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Developing ionic liquid forms of picloram with reduced negative effects on the aquatic environment

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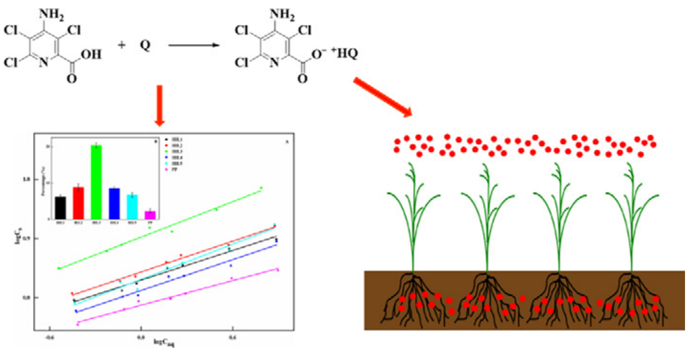
HIGHLIGHTS

- Five novel herbicidal ionic liquids (HILs) based on picloram were synthesized and characterized.
- The HILs exhibited moderate adsorption capacity and low leaching characteristic.
- The negative effects of picloram on the aquatic environment were reduced.
- A lower use dosage of picloram was achieved by application of HILs.

GRAPHICAL ABSTRACT



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ABSTRACT

As a widely used herbicide, picloram has been frequently detected in the aquatic environment due to its high leaching potential and low adsorption by soil. To reduce aquatic environmental risk of this herbicide caused by leaching and runoff, five herbicidal ionic liquids (HILs) based on picloram were prepared by pairing isopropylamine, octylamine, octadecylamine, 1-methylimidazole, 4-methylmorpholine respectively. Their physicochemical properties including water solubility, octanol-water partition coefficient, surface activity, leaching, as well as soil adsorption were compared. The results showed that these properties could be adjusted by appropriate selection of counter cations. The HILs with long alkyl chains in cations had low water solubility and leaching characteristics, good surface tension and lipophilicity, as well as high soil adsorption. Compared with currently used picloram in the forms of potassium salts, HIL3 had more excellent herbicidal activity against broadleaf weeds and may offer a lower use dosage. The HILs based on picloram can reduce its negative effects on the aquatic environment and can be used as a desirable alternative to commercial herbicidal formulations of picloram in future.

1. Introduction

Herbicides are an effective, economical and powerful management tool to destroy unwanted species of plants in farmland. However, the widespread use of herbicides has created serious environmental problems, especially water contamination (Masiá et al., 2013). Herbicides can enter aquatic environment via multiple pathways, e.g. surface

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water runoff and leaching from soils after application (Celis et al., 2005). It has been reported that many herbicides, including 2,4-D, atrazine, picloram, clopyralid and so on, have been frequently detected in surface and ground water (Dos Santos et al., 2010; Tizaoui et al., 2011; Ghoshdastidar and Tong, 2013; Chen et al., 2015). And these compounds usually have adverse effects on aquatic organisms and human health (Kniss, 2017).

As an auxin-type herbicide, picloram (4-amino-3,5,6-trichloropyridine-2-carboxylic acid) is widely used for controlling broad-leaved weeds in corn, wheat, pasture, pinus, sorghum and sugar cane (Massaroppi et al., 2003; Fairchild et al., 2009). It is a weak acid ($pKa = 2.3$) and usually marketed as potassium salt (Celis et al., 2002). The picloram acid water solubility is 560 mg L^{-1}, while its potassium salt is 400, 000 mg L^{-1} (Mayes and Dill, 1984; U.S.EPA, 1995). Because of its highly water-soluble and anionic characters, picloram displays low sorption on soil particles ($Koc = 3–53$ mL g^{-1}) (Bovey and Richardson, 1991; Oliveira et al., 2013; Steffens et al., 2015), and its major route of dissipation is leaching (U.S.EPA, 1995; Close et al., 1998). When picloram was applied on soil at an amount of 3.4 kg ha^{-1}, it could reach 50–75 cm depth by leaching (Oliveira et al., 2013). Moreover, picloram is mainly degraded by microorganisms in soil and is very stable to hydrolysis and anaerobic degradation with over 90% of the chemical not degraded after 300 days of incubation (Watson et al., 1989; U.S.EPA, 1995; Celis et al., 2002). Multiple studies have shown that picloram was frequently detected in a variety of environments and caused a contamination of ground and surface water at significant levels (Glass and Edwards, 1974; Bovey et al., 1975; Lavy et al., 1996; Muir and de Wit, 2010; Stuart et al., 2012; Maciel et al., 2013). The interim maximum acceptable concentration (IMAC) of picloram in drinking water is 0.19 mg L^{-1}, as proposed by the Health Canada (Faust and Aly, 1998). Besides, the environmental risks of picloram are also related to aquatic organisms via runoff, leaching, or discharge of contaminated ground water into surface water (U.S.EPA, 1995). One research reported that bull trout were very sensitive to this herbicide and whose maximum acceptable concentration of picloram is 0.80 mg L^{-1} for 30 days (Fairchild et al., 2009). Therefore, due to the characteristics of high water solubility and long persistence of picloram, improving its physicochemical properties and reducing its application dosage are very necessary to decrease the negative effects of this herbicide on aquatic environment.

Herbicidal ionic liquids (HILs) are a new type of ionic liquids (ILs), which usually contain targeted herbicidal anions and the counter cations (Syguda et al., 2016). This new group of organic compounds was first introduced by Pernak in 2011 (Pernak et al., 2011). Due to high biological activity as well as excellent physical and chemical properties, HILs as novel phytopharmaceuticals can be classified as the third-generations ILs (Hough et al., 2007; Shamshina et al., 2015). During the past several years, HILs have experienced a fast development in the field of agrochemistry. So far, numerous scientific reports have described HILs of currently available herbicides, such as 2,4-D, bentazone, bromoxynil, clopyralid, dicamba, fomesafen, glyphosate, metsulfuron methyl, MCPA, MCPB and MCPP (Cojocaru et al., 2013; Pernak et al., 2013; Ding et al., 2014; Kordala-Markiewicz et al., 2014; Pernak et al., 2014; Niemczak et al., 2015; Pernak et al., 2015a, 2015b; Wang et al., 2015; Zhu et al., 2015; Pernak et al., 2016a; Tang et al., 2017). The traditionally applied herbicidal formulations, such as inorganic salts (sodium, potassium or ammonium) and esters forms, have the disadvantages of high water solubility and vapor pressure (Pernak et al., 2017). As a new discovery in plant protection, HILs show unique and fascinating physicochemical properties (low volatility and water solubility, high stability, increased hydrophobicity and good surface activity) by selecting suitable counter ions (Pernak et al., 2016b). Additionally, the herbicidal activity of HILs is also enhanced along with the improvement of physicochemical, which gives us a way to reduce the consumption of the herbicide dose per hectare (Pernak et al., 2013; Ding et al., 2014; Pernak et al., 2015a, 2015b). Therefore, the HILs strategy is an appropriate choice to eliminate the negative impacts of current herbicidal formulations on the environment caused by leaching, runoff, volatilization and the use of large dosage.

The aim of this work is to prepare new HILs of picloram via acid-base reaction to optimize its physicochemical properties and confer picloram with high herbicidal activity and low mobility in the soils. The selected counter cations were isopropylamine, octylamine, octadecylamine, 1-methylimidazole, and 4-methylmorpholine. The water solubility, octanol-water partition coefficient, surface activity, soil adsorption, leaching, and herbicidal activity of the synthesized HILs were evaluated.

2. Material and methods

2.1. Materials

2.1.1. Chemicals

Picloram (96% purity) was purchased from Sichuan Lier Chemical Co., Ltd. Methanol, acetic acid, calcium chloride, sodium hydroxide, isopropylamine, octylamine, octadecylamine, 1-methylimidazole, and 4-methylmorpholine were analytical grade and purchased from Sinopharm Chemical Reagent Co., Ltd. (Beijing, China). Acetonitrile and methanol that were high-performance liquid chromatography (HPLC) grade were supplied from J. T. Baker (Phillipsburg, NJ, USA). Ultrapure water was collected in the laboratory by using a Millipore water purification system (Millipore, Billerica, MA, USA). Picloram potassium (PP) was prepared based on acid–base reaction in our laboratory.

2.1.2. Apparatus

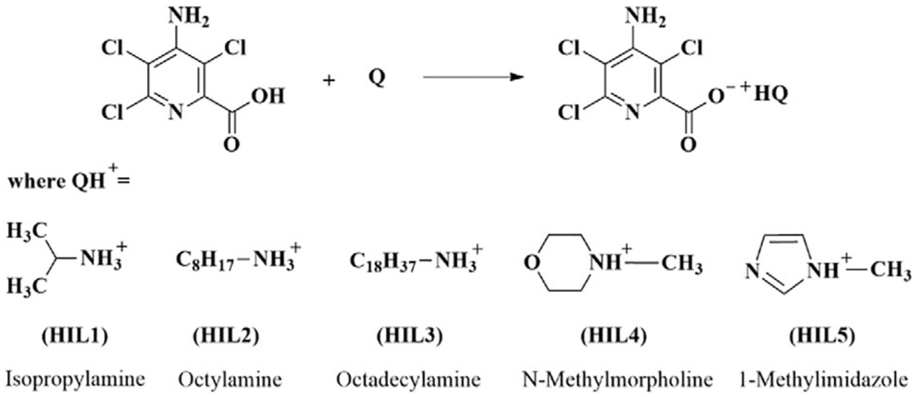
The identification of HILs: ^{1}H NMR spectra were determined on a Bruker Avance DPX 300 MHz NMR spectrometer (Bruker, Germany). CHN elemental analyses were performed at a 5E-CHN2000 elemental analyzer (Changsha Kaiyuan Instruments Co., Ltd., China). Physicochemical analyses: the water content was tested by using an AKF-1volumetric Karl-Fischer moisture titrator (Hogon Scientific Instrument Co., Ltd., China). The melting point was recorded by a SGWX-4B microscopic melting point apparatus (SPSIC, China). Surface tension measurements were carried out by a JK 99B analyzer (Powereach, China, resolution <0.05 mN m^{-1}). An HPLC system consisted of two LC-20ATvp pumps and a SPD-20Avp ultraviolet detector (Shimadzu) was used for detection of chemicals. A reversed phase kromasil ODS C18 column (250 mm × 4.6 mm, 5 μm) was used for separation at ambient temperature, and a Chromato Solution Light Chemstation for LC system was employed to acquire and process chromatographic data. The mobile phases were acetonitrile (eluent A) and water with 0.3% acetic acid (eluent B) (70/30, v/v). Injection volume was 20 μL, and the detection wavelength was 254 nm. The flow rate was constant at 1.0 mL min^{-1}, and the column was kept at normal temperature.

2.2. Preparation of HILs

The preparation method was as described in the previous work (Belieres and Angell, 2007; Brigouleix et al., 2010). In brief, a round-bottom flask, equipped with a magnetic stirrer, a thermometer, and a reflux condenser, the picloram (0.01 mol) was dissolved in 25 mL of methanol, followed by addition of 0.01 mol of amine. The mixture was stirred for 3 h at 50 °C until a clear reaction solution was obtained. Since the reaction was exothermic, the clear solution was cooled down to room temperature and stirred again for 2 h in ice bath. When the methanol was evaporated from the reaction solution at 45 °C for 0.5 h, the desirable HILs were obtained. The synthetic route of new HILs is shown in Scheme 1.

2.2.1. Propan-2-aminium 4-amino-3,5,6-trichloropicolinate, HIL1

90% yield. Elemental analysis calcd. (%) for $C_9H_{12}Cl_3N_3O_2$ ($M = 299.00$) C 35.96, H 4.02, N 13.98; found: C 35.93, H 4.02, N 13.96.



Scheme 1. Synthesis of HILs and the structure of cations.

2.2.2. Octan-1-aminium 4-amino-3,5,6-trichloropicolinate, HIL2

94% yield. Elemental analysis calcd. (%) for $C_{14}H_{22}Cl_3N_3O_2$ ($M = 369.08$) C 45.36, H 5.98, N 11.34; found: C 45.39, H 5.98, N 11.34.

2.2.3. Octadecan-1-aminium 4-amino-3,5,6-trichloropicolinate, HIL3

91% yield. Elemental analysis calcd. (%) for $C_{24}H_{42}Cl_3N_3O_2$ ($M = 509.23$) C 56.41, H 8.28, N 8.22; found: C 56.50, H 8.29, N 8.23.

2.2.4. 4-Methylmorpholin-4-ium 4-amino-3,5,6-trichloropicolinate, HIL4

92% yield. Elemental analysis calcd. (%) for $C_{11}H_{14}Cl_3N_3O_3$ ($M = 341.23$) C 38.56, H 4.08, N 12.26; found: C 38.54, H 4.06, N 12.33.

2.2.5. 1-Methyl-1H-imidazol-1-ium 4-amino-3,5,6-trichloropicolinate, HIL5

90% yield. Elemental analysis calcd. (%) for $C_{10}H_9Cl_3N_4O_2$ ($M = 321.98$) C 37.12, H 2.80, N 17.32; found: C 37.19, H 2.79, N 17.30.

2.3. Physicochemical properties

2.3.1. Water solubility

The solubilities of picloram and the synthesized HILs in water at different pH values (pH = 5, 6, 7, 8, 9) at 25 °C were performed with the shake method (The OECD Guidelines for the Testing of Chemicals, 1995a). HILs and picloram were weighed into each of three glass vessels that were filled with 10 mL of phosphate buffer solutions (PBS) with a certain pH until saturation occurred. All the glass vessels were tightly sealed and then were kept agitating on a shaker at 25 °C. One day later, the solution in one of the vessels reached equilibrium. Then its filtered supernatant was analyzed by HPLC. Similarly, the solutions in other two vessels were analyzed after initial equilibration for 48 h and 72 h respectively. All the treatments were replicated for three times in the test.

2.3.2. Octanol-water partition coefficient

The partition coefficients (n-octanol/water) of HILs and PP were determined by the shake flask method at 25 °C (The OECD Guidelines for the Testing of Chemicals, 1995b). Firstly, *n*-octanol and water were saturated by water and n-octanol, respectively. And then, 1.00 mL of HILs or PP solution in *n*-octanol and water (concentration being 0.01 mol L^{-1}) were added to 9.00 mL of water and *n*-octanol in tubes. All tubes were shaken on a shaker at 25 °C. After 24 h, the mixtures were centrifuged at 4000 rpm for 10 min and the water phase (1 mL) was collected. The concentrations of the sample in the water solution were analyzed by HPLC. All the treatments were replicated for three times in the test.

2.3.3. Surface activity

The surface tensions of PP and the synthesized HILs were determined at room temperature using the Wilhelmy plate method (Decroos et al., 2007). Before the tests started, a series of different concentrations of PP and HILs were prepared in purified water. Then the sensing platinum plate was slowly oriented perpendicular to the interface of the test solutions, and it was stopped when the equilibrium between liquid surface tension and other related forces was attained. The value of surface tension of the test compound was measured by the balanced sensor of the instrument. The values of critical micelle concentration (CMC) were determined from the intersection of two straight lines of surface tension γ versus logarithm bulk concentration (log C) of drugs. All the treatments were replicated for three times in the test.

2.3.4. Leaching experiment

The mobility of HILs and PP in the natural soils was tested via soil thin layer chromatograph (soil TLC) (U.S.EPA, 1998; Steurbaut and Pussemier, 2000). The air-dried soil was passed through a 250-μm meshed screen to obtain soil samples with homogeneous particles. Thin soil TLC plates (0.5 mm thickness) were prepared by spreading a soil/water slurry with a soil/water ratio of 4:3 onto 20 × 20 cm clean grass plates by using the help of a commercial TLC spreader. Then the plates were air-dried at room temperature for 24 h. Two horizontal lines were marked each plate at distance of 1.5 cm and 11.5 cm above the base. About 3 μg of test samples in methanol was used as spot onto the soil TLC plates at 1.5 cm from the bottom edge of the plates. The loaded plates were immersed into distilled water at a height of 0.5 cm at a suitable angle in a closed chromatographic chamber when the methanol was completely evaporated from the plates. The plates were taken out until the eluent reached the 11.5 cm line and dried at 25 °C. R_f values were the furthest distance traveled by the test compounds divided by the distance traveled by the eluent front. All the treatments were replicated for three times in the test.

2.3.5. Soil adsorption

Soil adsorption studies of HILs and PP were performed by using the batch equilibration method in 100 mL teflon centrifuge tubes (U.S.EPA, 2008). The test soil was sampled from the surface layer (0–20 cm) in Beijing China at 40°03′34″N 116°13′37″E, air-dried at 25 °C and sieved with a particle size <2 mm. In order to avoid picloram degradation caused by the microorganisms in the soil, the test soil was autoclaved at 180 °C for 4 h before used in the adsorption experiments. HILs or PP were dissolved in 0.01 M $CaCl_2$ aqueous solution. Concentrations ranged from 0.4–8 mg L^{-1} (seven concentration points) for each drug. Each sample consisted of 2 g sterilized soils mixed with 50 mL of HILs solution in the centrifuge tube. The tubes were equilibrated by shaking mechanically at 25 ± 2 °C for 24 h. After equilibration, the soil

Table 1
^{1}H NMR data of HILs.

HILs	δ (ppm)
HIL1	1.17 (s, 3H, CH_3), 1.19 (s, 3H, CH_3), 3.26 (m, 1H, CH), 6.74 (s, 2H, NH_2), 8.24 (brs, 3H, NH_3^+)
HIL2	0.86 (t, $J = 6.39$ Hz, 3H, CH_3), 1.24 (m, 10H, CH_2), 1.51 (m, 2H, CH_2), 2.73 (t, $J = 7.47$ Hz, 2H, CH_2), 6.75 (s, 2H, NH_2), 8.24 (brs, 3H, NH_3^+)
HIL3	0.85 (t, $J = 6.39$ Hz, 3H, CH_3), 1.23 (m, 30H, CH_2), 1.51 (m, 2H, CH_2), 2.73 (t, $J = 7.42$ Hz, 2H, CH_2), 6.72 (s, 2H, NH_2), 8.14 (brs, 3H, NH_3^+)
HIL4	2.58 (s, 3H, CH_3), 2.91 (m, 4H, CH_2), 3.76 (t, $J = 4.68$ Hz, 4H, CH_2), 6.96 (s, 2H, NH_2), 8–10 (brs, 1H, NH)
HIL5	3.74 (s, 3H, CH_3), 7.10 (s, 2H, NH_2), 7.15 (s, 1H, CH), 7.31 (s, 1H, CH), 8.10 (s, 1H, CH), 10–12 (brs, 1H, NH)

^{1}H NMR (300.13 MHz; $CDCl_3$; Me_4Si).

suspensions were centrifuged at 4000 rpm for 4 min and the concentrations of HILs or PP in supernatant were determined by HPLC. Preliminary experiments confirmed that there was no drug residue on the walls of the tubes and that 24 h allowed for the drugs sorption equilibrium was enough. All the treatments were replicated for three times in the test. In this study, the adsorption isotherms were described for each drug using Freundlich equation:

$$\log C_s = \log K_f + N \log C_{aq}$$

where C_s (mg kg^{-1}) represents the amount of adsorbed HILs or PP by soil, C_{aq} (mg L^{-1}) represents mass concentration of HILs or PP in the aqueous phase when reaching adsorption equilibrium, K_f (mg^{1-n} L^n kg^{-1}) and N are the empirical constants.

2.4. Herbicidal activity

The herbicidal efficacy tests were conducted in no-till farmland in the Haidian district in Beijing (40°02′25″N 116°17′42″E) in July 2016. The daytime temperature in farmland was 33 °C, night 24 °C. The photoperiod was about 16:8 for day:night. The test plants were almost all broadleaf weeds, including *Kochia scoparia* (around 70%) and *Chenopodium album* (around 25%). At the time of HILs application, the weed height was an average of 13 cm. Plot size was designed to be 2 m × 5 m areas. Aiming at avoiding mutual influence, the 1-metre-wide isolation zones were set up between different treatments. The HILs and PP were applied at dose of 100, 200, 400 g AI ha^{-1} (Chicoine, 1984). The synthetic HILs were dissolved in a mixture of methanol and water with the percent of methanol maintaining 0.1% of the total solution volume to increase solubility with little effects of organic solvent. PP was dissolved in water directly to obtain the solutions of the same concentrations. The spray volume of every drugs was 600 mL. Water was used as the control. In this experiment, the weed control efficacies at 21 days after treatment (DAT) were evaluated by growth weight reduction on a scale of zero (no weight reduction) to 100 (no weight left) (Cojocaru et al., 2013). Six seedlings of each weed were selected in each area. These seedlings were washed and air dried. The fresh weight reduction was calculated as follows: $FWR = (M_1 - M_2)/M_1 \times 100\%$, where FWR, M_1 and M_2 represent the fresh weight reduction, the fresh weight of the whole seedling from control areas, the fresh weight of the whole seeding from treated areas, respectively.

Table 3
Adsorption isotherm constants from Freundlich equations for HILs in Beijing soil.

Drugs	K_f (mg^{1-n} L^n kg^{-1})	N	R^2
PP	0.770 ± 0.008	0.623	0.976
HIL1	1.851 ± 0.036	0.750	0.977
HIL2	2.464 ± 0.071	0.780	0.987
HIL3	8.342 ± 0.179	0.898	0.975
HIL4	1.290 ± 0.020	0.780	0.970
HIL5	1.899 ± 0.017	0.890	0.960

3. Results and discussion

3.1. Preparation and characterization of HILs

Five HILs containing herbicidal anion-picloram were synthesized by the acid-base reaction in organic solvents. The structures of cations of HILs are shown in Scheme 1. The counter cations were isopropylamine, octylamine, octadecylamine, which represented amines with hydrocarbons of different lengths. 1-Methylimidazole and 4-methylmorpholine represented different heterocycles. These cations have surfactant character or additional biological activity (e.g., fungicidal or antibacterial activity) (Docherty and Kulpa, 2005; Cojocaru et al., 2013; Ławniczak et al., 2015). The structures of all the synthesized HILs were characterized by ^{1}H NMR spectroscopy and elemental analysis. The ^{1}H NMR spectra of five HILs are provided by in the supplementary information. Table 1 summarizes the ^{1}H NMR data of HIL1–5. The water content in the HILs was determined by coulometric Karl-Fischer titration and identified to be <500 mg L^{-1}. The physico-chemical properties of the obtained compounds, including water solubility, octanol-water partition coefficient, surface activity, melting point, and mobility (R_f) are summarized in Table 2.

In the ^{1}H NMR spectroscopy results, HIL1–3 presented the disappearance of the alkali-NH_2 peak and the appearance of alkali-NH_3^+ peak of the particular primary amine. For example, in HIL1, a single broad peak was located at 8.24 ppm. The protons of methyl located around the nitrogen atom of the cations in HIL4 and HIL5 shifted downfield (more over 0.1 ppm). These changes in the chemical shift of HILs fully bore out ionized nature of the compounds and were also consistent with previous report (Pernak et al., 2011; Zhu et al., 2015; Pernak et al., 2016a). All HILs were solid at room temperature with relatively high melting points (>120 °C) and may be classified as higher melting crystalline salt (Cojocaru et al., 2013). With the increase of alkyl chain length in the cations, the melting points of HILs showed a declining trend.

3.2. Physicochemical properties

3.2.1. Water solubility

The solubility of herbicides in water is a dominating factor that could influence their environmental fate. As 'designer' compounds, HILs could overcome this shortcoming of commonly applied herbicides by incorporation of appropriate cations. In this work, five HILs based on

Table 2
The physicochemical properties of HILs.

Drugs	Solubility at different pH (mg L^{-1})					Log (K_{ow})	γ_{CMC} (mN m^{-1})	R_f	Melting point (°C)
	5.0	6.0	7.0	8.0	9.0				
Picloram	2.93×10^3	3.23×10^3	1.95×10^4	3.21×10^4	3.81×10^4	-1.6773[a]	66.68[a]	0.86[a]	218
HIL1	2.68×10^4	7.80×10^4	1.12×10^5	1.41×10^5	1.40×10^5	-0.8570	65.60	0.78	176–178
HIL2	1.77×10^3	1.78×10^3	2.17×10^3	2.01×10^3	1.73×10^3	0.3644	35.95	0.46	134–136
HIL3	7.70×10^2	1.12×10^3	2.06×10^3	3.48×10^3	3.67×10^3	0.5646	28.13	0.42	122–124
HIL4	4.20×10^4	3.27×10^4	4.49×10^4	7.31×10^4	1.20×10^5	0.2217	53.44	0.78	142–144
HIL5	1.44×10^4	3.56×10^4	1.97×10^5	2.57×10^5	$>3.0 \times 10^5$	0.1364	62.13	0.82	130–134

[a] Measured in the form of potassium salt.

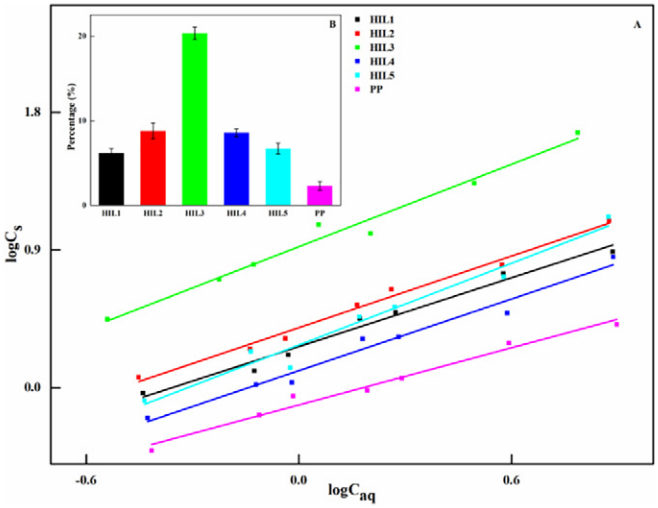


Fig. 1. A: The Freundlich adsorption isotherms of HILs and picloram potassium (PP) in Beijing soil; B: adsorption percentage after adsorption equilibrium of HILs and PP at the initial concentration of 2 mg L^{-1} in Beijing soil.

picloram demonstrated a significant difference on water solubility because of the structure variation of the cations. The solubilities of HILs and picloram in water with pH ranging from 5.0 to 9.0 at 25 °C are presented in Table 2. The solubility of picloram was increasing in the pH range of 5.0 to 9.0 while that of HILs were not apparently affected by pH. The solubilities of HIL2 (2.17×10^3 mg L^{-1}) and HIL3 (2.06×10^3 mg L^{-1}) were lower than that of picloram (1.95×10^4 mg L^{-1}) at pH 7.0. However, the HILs 1, 4 and 5 exhibited higher solubilities than picloram at same condition. The data of HIL1–3 also showed the solubilities of HILs decreased with the alkyl chain length of the amine increased. These results were consistent with the previous research (Ding et al., 2014; Pernak et al., 2017). Therefore, ionic liquid forms of picloram can reduce the amount of picloram into the aquatic environment by selection of appropriate counter ions, which could also reduce potential damage to the non-target organisms. In addition, the toxicity of picloram-based HILs to aquatic organisms might be worth considering in future studies.

3.2.2. Octanol-water partition coefficient

As an important physicochemical characteristic, the octanol-water partition coefficient is widely used to describe hydrophobic/hydrophilic properties of organic compounds. The high partition coefficient means that a compound has the large transfer free energy from water to octanol. In addition, this parameter is also used to assess the potential environmental risk of organic compounds associated with bioaccumulation or toxicity. The logarithms of the partition coefficients ($\log K_{ow}$) of HILs and PP were calculated and shown in Table 2. Based on the obtained data, it could be concluded that HILs were more liposoluble than PP, which was also verified by abovementioned solubility. Compared with different types of cations, the HILs consisted a longer alkyl chain had higher $\log K_{ow}$, which meant that it exhibited better lipophilicity. Due to the relationship between octanol-water partition coefficient and the cuticle-water partition coefficient of the plant cell membrane (Schönherr and Riederer, 1989), HILs with a good lipophilicity could make active ingredients (AIs) penetrate easily the cell membrane of the plant and enhance herbicidal activity. Although $\log K_{ow}$ values of HILs were increased in comparison to PP, a risk of bioaccumulation caused by HILs was not significant with $\log K_{ow}$ no >5 (Fisk et al., 1998).

3.2.3. Surface activity

The surface activity of herbicide spray solution has relation with herbicide efficacy by altering the surface properties of the droplet and affecting the availability of herbicide molecule. The surface activity of HILs can be evaluated by the surface tension at the CMC (γ_{CMC}). The γ_{CMC} values of PP and the synthesized HILs are summarized in Table 2. In the absence of surfactant, all the synthesized HILs could decrease the surface tension of water (72.8 mN m^{-1}). The order of decreasing surface tensions was PP, HIL1, HIL5, HIL4, HIL2, HIL3. Compared with PP, all the synthesized HILs had lower surface tensions. However, there was a significant difference in the surface tensions among the HILs. The surface tension of HIL3 (28.13 mN m^{-1}) was at least 2 times less that of HIL1 (65.60 mN m^{-1}). For the surface tensions of HIL4 and HIL5, the imidazole ring and morpholine ring had little influence on the surface activity of HILs. From the surface tensions of HIL1–3, the increase in the length of alkyl chain of the cations had a positive effect on reducing the surface tension, which also corresponds with the surfactant character of the cations. Therefore, the type of counter cation was decisive for the surface tension of HILs. The formed HILs could be considered as novel surface-active compounds decreasing surface tension. HILs with low surface tensions could permit a reduction in the contact angle between the spray droplet and a plant, enhance spray retention and promote absorption of AIs, which led to a more excellent herbicide efficacy especially for highly water-soluble herbicides (Ramsey et al., 2005; Pernak et al., 2011).

3.2.4. Leaching experiment

Soil TLC has been used successfully to study the mobility of pesticides in soils (Helling, 1971; Johnson et al., 2000). High R_f values indicate fast mobility under the conditions tested. Once herbicides are applied into the environment, their mobility capacities depend on the structures and water solubility, as well as the interactions between herbicides and organic matter in soils and sediments. The R_f values of HILs and PP are presented in Table 2. The R_f values of all the HILs were lower than that of PP (0.86) and followed the order of HIL3 (0.42) < HIL2 (0.46) < HIL1 (0.78) = HIL4 (0.78) < HIL5 (0.82), which meant that high leaching of picloram can be reduced by its ionic liquid forms. Due to the structure variation of the cations, different HILs exhibited different mobility. HIL3 contained long alkyl chain in cation had the weakest

Table 4
The fresh weight reduction of HILs against *Kochia scoparia* and *Chenopodium album* at 21 days after treatment in no-till farmland.

Drugs	Fresh weight reduction (%) with different dosage (g AI ha^{-1})					
	Kochia scoparia			*Chenopodium album*		
	100	200	400	100	200	400
PP[*]	10.0 ± 1.9 ab[**]	31.2 ± 4.3 c	56.2 ± 1.7 c	78.1 ± 1.1 bc	84.7 ± 3.0 c	92.9 ± 3.5 cd
HIL1	9.4 ± 1.0 ab	23.9 ± 1.6 b	55.4 ± 4.8 c	77.5 ± 1.7 bc	81.2 ± 2.0 bc	91.6 ± 1.3 c
HIL2	17.8 ± 1.9 c	38.8 ± 1.2 d	60.7 ± 1.5 cd	76.1 ± 2.2 b	82.1 ± 2.1 bc	96.5 ± 0.9 d
HIL3	21.5 ± 1.7 c	44.9 ± 1.2 e	66.6 ± 1.2 d	81.5 ± 2.5 c	91.1 ± 1.7 d	95.7 ± 2.0 cd
HIL4	7.2 ± 2.9 a	18.1 ± 1.3 a	37.2 ± 3.5 a	68.7 ± 2.4 a	71.7 ± 2.0 a	81.0 ± 2.5 a
HIL5	12.5 ± 4.2 b	21.0 ± 1.3 ab	45.2 ± 5.9 b	75.0 ± 3.5 b	77.0 ± 4.6 b	85.7 ± 2.4 b

[*] Picloram potassium.
[**] Fresh weight reduction values within each column followed by different letters are significantly different at $P < 0.05$, $n = 3$.

mobility. The weak leaching of HIL3 was attribute to its low water solubility. The highly lipophilic HILs bearing long alkyl substituents may be easy to interact with organic matter in soils and sediments, and thus being rather immobile (Jungnickel et al., 2011). As the R_f values decrease, HILs was not easy to reach the water table and was conducive for reducing potential risks to contamination of groundwater.

3.2.5. Soil adsorption

It was reported that the adsorption capacities were strongly affected by the cation size and the hydrophobic nature of ILs (Hassan et al., 2014). For this reason, HILs may be more likely to be adsorbed by soil than PP. The experimental sorption data of HILs and PP were fit by a Freundlich equation in the logarithmic form, and the values for the empirical constant K_f and N are presented in Table 3. The correlation coefficients (R^2) derived from the Freundlich equations are all above 0.960, indicating that the data were well represented by this model (Fig. 1A). The N values of HILs and PP were <1, which implied that as the initial concentrations of HILs and PP increased, the percentage adsorbed by the soil decreased (Dousset et al., 1994). The Freundlich constant K_f represented the degree or strength of adsorption and therefore was taken as an index of adsorption (Farmer and Aochi, 1974). The K_f of HIL3 was the largest, followed by HIL2, HIL1, HIL5, HIL4 and PP, respectively. It can be concluded that the HILs paired with ring compounds (morpholine ring and imidazole ring) or short-chain compounds had little impacts on the K_f. The difference of the K_f among HIL1–3 showed the adsorption capacity was strongly associated with the length of alkyl chain. Fig. 1B shows that adsorption percentage of all HILs was higher than that of PP at the initial drug concentration of 2 mg L^{-1}, which was coincident with the K_f values. The result of soil adsorption study was correlated with the leaching experiments previously and similar to previous study (Stepnowski et al., 2007). HILs with high K_f showed desirable absorption property of soils and could contribute to reducing the threats caused by picloram to surface and ground water. The increasing adsorption of picloram may be also in favor of degradation of picloram by microorganisms in soil.

3.3. Herbicidal activity

All the synthesized HILs were tested the herbicidal activity in no-till farmland. Table 4 illustrates that the herbicidal activity of HILs 1, 2, 4 and 5 had no significant difference with PP on the control efficacies of broadleaf weeds (*Kochia scoparia* and *Chenopodium album*). However, HIL3 showed an improved biological activity on the same broadleaf weeds than PP at dose of 100, 200, 400 g AI ha^{-1}, respectively. The fresh weight reduction of HIL3 on *Kochia scoparia* was 66.6% while that of PP was 56.2% at 21 days after treatment at dose of 400 g AI ha^{-1}. This result could also be explained by the low water solubility, good lipophilicity and surface activity of HIL3. And this was in a good accordance with previous studies (Ding et al., 2014; Kordala-Markiewicz et al., 2014; Zhu et al., 2015; Pernak et al., 2016b). In addition, the biological activity of all the HILs on *Chenopodium album* was better than that on *Kochia scoparia* at the same treatment. Therefore, the efficacy of HILs in field trials depended on species of weeds. The good herbicidal activities displayed by HIL3 may reduce the consumption of the starting herbicides in actual application.

4. Conclusions

In this work, five new picloram-based HILs with different types of cations were prepared via acid-base reaction and characterized by ^{1}H NMR spectra and elemental analyzer. The water solubility, octanol-water partition, surface activity, leaching, soil adsorption and herbicidal efficacy under field condition of HILs were analyzed. The physicochemical properties of HILs could be adjusted by selection of different cations. The HILs with long alkyl chains in cations had low water solubility and leaching characteristics, good surface tension and lipophilicity, as well as high soil adsorption. Compared with currently used picloram in the forms of potassium salts, HIL3 had more excellent herbicidal activity against broadleaf weeds and may offer a lower use dosage. With the improvement and optimization of these properties, the HILs based on picloram could reduce aquatic environmental risk of this herbicide caused by leaching, runoff and the use of large dosage. The HILs with long alkyl substituents in cations are promising herbicidal agents and may be an alternative to commercial herbicidal formulations of picloram in the future.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2017.10.288.

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