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Persistence of selected ammonium- and phosphonium-based ionic liquids in urban park soil microcosms

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ABSTRACT

Knowledge about biodegradability of ionic liquids (ILs) in terrestrial systems is limited. Here, using urban park soil microcosms spiked with either ammonium- or phosphonium-based ILs [didecyldimethylammonium 3-amino-1,2,4-triazolate, benzalkonium 3-amino-1,2,4-triazolate, trihexyl(tetradecyl)phosphonium chloride, or trihexyl(tetradecyl)phosphonium 1,2,4-triazolate], we studied their (i) 300-day primary biodegradation, and (ii) influence on CO_2 evolution from the microcosms. The primary biodegradation ranged from 21 to 33% of total compound in the dissolved phase. The evolution of CO_2 from spiked microcosms was either lower or within the range of background soil respiration, indicating no or small mineralization of the parent compounds and/or their metabolites, and their negligible or small toxicity to soil microorganisms. Our results suggest the potential for persistence of the four studied ILs in urban park soils.

Introduction

Ionic liquids (ILs) are a group of chemicals composed of an organic cation and an organic or inorganic anion. Due to a large number of cation–anion combinations, the number of ILs which may be obtained is tremendous (up to 10^{18}) (Rogers and Seddon, 2003). Various ILs are currently applied in catalysis and biocatalysis, and in organic synthesis (e.g., multi-ton scale use of imidazolium-based IL in the BASIL™ process developed by BASF) (Plechkova and Seddon, 2008; Quijano et al., 2010). Although there are no reports providing information about the presence of ILs in water or soil ecosystems yet, the increasing use of ILs in the industry is expected to lead to environmental pollution. Consequently, there has been an increasing number of studies dealing with ILs behaviour and impact on the environment (Ranke et al., 2007; Pham et al., 2010; Petkovic et al., 2011; Cvjetko Bubalo et al., 2014).

Low volatility of ILs excludes emission into air as an exposure route, but there can be direct release routes to freshwater or soil. It is generally thought that relatively high thermal and chemical stability of ILs contributes to their low biodegradability (Quijano et al., 2011; Neumann et al., 2012), primarily on in aquatic environments (Coleman and Gathergood, 2010; Ford et al., 2010; Stolte et al., 2011). This is true for ammonium-, imidazolium-, phosphonium- and pyridinium-based ILs. In soils, Modelli et al. (2008), demonstrated that at the end of a 180-day respirometric experiment, none of the four imidazolium-based ILs was mineralized completely, and the amount of evolved CO_2 depended on both the type of cation and the type of anion. Primary biodegradation, defined as an “alteration in the chemical structure of a substance, brought about by biological action, resulting in the loss of a specific property of that substance” (OECD, 301, 1992) of imidazolium-, morpholinium-, piperidinium-, pyridinium- and pyrrolidinium-based ILs, has been studied (Stolte et al., 2008; Neumann et al., 2014) and formation of biotransformation products of some

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imidazolium- and pyridinium-based ILs documented (Stolte et al., 2008; Pham et al., 2009; Docherty et al., 2010). Sorption of ILs onto the soil matrix can occur, depending on soil parameters (such as organic carbon content or cation exchange capacity), which can lead to a decrease of their bioavailability and biodegradability and contribute to the potential persistence (Stepnowski, 2005; Studzińska et al., 2008; Mrozik et al., 2012). Most published studies focused on toxicity of ILs to single, isolated microbial strains (Pham et al., 2010; Cvjetko Bubalo et al., 2014), but little is known about the influence of ILs on the activity of soil microbiota. Recently, in a 28-day respirometric assay Peric et al. (2014) showed that various protic and aprotic ILs inhibited soil respiration in the concentration range from 100 mg kg^{-1} to 10,000 mg kg^{-1} depending on the ILs' structure. Despite these advances, knowledge about the long-term fate of ILs in terrestrial environments, is still limited.

The aim of our study was to investigate primary, 300-day biodegradation of ammonium- and phosphonium-based ILs in urban park soil microcosms, simulating an accidental spill, and their influence on CO_2 evolution from the microcosms over the course of biodegradation. The four ILs studied were: (i) didecyldimethylammonium 3-amino-1,2,4-triazolate ([DDA][3AT]), (ii) benzalkonium 3-amino-1,2,4-triazolate ([BDA][3AT]), (iii) trihexyl(tetradecyl)phosphonium chloride ($[P_{66614}][Cl]$), and (iv) trihexyl(tetradecyl)phosphonium 1,2,4-triazolate ($[P_{66614}][Tr]$). Apart from $[P_{66614}][Cl]$, the studied ILs have antifungal properties. The triazole-based ILs were previously described as novel antimicrobial and anti-fungal plant protection agents with a broad spectrum of activity (Walkiewicz et al., 2010), and are thus expected to be toxic to the microorganisms present in the soil. An urban park soil of known biodegrading potential toward petroleum hydrocarbons (Sydow et al., unpublished results) was employed. The primary biodegradation (300-day) was studied by measuring ILs' residues in the soil, while CO_2 evolution from spiked microcosms was measured using a respirometric test.

Materials and methods

Synthesis of ionic liquids

The ammonium-based ILs were synthesized with the use of quaternary ammonium bromides, which were obtained in reaction of equimolar amount of amine (decyldimethylamine or benzyldimethylamine) with appropriate bromoalkane (1-bromodecane or 1-bromododecane, respectively). The reaction was carried out using anhydrous acetonitrile as solvent at 70 °C for 24 h. After cooling the reaction mixture to room temperature, quaternary ammonium bromides were precipitated by adding cold ethyl acetate. The bromides were filtered and dried under vacuum at 50 °C. Product yield was over 95%. Next, 3-amino-1,2,4-triazolate ILs were prepared by *in situ* deprotonation of corresponding azole with sodium or potassium hydroxide in methanol and mixed with an equimolar amount of appropriate quaternary ammonium bromides, according to the method described in Walkiewicz et al. (2010). The phosphonium-based ILs were prepared according to method described by Cieniecka-Rosłonkiewicz et al. (2005). Briefly, trihexyl(tetradecyl)phosphonium chloride was prepared in reaction of trihexylphosphine and 1-bromotetradecane. The 1,2,4-triazolate was obtained by *in situ* deprotonation of corresponding azole with sodium hydroxide in methanol, followed by reaction with chloride precursor. Water content of the synthesized ILs was determined by Karl Fisher method for all prepared compounds, and was less than 0.1%. The list of the studied ILs is given in Table 1.

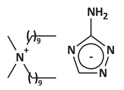
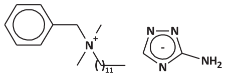
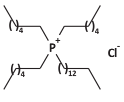
Soil

The soil used in the experiments was collected from a city park in Poznań, Poland (N 52.4011445, E 16.9222993) and according to Unified Soil Classification System, was characterized as fine grained silt loam type OL belonging to organic silts and organic silty clays of low plasticity. The composition of experimental soil was as follows: clay 4 ± 1 [%]; silt 83 ± 3 [%]; sand 13 ± 2 [%]. Detailed characteristics of the soil: organic carbon 5.44 ± 0.31 [g kg^{-1}]; nitrogen 0.57 ± 0.07 [g kg^{-1}]; phosphorous 0.080 ± 0.005 [g kg^{-1}]; pH 6.95 ± 0.7; bulk density 1.41 ± 0.06 [Mg m^{-3}]; porosity 0.455 ± 0.03 [m^3 m^{-3}]; moisture 18 ± 1 [%]; cation exchange capacity 22.1 ± 0.8 [$cmol_c$ kg^{-1}]. A sign ± represents standard deviation (n = 3).

Primary biodegradation

Each primary biodegradation experiment was set up with four replicates. Three replicates were used to analyze ions residues with the use of HPLC–MS, while one replicate was used for moisture monitoring over the course of the experiment. The samples were prepared as follows: 10 g of non-sterilized soil was added into bottles and then spiked with a methanol solution of each IL to reach an approximate concentration of 4000 mg kg^{-1} of IL per sample. The concentration in this range is typically used in hydrocarbon biodegradation tests (Lisiecki et al., 2014). Next, methanol was

Table 1
Ionic liquids used during the study.

Type	Name	Acronym	Structure
Ammonium-based	Didecyldimethylammonium 3-amino-1,2,4-triazolate	[DDA][3AT]	
	Benzalkonium 3-amino-1,2,4-triazolate	[BDA][3AT]	
Phosphonium-based	Trihexyl(tetradecyl)phosphonium chloride	$[P_{66614}][Cl]$	
	Trihexyl(tetradecyl)phosphonium 1,2,4-triazolate	$[P_{66614}][Tr]$