



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



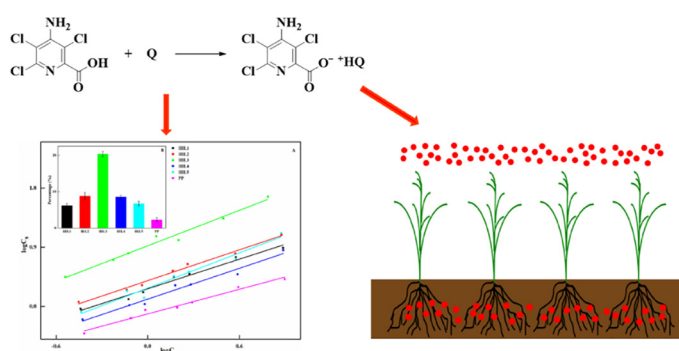
Gang Tang, Baitao Wang, Guanglong Ding, Wenbing Zhang, You Liang, Chen Fan, Hongqiang Dong, Jiale Yang, Dandan Kong, Yongsong Cao\*

College of Plant Protection, China Agricultural University, Beijing, China

### 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.

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\* Corresponding author at: NO.2 Yuanmingyuan West Road, China Agricultural University, Beijing 100193, China.

E-mail address: [caoy@cau.edu.cn](mailto:caoy@cau.edu.cn) (Y. Cao).

### 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

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 ( $pK_a = 2.3$ ) and usually marketed as potassium salt (Celis et al., 2002). The picloram acid water solubility is  $560 \text{ mg L}^{-1}$ , while its potassium salt is  $400,000 \text{ mg L}^{-1}$  (Mayes and Dill, 1984; U.S.EPA, 1995). Because of its highly water-soluble and anionic characters, picloram displays low sorption on soil particles ( $K_{oc} = 3\text{--}53 \text{ mL g}^{-1}$ ) (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  $3.4 \text{ kg ha}^{-1}$ , 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  $0.19 \text{ mg L}^{-1}$ , 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  $0.80 \text{ mg L}^{-1}$  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-generation 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 (Cojocar 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:  $^1\text{H}$  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-1 volumetric 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  $<0.05 \text{ mN m}^{-1}$ ). 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 ( $250 \text{ mm} \times 4.6 \text{ mm}$ ,  $5 \mu\text{m}$ ) 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  $20 \mu\text{L}$ , and the detection wavelength was 254 nm. The flow rate was constant at  $1.0 \text{ mL min}^{-1}$ , 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  $50 \text{ }^\circ\text{C}$  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  $45 \text{ }^\circ\text{C}$  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  $\text{C}_9\text{H}_{12}\text{Cl}_3\text{N}_3\text{O}_2$  ( $M = 299.00$ ) C 35.96, H 4.02, N 13.98; found: C 35.93, H 4.02, N 13.96.

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