective quantity of glyphosate previously adsorbed. Greater Fe/Al WTR amendment rate resulted in greater glyphosate sorption quantities, and a lesser proportion of the adsorbed glyphosate was desorbed from Fe/Al WTR-amended TJ and SD soils as the WTR amendment rate increased. As the quantity of

glyphosate previously adsorbed increased, the proportion of desorbed glyphosate increased from 15% to 33% and from 8.0% to 20% in the TJ and SD soils without Fe/Al WTR amendment, respectively. In comparison, although the quantities of glyphosate adsorbed to TJ and SD soils amended with 10% (w/w) Fe/Al WTR were 4-fold greater than non-amended TJ and SD soils, the maximum proportion of desorbed glyphosate from TJ and SD soils amended with 10% (w/w) Fe/Al WTR was only 8.1% and 5.6%, respectively. Thus, the quantity of glyphosate desorbed from Fe/Al WTR-amended soils was dependent on both the quantity of previously adsorbed glyphosate and the rate of Fe/Al WTR amendment.

2.4. Fractionation of glyphosate from WTR and WTR-amended soils

In order to elucidate the mechanism(s) of glyphosate retention in Fe/Al WTR-amended soils and inform glyphosate desorption behavior, four major glyphosate fractions in soils with and without Fe/Al WTR amendments were chemically extracted sequentially (Ivanoff et al., 1998; Zhang et al., 2008), including NaHCO_3 -glyphosate, HCl-glyphosate, NaOH-glyphosate and

Table 3 – Isotherm parameters for glyphosate sorption to TJ and SD soils amended with Fe/Al WTR at rates between 0 and 10% (w/w).

Samples		Freundlich equation			Langmuir equation		
		$Q_e = K_F C_e^n$			$Q_e = \frac{K_L Q_m C_e}{1 + K_L C_e}$		
		K_F ($\text{mg}^{1-n} \text{L kg}^{-1}$)	n	R^2	K_L (L/mg)	Q_{\max}^{***} (mg/kg)	R^2
TJ soil	WTR ^a	10350	0.31	0.994	0.190	37900	0.936
	0% WTR	140*	0.30	0.947	0.066	690**	0.922
	2% WTR	147*	0.45	0.981*	0.020	1836**	0.951
	5% WTR	493*	0.30	0.937	0.058	2255**	0.984
	10% WTR	525*	0.39	0.981	0.070	3307**	0.990
SD soil	0% WTR	132*	0.35	0.982	0.040	871**	0.911
	2% WTR	278*	0.30	0.956	0.082	1284**	0.966
	5% WTR	374*	0.35	0.991	0.059	2231**	0.967
	10% WTR	644*	0.37	0.982	0.104	3389**	0.973

* and ** represent a significant increase in the values of K_F and Q_{\max} resulted from the increasing rate of Fe/Al WTR amendment within soils at $p < 0.05$ and $p < 0.001$ level, respectively.

^a Batch equilibrium studies for glyphosate sorption on Fe/Al WTR were conducted (Figs. S3, S4).

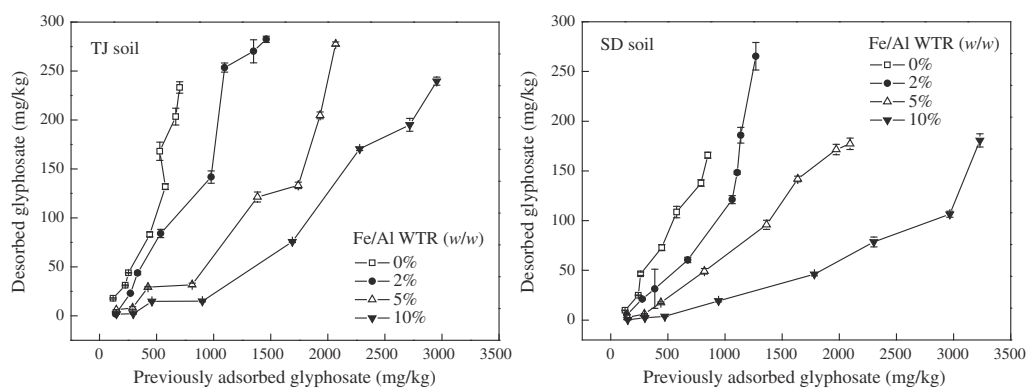


Fig. 2 – Desorption of previously adsorbed glyphosate from TJ and SD soils amended with Fe/Al WTR at rates of 0, 2%, 5% and 10% (w/w).

residual glyphosate. As generally observed in sequential chemical fractionation techniques, the proportion of adsorbed glyphosate recovered as the chemical fractionation sequence proceeds represents the proportion of the total adsorbed glyphosate associated with the solid phase in increasingly stable complexes. Thus, in the present study, NaHCO_3 -glyphosate is considered the readily labile fraction and represents glyphosate adsorbed to soil mineral surfaces, HCl -glyphosate is considered a moderately labile fraction and represents the proportion of glyphosate chemisorbed to minerals, and the NaOH -glyphosate fraction includes the bulk of the moderately labile glyphosate associated with soil fulvic acid and some nonlabile glyphosate associated with humic acid (Ivanoff et al., 1998; Zhang et al., 2008). The residual glyphosate obtained after soil residue ashing and dissolution in H_2SO_4 is the highly resistant, non-labile fraction and represents the most stable proportion of adsorbed glyphosate.

The greatest proportion of glyphosate adsorbed to non-amended TJ and SD soils was associated with the NaHCO_3 -extractable, or readily labile fraction (NaHCO_3 -GLY in Fig. 3). The NaHCO_3 -glyphosate comprised 86% and 98% of the total adsorbed glyphosate in the non-amended TJ and SD soils, respectively. Within the Fe/Al WTR, adsorbed glyphosate was primarily within the readily labile (NaHCO_3 -glyphosate) and moderately labile (HCl -glyphosate) fractions, accounting for 51% and 42% of the total adsorbed glyphosate, respectively. Following amendment of the TJ and SD soils with 10% (w/w) Fe/Al WTR, the relative proportion of total adsorbed glyphosate present in the readily labile fraction (NaHCO_3 -glyphosate) declined to 68% and 70%, respectively. The relative proportion of total adsorbed glyphosate within the moderately labile fraction (HCl -glyphosate) increased to 28% and 22%, respectively, following amendment of TJ and SD soils with 10% (w/w) Fe/Al WTR, but there was a negligible change in the relative proportions of NaOH -glyphosate and residual glyphosate.

2.5. Effects of solution chemistry on glyphosate sorption by WTR-amended soils

2.5.1. Solution pH

Fig. 4 shows the glyphosate sorption by Fe/Al WTR-amended TJ and SD soils as a function of pH. Glyphosate sorption varied inversely with solution pH at each rate of WTR amendment.

Statistical analyses indicated that the pH increase from 4 to 10 significantly reduced glyphosate sorption in the non-amended TJ and SD soils ($p < 0.01$), but the inhibitory effect on glyphosate sorption to TJ and SD soils amended with 5% and 10% (w/w) Fe/Al WTR was not significant ($p > 0.05$). Specifically, as the pH increased from 4.5 to 10.2, the glyphosate sorption to non-amended soils declined by 22% (TJ–0%) and 33% (SD–0%), whereas the same increase in solution pH resulted in only 12% and 14% reduced glyphosate sorption to TJ and SD soils amended with 10% (w/w) Fe/Al WTR, respectively. Overall, increasing pH decreased glyphosate sorption to TJ and SD soils; however, soil amendment with Fe/Al WTR minimized the inhibitory effect of increasing pH on glyphosate sorption.

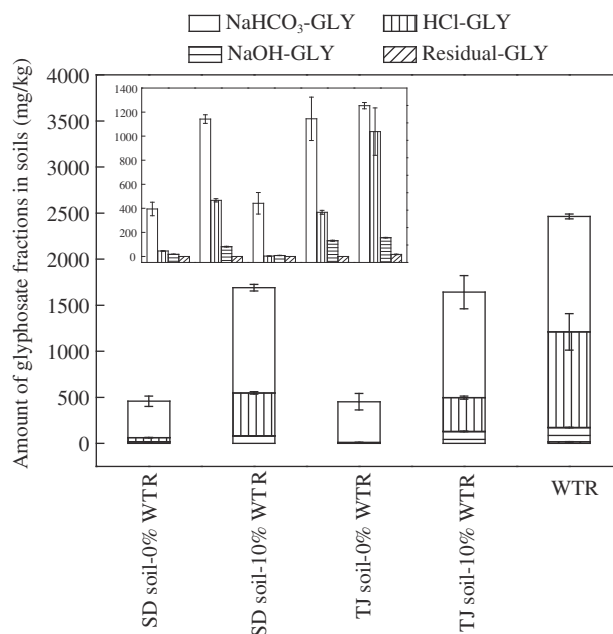


Fig. 3 – Distribution of adsorbed glyphosate (GLY) among fractions chemically extracted from Fe/Al WTR and TJ and SD soils amended with WTR at rates of 0 and 10% (w/w). Soil–0% WTR, Soil–5% WTR and Soil–10% WTR represent soil amended with 0, 5% and 10% WTR, respectively.

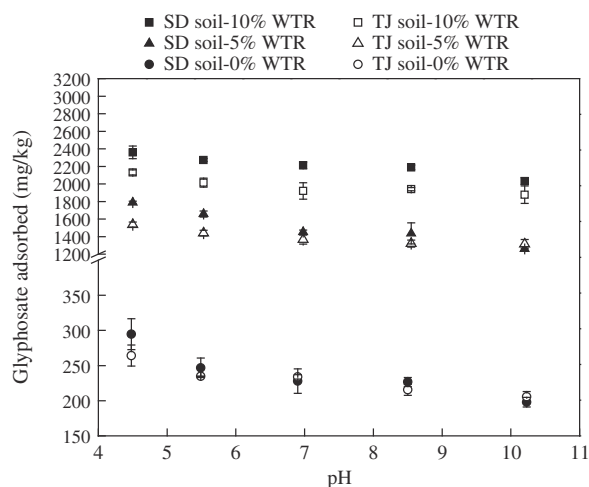


Fig. 4 – Effect of solution pH on glyphosate sorption to TJ and SD soils amended with WTR at rates of 0%, 5% and 10% (w/w). Soil—0% WTR, Soil—5% WTR and Soil—10% WTR represent soil amended with 0, 5% and 10% WTR, respectively.

2.5.2. Solution ionic strength and electrolyte composition

Solution cation composition significantly affected glyphosate sorption; the presence of Ca^{2+} significantly promoted glyphosate sorption in comparison to K^+ ($p < 0.001$) in both TJ and SD soils (Fig. 5). Similar effects were observed in both TJ and SD soil solutions following increases in soil solution ionic strength using either K^+ or Ca^{2+} . Glyphosate sorption by non-amended TJ and SD soils was significantly enhanced with increasing solution ionic strength, regardless of whether K^+ or Ca^{2+} was the dominant cation in the background electrolyte solution ($p < 0.05$). With solution K^+ and Ca^{2+} concentration increasing from 0.005 to 0.05 mol/L, glyphosate sorption increased by 21% and 32% in non-amended TJ soil and by 15% and 38% in non-amended SD soil, respectively. In contrast, increasing ionic strength of

both K^+ and Ca^{2+} solutions did not significantly affect ($p > 0.05$) glyphosate sorption to Fe/Al WTR-amended TJ and SD soils (5% and 10% w/w). The maximum observed decrease in glyphosate sorption in soils amended with 10% (w/w) Fe/Al WTR as a result of increasing solution ionic strength was 14% and 9% for TJ and SD soils, respectively. These results indicate that the soil amendment with Fe/Al WTR reduced the impact of solution ionic strength on glyphosate sorption.

3. Discussion

3.1. Effect of Fe/Al WTR amendments on glyphosate sorption capacity of agricultural soils

The Q_{max} for Fe/Al WTR was 44 times greater than both the soils, and the glyphosate sorption capacity of both soils was significantly increased with increasing amendment rate in the order of $0\% < 2\% < 5\% < 10\%$ (w/w) WTR addition (Fig. 1 and Table 3). This demonstrates that amendment of agricultural soils with Fe/Al WTR could effectively enhance glyphosate sorption capacity. It has previously been reported that glyphosate sorption in soils is primarily controlled by soil pH (Gimsing et al., 2004) and amorphous Fe/Al hydroxides (Piccolo et al., 1994). In the present study, both the TJ and SD soils exhibited low glyphosate sorption capacity mainly due to their alkaline properties and low Fe-ox and Al-ox contents. The soil pH decreased with the increasing amount of Fe/Al WTR added, and 10% Fe/Al WTR amendment (w/w) reduced the soil pH by 0.15 and 0.28 units for TJ and SD soils, respectively (Table S3). The slightly lower soil pH following Fe/Al WTR amendment contributed to the enhancement of glyphosate sorption by soils. Moreover, the Fe-ox and Al-ox contents of the Fe/Al WTR used herein were each >50 times greater than those of the TJ and SD soils. Amendment of the TJ and SD soils with 10% Fe/Al WTR (w/w) resulted in 10 to 13-fold increase in Fe-ox and Al-ox contents, thereby substantially enhancing the glyphosate sorption capacity of the amended soils due to the increase in

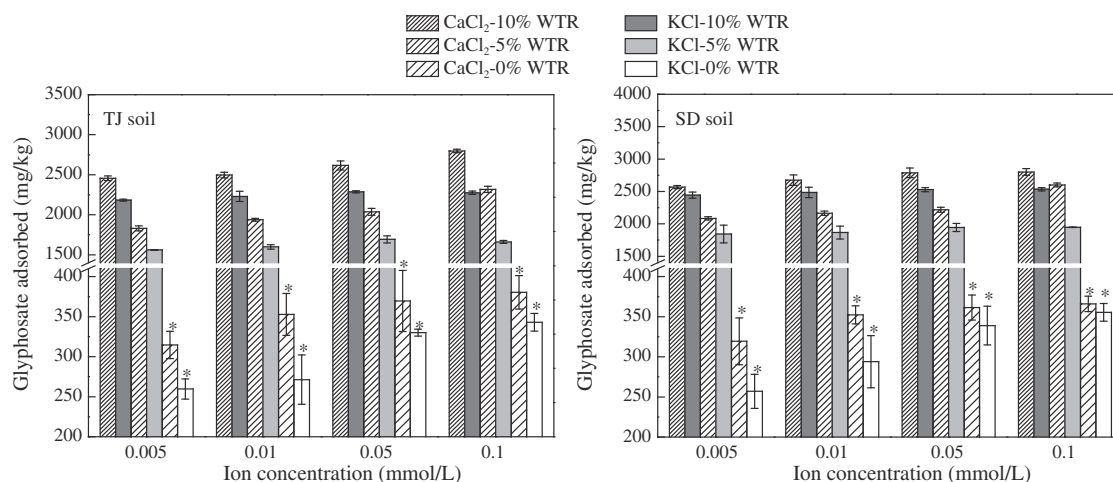


Fig. 5 – Effects of solution ionic strength and electrolyte composition on glyphosate sorption to TJ soil and SD soil (amended with Fe/Al WTR at rates of 0, 5% and 10% (w/w)). * represents statistically significant differences caused by increasing ionic strength of K^+ and Ca^{2+} solutions at $p < 0.05$ level.

the availability of glyphosate sorption sites. High P and OM content would reduce the glyphosate sorption by soils (De Jonge et al., 2001; Vereecken, 2005). The lesser glyphosate sorption capacity of TJ soil relative to the SD soil may be attributed to its greater P and OM contents (Table 2). Soil P may reduce glyphosate sorption via competitive sorption processes, whilst OM can reduce glyphosate sorption by blocking available sorption sites (Borggaard and Gimsing, 2008; De Jonge et al., 2001).

3.2. Effect of Fe/Al WTR amendments on glyphosate lability in agricultural soils

The proportion of adsorbed glyphosate subsequently desorbed from the Fe/Al WTR-amended soils was inversely related to the WTR application rate (Fig. 2). Glyphosate fractionation results (Fig. 3) showed that adsorbed glyphosate in both WTR-amended TJ and SD soils was present in a relatively more stable form (HCl-glyphosate) compared to non-amended soils, resulting in decreased glyphosate lability in WTR-amended TJ and SD soils. The majority of Fe and Al within the amended TJ and SD soils was solubilized during HCl extraction (Table S4), indicating that the HCl-glyphosate fraction extracted from Fe/Al WTR-amended soils included glyphosate adsorbed by Fe/Al hydroxides. This suggests that the decrease in glyphosate lability in the TJ and SD soils amended with Fe/Al WTR is likely attributable to the proportionally greater Fe/Al hydroxide content following WTR amendment.

3.3. Effect of solution chemistry on glyphosate sorption by Fe/Al WTR amended soils

Amendment of TJ and SD soils with Fe/Al WTR minimized the inhibitory effect on glyphosate sorption observed with increasing solution pH and mitigated the effects of increasing solution ionic strength. The high proportion of glyphosate adsorbed to soil mineral surfaces (NaHCO₃-glyphosate) reflects the importance of net electrostatic repulsion in the glyphosate sorption process. With glyphosate pK_a values of 2, 2.6, 5.6 and 10 (Sprankle et al., 1975), glyphosate exists as a negative ion within the solution pH range of 4.5–10.2 used in this study. The inhibitory effect of increasing pH on glyphosate sorption was likely associated with the greater net negative charge of the glyphosate caused by the deprotonation of the three functional groups (amine, carboxylate, and phosphonate) at higher solution pH, resulting in less interaction between the negatively charged soil surface and glyphosate (De Jonge and De Jonge, 1999; McConnell and Hossner, 1985). These results are consistent with those obtained by others investigating glyphosate sorption to goethite, hematite, kaolin and other soils (McConnell and Hossner, 1985; Pessagno et al., 2008; Sheals et al., 2002). In comparison to K⁺, divalent Ca²⁺ may act as a bridge between glyphosate and negatively-charged soil particles, thereby promoting glyphosate sorption to soils. An increase in solution ionic strength can compress the electric double layer, resulting in the decrease of electrostatic repulsion and hence enhancing the sorption capacity. As demonstrated herein, the quantities of adsorbed glyphosate in soils without WTR amendment significantly declined with increasing pH and increased as ionic strength increased.

Following the WTR amendment, the relative importance of glyphosate surface sorption (NaHCO₃-glyphosate) decreased due to the increased proportion of glyphosate chemisorbed to Fe/Al hydroxides (HCl-glyphosate), where net electrostatic repulsion has relatively little impact. Meanwhile, the higher isoelectric point (IEP) of the Fe/Al hydroxides within the Fe/Al WTR compared to the non-amended soils may result in a lesser net negative charge for soils in solution, decreasing the net electrostatic repulsion between glyphosate and solid surfaces. These two factors mentioned above are the most likely explanations for the diminished effects of solution pH and ionic strength observed for glyphosate sorption to soils amended with WTR.

3.4. Implications for practical application

Buffer zones such as wetlands, drainage ditches and buffer strips have been implemented as best management practices to minimize the release of pesticides into surrounding waters (Rogers and Stringfellow, 2009). The results of the present work indicate that Fe/Al WTR may be a useful addition to the substrates of wetlands or soils of drainage ditches and buffer strips to enhance the glyphosate sorption capacity and increase the retention time of glyphosate in these systems, thus minimizing glyphosate movement with irrigation or stormwater and allowing sufficient time for biodegradation or plant absorption.

Studies have proved that Al toxicity is not an issue for land application of WTR. The Al within WTR was stable and almost no Al was released from WTR under solution pH 4.2–8.9 (Wang et al., 2014). Mahdy et al. (2009) found that amendment with 4% WTR did not increase the extractable Al contents in soils. It has also been reported that neither reduced yields nor increased plant Al phytoavailability was observed during 2-year treatment with 1% WTR surface applied (w/w) in field (Oladeji et al., 2009). However, given the documented crop P deficiency in agricultural soils amended with 10% (w/w) Fe/Al WTR in previous work (Dayton and Basta, 2001), field trials are necessary to determine the optimal Fe/Al WTR amendment rate to ensure the growth of vegetation in buffer zones.

4. Conclusions

Amendment of agricultural soils with Fe/Al WTR, which contained a substantial quantity of amorphous Fe and Al hydroxide minerals, effectively enhanced glyphosate retention by two representative agricultural soils from China. Results presented herein indicate that the use of Fe/Al WTR as a soil amendment to enhance the retention of glyphosate by soils could be a suitable beneficial re-use of this by-product.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.jes.2015.01.030>.

REFERENCES

- Abrantes, N., Pereira, R., Gonçalves, F., 2010. Occurrence of pesticides in water, sediments, and fish tissues in a lake surrounded by agricultural lands: concerning risks to humans and ecological receptors. *Water Air Soil Pollut.* 212 (1–4), 77–88.
- Agyin-Birikorang, S., Oladeji, O.O., O'Connor, G.A., Obreza, T.A., Capece, J.C., 2009. Efficacy of drinking-water treatment residual in controlling off-site phosphorus losses: a field study in Florida. *J. Environ. Qual.* 38 (3), 1076–1085.
- Andréa, M.M., Peres, T.B., Luchini, L.C., Bazarin, S., Papini, S., Matallo, M.B., et al., 2003. Influence of repeated applications of glyphosate on its persistence and soil bioactivity. *Pesq. Agrop. Brasileira* 38 (11), 1329–1335.
- Aparicio, V.C., De Gerónimo, E., Marino, D., Primost, J., Carriquiriborde, P., Costa, J.L., 2013. Environmental fate of glyphosate and aminomethylphosphonic acid in surface waters and soil of agricultural basins. *Chemosphere* 93 (9), 1866–1873.
- Askew, S.D., Wilcut, J.W., 1999. Cost and weed management with herbicide programs in glyphosate-resistant cotton (*Gossypium hirsutum*). *Weed Technol.* 13 (2), 308–313.
- Aslam, S., Garnier, P., Rumpel, C., Parent, S.E., Benoit, P., 2013. Adsorption and desorption behavior of selected pesticides as influenced by decomposition of maize mulch. *Chemosphere* 91 (11), 1447–1455.
- Avigliano, L., Alvarez, N., Mac Loughlin, C., Rodríguez, E.M., 2014. Effects of glyphosate on egg incubation, larvae hatching and ovarian re-maturation, in the estuarine crab *Neohelice granulata*. *Environ. Toxicol. Chem.* 33 (8), 1879–1884. <http://dx.doi.org/10.1002/etc.2635>.
- Babatunde, A.O., Zhao, Y.Q., 2007. Constructive approaches toward water treatment works sludge management: an international review of beneficial reuses. *Crit. Rev. Environ. Sci. Technol.* 37 (2), 129–164.
- Barrett, K.A., McBride, M.B., 2007. Phosphate and glyphosate mobility in soil columns amended with Roundup. *Soil Sci.* 172 (1), 17–26.
- Borggaard, O.K., Gimsing, A.L., 2008. Fate of glyphosate in soil and the possibility of leaching to ground and surface waters: a review. *Pest Manag. Sci.* 64 (4), 441–456.
- Bott, S., Tesfamariam, T., Kania, A., Eman, B., Aslan, N., Römhild, V., et al., 2011. Phytotoxicity of glyphosate soil residues re-mobilised by phosphate fertilisation. *Plant Soil* 342 (1–2), 249–263.
- Cuhra, M., Traavik, T., Bøhn, T., 2013. Clone- and age-dependent toxicity of a glyphosate commercial formulation and its active ingredient in *Daphnia magna*. *Ecotoxicology* 22 (2), 251–262.
- Dayton, E.A., Basta, N.T., 2001. Characterization of drinking water treatment residuals for use as a soil substitute. *Water Environ. Res.* 73 (1), 52–57.
- De Jonge, H., De Jonge, L.W., 1999. Influence of pH and solution composition on the sorption of glyphosate and prochloraz to a sandy loam soil. *Chemosphere* 39 (5), 753–763.
- De Jonge, H., De Jonge, L.W., Jacobsen, O.H., Yamaguchi, T., Moldrup, P., 2001. Glyphosate sorption in soils of different pH and phosphorus content. *Soil Sci.* 166 (4), 230–238.
- Dill, G.M., Cajacob, C.A., Padgett, S.R., 2008. Glyphosate-resistant crops: adoption, use and future considerations. *Pest Manag. Sci.* 64 (4), 326–331.
- Elkhatib, E.A., Mahdy, A.M., ElManeahet, M.M., 2013. Effects of drinking water treatment residuals on nickel retention in soils: a macroscopic and thermodynamic study. *J. Soil. Sediment.* 13 (1), 94–105.
- EPA, 2010. Fate, transport, and transformation test guidelines. Adsorption/Desorption (Batch Equilibrium) (Available at: <http://www.epa.gov/oppts>. Date accessed: 28 February 2010).
- Giesy, J.P., Dobson, S., Solomon, K.R., 2000. Ecotoxicological risk assessment for Roundup® herbicide. In: Ware, G.W. (Ed.), *Reviews of Environmental Contamination and Toxicology*. Springer-Verlag New York Inc, pp. 35–120.
- Giles, C.H., MacEwan, T.H., Nakhwa, S.N., Smiths, D., 1960. A system of classification of solution adsorption isotherms, and its use in diagnosis of adsorption mechanisms and in measurements of specific surface areas of solids mechanisms and in measurement of specific surface areas of solids. *J. Chem. Soc.* 4, 3973–3993.
- Gimsing, A.L., Borggaard, O.K., Bang, M., 2004. Influence of soil composition on adsorption of glyphosate and phosphate by contrasting Danish surface soils. *Eur. J. Soil Sci.* 55 (1), 183–191.
- Gjettermann, B., Petersen, C.T., Hansen, S., Koch, C.B., Styczen, M., 2011. Kinetics of glyphosate desorption from mobilized soil particles. *Soil Sci. Soc. Am. J.* 75 (2), 434–443.
- Glozier, N.E., Struger, J., Cessna, A.J., Gledhill, M., Rondeau, M., Ernst, W.R., et al., 2012. Occurrence of glyphosate and acidic herbicides in select urban rivers and streams in Canada, 2007. *Environ. Sci. Pollut. Res.* 19 (3), 821–834.
- Goldsborough, L.G., Brown, D.J., 1993. Dissipation of glyphosate and aminomethylphosphonic acid in water and sediments of boreal forest ponds. *Environ. Toxic. Chem.* 12 (7), 1139–1147.
- Hovsepian, A., Bonzongo, J.C.J., 2009. Aluminum drinking water treatment residuals (Al-WTR) as sorbent for mercury: implications for soil remediation. *J. Hazard. Mater.* 164 (1), 73–80.
- Hu, Y.S., Zhao, Y.Q., Sorohan, B., 2011. Removal of glyphosate from aqueous environment by sorption using water industrial residual. *Desalination* 271 (1–3), 150–156.
- Ippolito, J.A., Scheckel, K.G., Barbarick, K.A., 2009. Selenium adsorption to aluminum-based water treatment residuals. *J. Colloid Interface Sci.* 338 (1), 48–55.
- Ippolito, J.A., Barbarick, K.A., Elliott, H.A., 2011. Drinking water treatment residuals: a review of recent uses. *J. Environ. Qual.* 40 (1), 1–12.
- Ivanoff, D.B., Reddy, K.R., Robinson, S., 1998. Chemical fractionation of organic phosphorus in selected histisols. *Soil Sci.* 163 (1), 36–45.
- Jones, D.K., Hammond, J.I., Relyea, R.A., 2011. Competitive stress can make the herbicide Roundup® more deadly to larval amphibians. *Environ. Toxicol. Chem.* 30 (2), 446–454.
- Le Bot, B., Colliaux, K., Pelle, D., Briens, C., Seux, R., Clément, M., 2002. Optimization and performance evaluation of the analysis of glyphosate and AMPA in water by HPLC with fluorescence detection. *Chromatographia* 56 (3–4), 161–164.
- Li, R.J., Wen, B., Zhang, S.Z., Pei, Z.G., Shan, X.Q., 2009. Influence of organic amendments on the sorption of pentachlorophenol on soils. *J. Environ. Sci.* 21 (4), 474–480.
- López-Piñero, A., Peña, D., Albarrán, A., Becerra, D., Sánchez-Llerena, J., 2013. Sorption, leaching and persistence of metribuzin in Mediterranean soils amended with olive mill waste of different degrees of organic matter maturity. *J. Environ. Manag.* 122, 76–84.
- Mahdy, A.M., Elkhatib, E.A., Fathi, N.O., Lin, Z.Q., 2009. Effects of co-application of biosolids and water treatment residuals on corn growth and bioavailable phosphorus and aluminum in alkaline soils in Egypt. *J. Environ. Qual.* 38 (4), 1501–1510.
- Makris, K.C., Harris, W.G., O'Connor, G.A., Obreza, T.A., Elliott, H.A., 2005. Physicochemical properties related to long-term phosphorus retention by drinking-water treatment residuals. *Environ. Sci. Technol.* 39 (11), 4280–4289.
- Makris, K.C., Sarkar, D., Datta, R., 2006. Aluminum-based drinking-water treatment residuals: a novel sorbent for perchlorate removal. *Environ. Pollut.* 140 (1), 9–12.

- Mallat, E., Barceló, D., 1998. Analysis and degradation study of glyphosate and of aminomethylphosphonic acid in natural waters by means of polymeric and ion-exchange solid-phase extraction columns followed by ion chromatography–post-column derivatization with fluorescence detection. *J. Chromatogr. A* 823 (1), 129–136.
- McConnell, J.S., Hossner, L.R., 1985. pH-Dependent sorption isotherms of glyphosate. *J. Agric. Food Chem.* 33 (6), 1075–1078.
- Morillo, E., Undabeytia, T., Maqueda, C., Ramos, A., 2000. Glyphosate adsorption on soils of different characteristics: influence of copper addition. *Chemosphere* 40 (1), 103–107.
- Morillo, E., Undabeytia, T., Maqueda, C., Ramos, A., 2002. The effect of dissolved glyphosate upon the sorption of copper by three selected soils. *Chemosphere* 47 (7), 747–752.
- Murphy, J., Riley, J.P., 1962. A modified single-solution method for the determination of phosphorus in natural water. *Anal. Chim. Acta* 27, 31–36.
- Nagar, R., Sarkar, D., Makris, K.C., Datta, R., 2010. Effect of solution chemistry on arsenic sorption by Fe- and Al-based drinking-water treatment residuals. *Chemosphere* 78 (8), 1028–1035.
- Nelson, D.W., Sommers, L.E., 1996. Total carbon, organic carbon, and organic matter. In: Page, A.L., Miller, R.H., Keeney, D.R. (Eds.), *Methods of Soil Analysis Part 3—Chemical Methods*. American Society of Agronomy Inc., Madison, pp. 961–1010.
- Oladeji, O.O., Sartain, J.B., O'Connor, G.A., 2009. Land application of aluminum water treatment residual: aluminum phytoavailability and forage yield. *Commun. Soil Sci. Plan.* 40 (9–10), 1483–1498.
- Owen, P.G., 2002. Water-treatment works' sludge management. *Water Environ. J.* 16 (4), 282–285.
- Pessagno, R.C., Torres Sánchez, R.M., Dos Santos Afonso, M., 2008. Glyphosate behavior at soil and mineral–water interfaces. *Environ. Pollut.* 153 (1), 53–59.
- Piccolo, A., Celano, G., Arienzo, M., Mirabella, A., 1994. Adsorption and desorption of glyphosate in some European soils. *J. Environ. Sci. Health B* 29 (6), 1105–1115.
- Ratcliff, A.W., Busse, M.D., Shestak, C.J., 2006. Changes in microbial community structure following herbicide (glyphosate) additions to forest soils. *Appl. Soil Ecol.* 34 (2), 114–124.
- Rogers, M.R., Stringfellow, W.T., 2009. Partitioning of chlorpyrifos to soil and plants in vegetated agricultural drainage ditches. *Chemosphere* 75 (1), 109–114.
- Sanchís, J., Kantiani, L., Llorca, M., Rubio, F., Ginebreda, A., Fraile, J., et al., 2012. Determination of glyphosate in groundwater samples using an ultrasensitive immunoassay and confirmation by on-line solid-phase extraction followed by liquid chromatography coupled to tandem mass spectrometry. *Anal. Bioanal. Chem.* 402 (7), 2335–2345.
- Sarkar, D., Makris, K.C., Vandanapu, V., Datta, P., 2007. Arsenic immobilization in soils amended with drinking-water treatment residuals. *Environ. Pollut.* 146 (2), 414–419.
- Shang, C., Zelazny, L.W., 2008. Selective dissolution techniques for mineral analysis of soils and sediments. In: Ulery, A.L., Drees, L.R. (Eds.), *Methods of Soil Analysis Part 5—Mineralogical Methods*. Soil Science Society of America Inc., Madison, pp. 33–80.
- Sheals, J., Sjöberg, S., Persson, P., 2002. Sorption of glyphosate on goethite: molecular characterization of surface complexes. *Environ. Sci. Technol.* 36 (14), 3090–3095.
- Shushkova, T., Ermakova, I., Leontievsky, A., 2010. Glyphosate bioavailability in soil. *Biodegradation* 21 (3), 403–410.
- Soso, A.B., Barcellos, L.J.G., Ranzani-Paiva, M.J., Kreutz, L.C., Quevedo, R.M., Anziliero, D., et al., 2007. Chronic exposure to sub-lethal concentration of a glyphosate-based herbicide alters hormone profiles and affects reproduction of female Jundiá (*Rhamdia quelen*). *Environ. Toxicol. Pharmacol.* 23 (3), 308–313.
- Sprankle, P., Meggitt, W.F., Penner, D., 1975. Adsorption, mobility, and microbial degradation of glyphosate in the soil. *Weed Sci.* 23 (3), 229–234.
- Thomas, G.W., 1982. Exchangeable cations. In: Page, A.L. (Ed.), *Methods of Soil Analysis Part 2—Chemical and Microbiological Properties*. Soil Science Society of America Inc., Madison, pp. 159–165.
- Van Stempvoort, D.R., Roy, J.W., Brown, S.J., Bickerton, G., 2014. Residues of the herbicide glyphosate in riparian groundwater in urban catchments. *Chemosphere* 95, 455–463.
- Vereecken, H., 2005. Mobility and leaching of glyphosate: a review. *Pest Manag. Sci.* 61 (12), 1139–1151.
- Verlicchi, P., Masotti, L., 2001. Reuse of drinking water treatment plants sludges in agriculture: problems, perspectives and limitations. In: Sangiorgi, F. (Ed.), *Technology transfer. Proceedings of the 9th International Conference on the FAO ESCORENA Network on recycling of agricultural, municipal and industrial residues in agriculture*, Gargano, Italy, 6–9 September 2000, pp. 67–73 (www.ramiran.net/doc).
- Waiman, C.V., Avena, M.J., Garrido, M., Band, B.F., Zanini, G.P., 2012. A simple and rapid spectrophotometric method to quantify the herbicide glyphosate in aqueous media. Application to sorption isotherms on soils and goethite. *Geoderma* 170, 154–158.
- Wang, C.H., Zhao, Y.Y., Pei, Y.S., 2012. Investigation on reusing water treatment residuals to remedy soil contaminated with multiple metals in Baiyin, China. *J. Hazard. Mater.* 237–238, 240–246.
- Wang, C.H., Liu, J.F., Pei, Y.S., 2013a. Effect of hydrogen sulfide on phosphorus lability in lake sediments amended with drinking water treatment residuals. *Chemosphere* 91 (9), 1344–1348.
- Wang, C.H., Bai, L.L., Pei, Y.S., 2013b. Assessing the stability of phosphorus in lake sediments amended with water treatment residuals. *J. Environ. Manag.* 122, 31–36.
- Wang, C.H., Yuan, N.N., Pei, Y.S., 2014. Effect of pH on metal lability in drinking water treatment residuals. *J. Environ. Qual.* 43 (1), 389–397.
- Yu, Y., Zhou, Q.X., 2005. Adsorption characteristics of pesticides methamidophos and glyphosate by two soils. *Chemosphere* 58 (6), 811–816.
- Yu, X.Y., Pan, L.G., Ying, G.G., Kookana, R.S., 2010. Enhanced and irreversible sorption of pesticide pyrimethanil by soil amended with biochars. *J. Environ. Sci.* 22 (4), 615–620.
- Zbytniewski, R., Buszewski, B., 2005. Characterization of natural organic matter (NOM) derived from sewage sludge compost. Part 1: chemical and spectroscopic properties. *Bioresour. Technol.* 96 (4), 471–478.
- Zhang, R.Y., Wu, F.C., Liu, C.Q., Fu, P.Q., Wen, L., Wang, L.Y., et al., 2008. Characteristics of organic phosphorus fractions in different trophic sediments of lakes from the middle and lower reaches of Yangtze River region and Southwestern Plateau, China. *Environ. Pollut.* 152 (2), 366–372.
- Zhang, X.K., He, L.Z., Sarmah, A.K., Lin, K.D., Liu, Y.K., Li, J.W., et al., 2014. Retention and release of diethyl phthalate in biochar-amended vegetable garden soils. *J. Soil. Sediment.* 14 (11), 1790–1799. <http://dx.doi.org/10.1007/s11368-014-0929-x>.
- Zhao, Y.Y., Wang, C.H., Wendling, L.A., Pei, Y.S., 2013. Feasibility of Using Drinking Water Treatment Residuals as a Novel Chlorpyrifos Adsorbent. *J. Agric. Food Chem.* 61 (31), 7446–7452.
- Zhou, Y.F., Haynes, R.J., 2011. Removal of Pb (II), Cr (III) and Cr (VI) from aqueous solutions using alum-derived water treatment sludge. *Water Air Soil Pollut.* 215 (1–4), 631–643.