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Mobility and biodegradability of an imidazolium based ionic liquid in soil and soil amended with waste sewage sludge†

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Sorption on solids and biodegradation are main phenomena that can mitigate the pollution of soil and water by ionic liquids (ILs). ILs sorbed on soil particles become immobilized (temporarily or permanently) which prevents them from spreading into deeper layers of soil or groundwater but which also makes them less bioavailable. In this study we attempt to examine if amendment of soil with waste sludge has a potential to mitigate the transport and enhance biodegradation of ILs using 1-methyl-3-octylimidazolium chloride ([OMIM][Cl]) as an example. We present the results of adsorption test (batch and column) and ultimate biodegradation of [OMIM][Cl] using microbial communities derived from soil. Finally, we combine all of these processes together to examine the fate of [OMIM][Cl] in a continuous column flow-through system in soil amended with waste sewage sludge. Addition of sludge serves two purposes: firstly increasing soil organic matter (formerly proved to facilitate retardation), and secondly augmenting soil with versatile microbial communities previously shown to successfully degrade ILs.

Environmental impact

Ionic liquids, recently described as contaminants on the horizon, are finding increasing application in industrial processes. Investigating their mobility and finding suitable ways to deal with possible pollution become an important issue. Phenomena that can prevent the pollution of soil and water by ILs are sorption on solids and biodegradation. The amendment of soils with sewage sludge may prevent spreading of these chemicals into groundwater and facilitate biodegradation. Herby we test the transport and the biodegradability of the an exemplar ionic liquid – methyl-octylimidazolium chloride [OMIM][Cl]. We have found that transport of ILs in low organic matter soils will be relatively fast and only slightly hindered in soils amended with organic matter. Additionally we detected transformation products in both columns containing soil and soil with sewage sludge indicating that biodegradation occurred in the dynamic flow-though system.

Introduction

Ionic liquids (ILs) are liquid salts formed by cations and anions, in which one or both are organic.[1] This class of substances is gaining increasing attention due to the broad range of potential applications and successful implementation of ILs-based technologies.[2,3] When a compound is utilized commercially a question of waste treatment and waste disposal arises. Imidazolium cation coupled with simple halide anion results in readily water soluble, moderately to poorly biodegradable ILs.[4–7] Such compounds might break through wastewater treatment plants (WWTPs) and reach natural waters and soils where they can become persistent pollutants. Therefore, investigating the mobility and finding suitable ways to deal with possible pollution become a pressing issue.

Phenomena that can mitigate the pollution of soil and water by ILs are sorption on solids and biodegradation, since at least the common 1-alkyl-3-methylimidazolium based ILs, are relatively hydrolytically and photochemically stable.[8] ILs sorbed on soil particles become immobilized (temporarily or permanently) which prevents them from spreading into deeper layers of soil or groundwater but which also makes them less bioavailable.

Sorption and transport in soils

Sorption in laboratory conditions is measured either in batch or in column test. In batch test (stationary system) the equilibrium can be achieved relatively fast since no macroscopic mass transfer hindrance is expected to occur thanks to efficient mixing. Column tests involve packing solid into a column and

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either spiking it with the target compound and flushing with artificial rainwater or continuously pumping solution of the compound through the column. Breakthrough curves (BTC) can be created and a partition coefficient (K_D) may be obtained.[9,10] Even though the goal of both tests is similar the results, in terms of numerical value of partition coefficients, can be different.[9,10] This is due to several aspects: (1) in a column the porous structure, imitating soil profiles, is maintained reassembling soil core samples or field conditions; (2) unlike in batch test in packed columns flow is rather advective and/or dispersive and mass transfer from one phase to another is somehow hindered and the contact time limited by flow; (3) solid/liquid ratios in column test are higher (closer to field condition) and both saturated and unsaturated conditions can be created.[10] Batch tests are often preferred due to their simplicity and much shorter duration especially for strongly sorbing solids, nevertheless results of batch test (*e.g.* K_D values) should be treated as a 'worst case' estimation.[9] If a prognosis of mobility or the possibility of leaching in soils is to be assessed – column test should be employed.

The extent of adsorption of ILs in soils is an interplay of properties of soil and properties of the IL molecule.[11] For soils it is affected most readily by organic matter content though clay content (especially presence of swelling clays) is also important.[12–15] For IL cations the length of alkyl substituent plays an important role.[11,16] In batch sorption tests, double layer sorption was observed resulting from surfactant-like properties of, especially long chain, ILs.[17,18] The studies of transport of IL cations in soil columns showed that short chained ILs were very mobile in soils, especially those low in organic matter and the presence of terminal hydroxyl groups resulted in even higher mobility.[16,19] IL cations with longer alkyl substituents were interacting with soil to slightly higher extent but were also easily leachable.[16,19] Therefore, upon entering terrestrial environment IL cations will most probably quickly migrate to deeper layers of soil or possibly groundwater and retardation will be negligible.[16] Waste sewage sludge, due to its high organic matter content, may serve as a passive sink for ILs (or other organic pollutants) decreasing their mobility and preventing for example ground water contamination. Additionally, as sludge contains a versatile microbial community, it might also increase the degradative capacity of soil indigenous microorganisms.

Biodegradability in soils

In most biodegradation tests activated sewage sludge is used as a source of inoculum due to the enormous microbial versatility or in order to obtain some kind of approximation of degradation during wastewater treatment. The 1-methyl-3-octyl imidazolium chloride ([OMIM][Cl]) undergoes full primary degradation in standard laboratory tests when microbial community derived from WWTP is used indicating that the structure is to some extant susceptible to degradation.[4,5] We have shown that some factors *e.g.* presence of alternative nutrient sources might prevent degradation and others like microbial adaptation might increase the degradation rate.[20] If ILs will emerge in the soil environment their degradation might

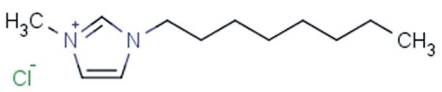

Fig. 1 Chemical structure of 1-methyl-3-octylimidazolium chloride ([OMIM][Cl]).

be different due to the differences in composition of microbial community and specificity of soli environment. Examining biodegradation in soils is of high environmental relevance as soils are one of ultimate sinks of pollutants, nevertheless the research directed at biodegradability of ILs in soils are far more scarce that reports on biodegradability in aquatic environment.

Biodegradation of ILs by soil microbial communities was examined by Modelli *et al.* and degradation of 1-butyl-3-methylimidazolium cations ranging from 20 to 60% depending on anion was reported during a three month period.[21]

In this study we attempt to investigate the influence of amendment of soils with waste sludge on mobility and biodegradability of an exemplary IL – [OMIM][Cl] (structure is given in Fig. 1).

We have shown before that even though [OMIM][Cl] is to some extent biodegradable, adsorption on sewage sludge flocs may be a far more important mechanism of removal in wastewater treatment process.[4] Here, we present the results of adsorption test (batch and column) and ultimate biodegradation using microbial communities derived from soil and sludge. Finally, we combine all of these processes together to examine the fate of [OMIM][Cl] in a continuous column flow-through system in soil amended with sewage sludge. Addition of sewage serves two purposes: firstly increasing soil organic matter (formerly proved to facilitate retardation), and secondly augmenting soil with versatile microbial communities previously proved to successfully degrade this IL cation. The question posed is whether in soil amended with waste sludge the retardation and biodegradation will be higher than in unamended soil. Test conditions were chosen in such a way as to resemble natural, field conditions such as: continuous flow resulting in limited mass transfer of [OMIM][Cl] between the aqueous phase, soil and microbial cells.

Results and discussion

Sorption batch tests

The results of the sorption batch tests for LUFA soil, sand and sewage sludge over range of concentrations are shown in Fig. 2. The sorption isotherm displays the well-known two-plateau shape. This kind of isotherm is characteristic for surface active agents and was also reported for ILs.[12,17,18] The isotherms were fitted using Langmuir and Freundlich adsorption models according to eqn (1) and (2) respectively:

$$C_s = K_D C_{aq} \quad (1)$$

$$C_s = K_f C_{aq}^{1/n} \quad (2)$$

where C_s is a concentration per unit mass of sorbent, K_D is a Langmuir solid/liquid distribution coefficient, K_f is a

Freundlich solid/liquid distribution coefficient, $1/n$ is a Freundlich exponent and C_{aq} is an aqueous concentration per unit volume at equilibrium. The results of fitting are given in Table 1. Both models gave relatively good fit.

Two Langmuir distribution coefficients (K_D) and two sets of Freundlich parameters were determined for each sorbent. The partition coefficients for soils and sand have comparable values whereas for sludge they are two to three orders of magnitude higher indicating high affinity of [OMIM][Cl] to that sorbent. In Langmuir model K_{D1} corresponds to the partitioning of [OMIM][Cl] between solid and solution, whereas the K_{D2} describes the sorption of the second layer of [OMIM][Cl] onto solid modified by the adsorption of the previous layer. K_{D1}s are larger than K_{D2}s which is due to K_{D1} summing both coulombic and dispersive interactions, while K_{D2} only accounts for the dispersive interaction between already sorbed IL molecules and IL molecules forming the second layer.

The initial concentration at which the second increase on the sorption isotherm occurs, described by the K_{D2}, must exceed 150 mM for sand, 200 mM for LUFA soil and 250 mM for sludge. The presence of such high concentration of [OMIM][Cl] in the environment is very unlikely and can be envisaged only as a result of an accidental spill of a pure compound or concentrated solution. Additionally, it would be encountered only locally and probably would be dissipated quickly due to the excellent miscibility with water. Therefore, only the lower range of concentrations, characterized by K_{D1} will be considered further. Knowing that $K_D = C_s/C_{aq}$ dissolved fraction (f_w) can be calculated according to the formula:

$$f_w = \frac{C_w V_w}{C_w V_w + C_s M_s} = \frac{V_w}{V_w + K_D M_s} \quad (3)$$

Dissolved fraction is therefore equal to 0.79 in LUFA soil/water, 0.80 in sand/water and 0.08 for sludge/water system, which indicates rather high mobility in the soil environment. As can be clearly seen the sorption of the IL on the sewage is one to two orders of magnitude higher than on both LUFA soil and sand.

Table 1 Fitting parameters of Langmuir and Freundlich model

	Langmuir model				Freundlich model		
Sorbent	K_{D1}	R^2	K_{D2}	R^2	K_f	n	R^2
Sand	2.47	0.994	1.81	0.884	1.28	1.31	0.980
LUFA	2.65	0.996	1.63	0.951	1.25	1.30	0.985
Sewage	123	0.991	138	0.925	62.0	1.12	0.933

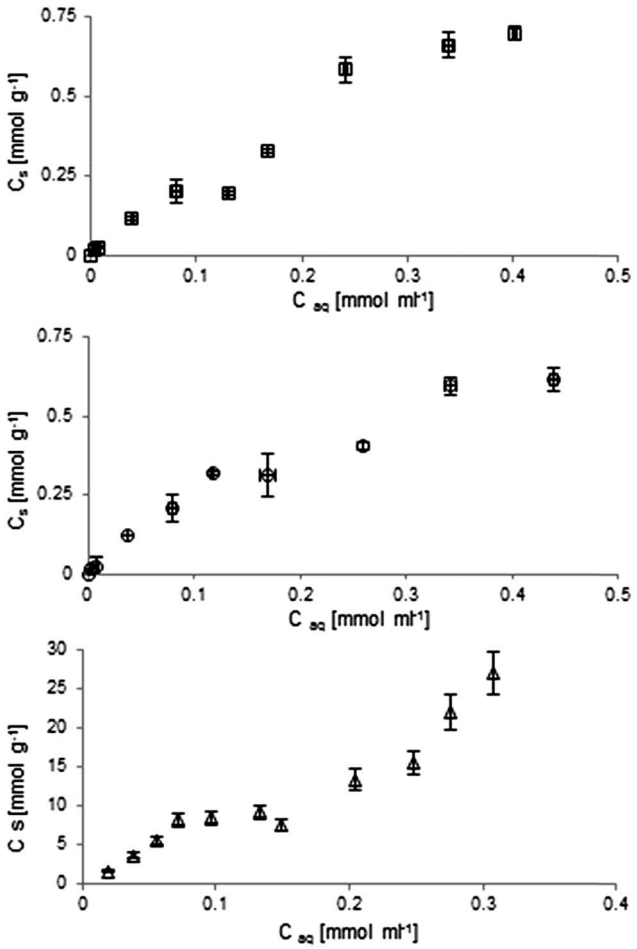

Fig. 2 Sorption isotherm of [OMIM][Cl] solution on sand (squares) LUFA soil (circles) and sewage (triangles) obtained in batch experiments.

Column flushing

Since organic matter has a potential to increase sorptive capacity of soil especially for more hydrophobic ILs and we observed high affinity of [OMIM][Cl] to sludge within this and previous studies the sludge biomass was used to amend soils.[4,20,22] One set of columns was packed with sand or LUFA soil to simulate natural, porous profile of soil. Another set of columns was packed with the same type of solid and additionally amended with dewatered sewage sludge (10% on the wet mass basis). The purpose of this is to examine the effect of adding waste sludge to soil in order to: first enrich soil in organic matter, and thus retard the movement of the IL, and second diversify microbial community. The diversification of the microbial community through the addition of the sewage, aims to provide organisms that might be able to degrade IL. The columns were first equilibrated with artificial rain water. A solution of [OMIM][Cl] (0.25 mM) was continuously pumped through all columns and leachate was collected and analysed for [OMIM][Cl]. In this way breakthrough curves (BTC) (Fig. 3 and 4) were obtained showing how fast IL can move through porous bed of soil. The amount of flushing solution pumped through column was expressed as multiples of the pore volume (PV).

The breakthrough occurs slightly faster in columns filled with LUFA soil or sand only, as no lag is visible and the concentration at the outlet of the column equals inlet concentration after approximately 10.5–11 PV. For columns amended with sewage sludge lag of 1–2 PV occurs before ILs can be

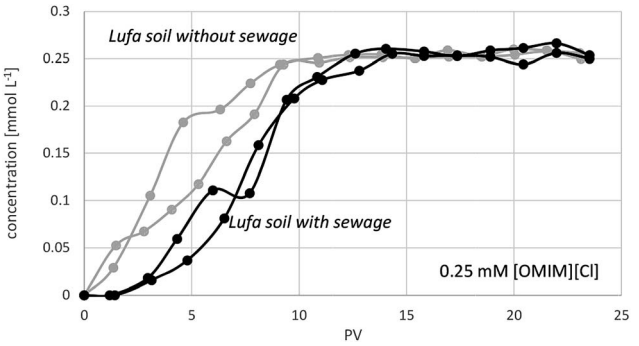

Fig. 3 Breakthrough curves of [OMIM][Cl] for two columns packed with a LUFA soil (grey) and two columns packed with a mixture of LUFA soil and sewage sludge (black).

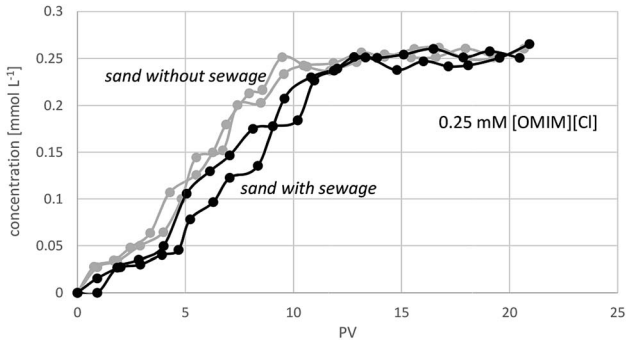

Fig. 4 Breakthrough curves of [OMIM][Cl] for two columns packed with sand (grey) and two columns packed with a mixture of sand and sewage sludge (black).

detected at the outlet of the column and maximum concentration is reached after 12.5 PV. A similar breakthrough pattern occurs in columns filled with sand or sand and sewage (Fig. 4).

Based on the total mass balance in the column the soil/solution partition coefficient (K_D) was calculated as the ratio between amount sorbed per unit mass of sorbent in the column and amount dissolved per unit volume of water taking into account the linear portion of the BTC until the sorbent was saturated. The results are given in Table 2. Both partition coefficient values for unamended solids are lower than those measured in batch tests (K_{D1} or even K_{D2} values). This suggests that even though the column system reached the dynamic equilibrium (at the point where the breakthrough occurs) it is not necessarily fully equilibrated with the sorbent. Such differences between solid/liquid partition coefficients measured in column and batch tests were previously reported.[23–25] Column tests represent a dynamic system in which the various ions may sorb/desorb in a reaction zone within the column. This may result in incomplete sorption in the column.

In general the most important factors causing differences between static and dynamic system result from the inherent properties of the test system and include: differences in solid to liquid ratio (usually much higher in column tests, here 7–8 times higher), reduction in available particle surface area, non-ideal mixing due to tighter packing, the presence of immobile water regions or preferential flow areas in dynamic systems.[23–25] Both tests for partition coefficient determination supply useful information having, nevertheless different significance. The batch K_D should be understood as equilibrium, maximum saturation parameter whereas the column K_D tends to be lower probably due to the fact that maximum saturation can rarely be achieved. The distribution coefficient obtained in batch testing is seemingly influenced by fewer variables, as a result it should be more robust and less likely to be influenced by *e.g.* lab to lab variations. There are, however, proofs showing that it is the column derived K_D that shows less variability regardless of geometry of columns, grain size and leaching time.[10] Therefore the batch K_D can be useful if a comparison between different sorbents or sorbates needs to be made, mainly because of less demanding experimental setup. On the other hand column derived coefficient is most probably a closer approximation of environmental partitioning.

Amending soil or sand with waste sludge approximately doubles the distribution coefficient, indicating that indeed the capacity for sorption of [OMIM][Cl] can be increased in this way. Nevertheless the differences between K_D values for unamended and amendet soil and sand were not statistically significant (Tables 2 and S1†).

A similar amount of artificial rainwater is required to flush IL cation out of unamended columns and columns amended with sewage (only columns with LUFA soil are shown in Fig. 5). [OMIM][Cl] is retained in all columns to a small extent. Based on mass balance about 15% and 20% of compound remains retained in the columns packed with LUFA soil and amended LUFA soil respectively indicating that this IL cation will be rather mobile.

Transformation products

The leachate from the columns was in addition analyzed by mass spectrometer (Fig. S1–S3†), to detect possible transformation products. It was found that in all columns the level of the hydroxylated parent compound increased significantly

Table 2 Solid/liquid partition coefficients for sand, LUFA soil and mixture of sand with sewage sludge and LUFA soil with sewage sludge (amount of sewage sludge in both cases 10% on wet mass basis)

Sorbent	Sand	Sand + sludge	LUFA soil	LUFA soil + sludge
$K_D \pm 1\sigma$ [mL g^{-1}]	1.66 ± 0.16	2.16 ± 0.24	1.78 ± 0.03	2.77 ± 0.28
p-value[a]	0.135		0.083	

[a] For comparison of two K_D values (with and without sludge addition) at $\alpha = 0.05$.

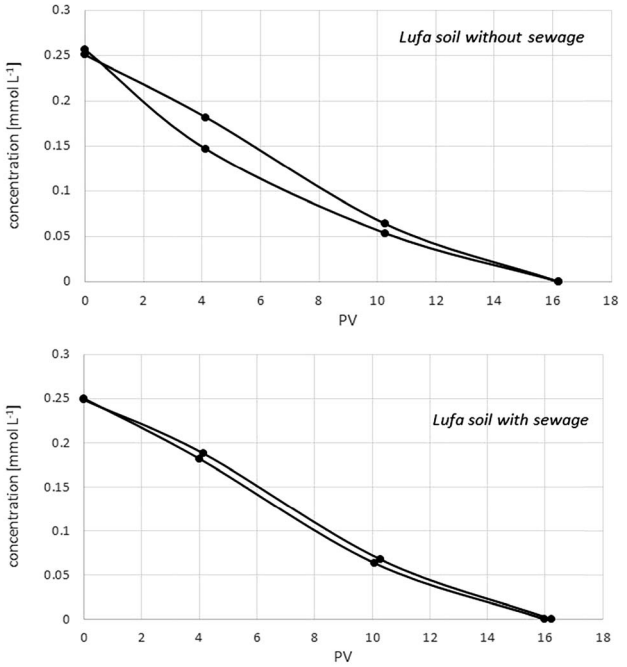

Fig. 5 Desorption of [OMIM][Cl] from columns containing LUFA soil (upper) and mixture of LUFA soil and sewage sludge (lower).

($m/z^+ = 211$). This indicates that both the indigenous bacteria and supplemented sewage bacteria are able to initialize degradation of [OMIM][Cl] under dynamic flow conditions. The degradation is of course not as efficient as that in the well mixed biodegradation experiments, and therefore the same level of degradation cannot be expected. A number of other metabolites were detected ($m/z^+ = 155$, 169 and 183), which correspond to various hydroxylated and carboxylated imidazolium compounds, with shorter alkyl chains.[5,20] The intensities of these peaks in the MS however were small. The biodegradation pathway with mass to charge ratios of detected transformation products is shown in Fig. 6.[5]

The difficulty to accurately determine and quantify these degradation products (*via* HPLC) lies in the fact that they, like the parent compound, continually sorb into the soil matrix. Therefore an accurate mass balance of the metabolites cannot be calculated, unless the sorption coefficients of each transformation products are measured independently.

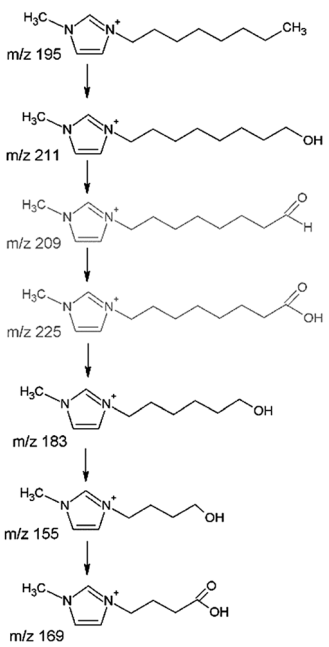

Fig. 6 Biodegradation pathway of OMIM cation according to Stolte *et al.*[5] Transformation products detected in this study are presented in black together with corresponding mass to charge ratios.

Biodegradation

We conducted biodegradability test of [OMIM][Cl] and sodium glutamate (positive control) measuring reduction in biological oxygen demand (BOD) over a period of 60 days (Fig. 7) using manometric respirometry method according to OECD 301F.[26] Activated sludge from WWTP treating predominantly municipal wastewater and microbial community derived from non-agricultural soil (no known history of chemical treatment) were used as sources of inoculum.

Viability of both inocula was confirmed, as full biodegradation of sodium glutamate took place. Nevertheless, in samples containing activated sewage sludge sodium glutamate degradation was completed after four days and in soil derived community degradation lasted 25 days. Degradation of the IL proceeded much slower in both cases and was not completed within 60 days. The final level of degradation of the IL cation was lower for soil derived community and reached around 30% upon test termination. Biodegradation of [OMIM][Cl] by activated sludge exceeded 60% yet was too slow to be classified as readily biodegradable (the condition of achieving 60% of ThOD removal within 10 days counted from the moment when biodegradation exceeds 10% was not met). Based on the mass balance and considering recent investigations it is assumed that the biodegradation observed in the sewage microbial community was due to side chain degradation whereas the core structure remained recalcitrant toward biodegradation.[5,20]

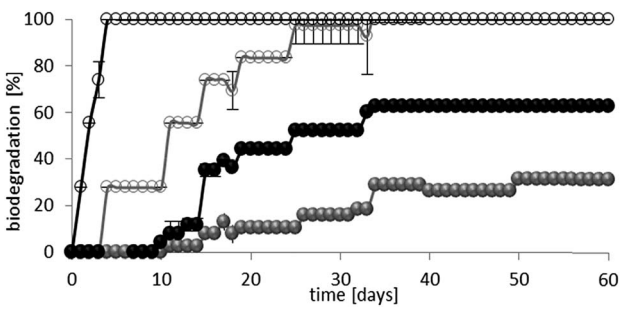

Fig. 7 Biodegradation of [OMIM][Cl] (closed symbols) and sodium glutamate (open symbols) by activated sewage sludge (black) and soil derived microbial community (grey).

Experimental

Chemicals

The investigated IL 1-methyl-3-octylimidazolium chloride was purchased from Merck KGaA (Darmstadt, Germany) with a purity of ≥98%. Inorganic components of mineral medium used for 'Manometric respirometry' test as well as anhydrous calcium chloride were purchased from POCh (Gliwice, Poland). Standard LUFA 2.1 soil was obtained from LUFA Speyer (Speyer, Germany). Sand was obtained from Brzeźno, Gdańsk, thoroughly flushed with demineralized water and air dried before use. The properties of soil and sand are listed in Table 3.

Parameters of LUFA soil are presented according to supplier's information. Organic carbon content of sand was analysed by liquid TOC II (Elementar Analysensysteme, Hanau, Germany), pH was measured in 0.01 M $CaCl_2$ solution with a pH electrode. Cation exchange capacity (CEC) was measured by barium chloride compulsive exchange method according to Ross.[27] An overview of the complete experimental plan is given in Fig. S4.†

Sorption of [OMIM][Cl] to sand, LUFA soil and sewage – batch experiment

Sorption batch test was conducted according to OECD 106 'Adsorption–desorption using a batch equilibrium method' procedure.[28] The initial concentration of IL was 0; 5; 10; 50; 100; 150; 200; 300; 400 and 500 mmol L^{-1} for LUFA soil or sand and 25; 50; 75; 100; 125; 150; 200; 250; 300; 350; 400 for sludge. 2 g of LUFA soil, sand or sewage were weighed into the test vessel and were equilibrated by shaking overnight with 10 mL of 0.01 M $CaCl_2$ solution. The IL stock solution with 0.01 M $CaCl_2$ was added (10 mL) and the mixture was shaken for another 24 hours at room temperature, then centrifuged at 15 000*g* for four minutes to remove solids. The supernatant was recovered for HPLC/UV analysis (exemplary chromatogram is given in Fig. S4†). All experiments were performed in duplicate accompanied by blank and control samples to exclude sorption on the test vessel or degradation as potential factors influencing the final results. Sorption isotherms for each solid were plotted and solid/liquid partition coefficients were derived as the slope of the linear part of the isotherm.

Soil column tests

Soil columns test was performed according to OECD 312 – leaching in soil columns. Columns of smaller dimensions were used as reported before by Mrozik *et al.*[16] and Studzińska *et al.*[19] Cylindrical columns made of stainless steel 21 mm in diameter and 65 mm in length (internal volume 22.5 cm^3) with Swagelok connectors were equipped with filters made of mineral wool to prevent flushing of solid. Columns were mounted vertically on stands and connected to a multichannel peristaltic pump *via* stainless steels tubes and TYGON® tubes inside of pump head. Unamended columns were filled with soil or sand (35 g on dry mass basis). Amended columns were filled with soil/activated sewage sludge or sand/activated sewage sludge (35 g soil/sand and 3.5 g of concentrated activated sewage sludge). Each column was initially equilibrated with 0.01 M $CaCl_2$ solution by flushing from top to bottom until conductivity of leachate measured using conductivity probe was equal to the conductivity of 0.01 M $CaCl_2$ solution. Subsequently the feed was changed for IL solution (0.25 mM in 0.01 M $CaCl_2$) and the direction of flushing was reversed and kept at the flow rate of 0.5 mL h^{-1} for 36 days. The soil/solution partition coefficient (K_D) was calculated as the ratio between amount sorbed per unit mass of sorbent in the column and amount dissolved per unit volume of water taking into account the linear portion of the BTC until the sorbent was saturated. The means of partition coefficients obtained from amended and unamended columns were compared for statistical significance using *t*-test. Additionally the composition of leachate was examined by direct infusion into MS in order to check for possible metabolites. All columns were prepared in duplicate. After 36 days, the IL solution was replaced with 0.01 M $CaCl_2$ solution and columns were flushed with a flow rate of approximately 10 mL h^{-1}, samples were collected from each column. Activated sewage sludge was obtained from the aeration chamber of municipal wastewater treatment plant Delmenhorst, Germany. Sewage flocs were centrifuged at 2000*g* for five minutes and the supernatant was discarded. The remaining pellet (dry mass 42.7 g L^{-1}, 40.85 g dry mass/1000 g wet mass) was used for packing sewage amended columns. All collected samples were centrifuged at 2000*g* for 15 min in order to remove any remaining solids and transferred to 1 mL vials. Concentration of [OMIM][Cl] in samples was determined using the HPLC/UV VWR Hitachi system containing the L2130 pump, L2130 degasser, L2200 autosampler, L2300 column oven, L2450 diode array detector and the EZChrom Elite software. A cation exchange column (250/3 NUCLEOSIL 100-5 SA) purchased from Macherey-Nagel (Dürren, Germany) was used. The mobile phase consisted of 55% acetonitrile (HPLC grade) and 45% aqueous 20 mM KH_2PO_4/3.9 mM H_3PO_4 buffer. A flow rate of 0.7 mL min^{-1}, temperature of 40 °C and a detection wavelength of 212 nm were used. Analytical performance parameters have been checked, a limit of quantification of 19.7 μM and a limit of detection of 6.9 μM were determined.

Table 3 Properties of soils used in the study

Parameter	Sand	LUFA soil
Organic carbon content [%]	0.12 ± 0.05	0.62 ± 0.07
Cation exchange capacity [meq./100 g]	2.78 ± 0.37	4.0 ± 0.7
pH (measured in 0.01 M $CaCl_2$)	6.8 ± 0.5	5.1 ± 0.4
Soil type	Sand	Silty sand

Degradation of [OMIM][Cl] by soil and sewage bacterial community

Biodegradation using soil and activated sewage sludge derived microbial communities was conducted according to OECD 301 F 'Manometric respirometry' procedure.[26] [OMIM][Cl] was used as an exemplary IL and sodium glutamate as a reference substance, both in concentrations of 0.25 mM. Activated sewage

sludge was obtained from an aeration chamber of the municipal wastewater treatment plant 'Wschód' (Gdańsk, Poland). Flocs were allowed to settle and the supernatant was used as an inoculum. Soil for biodegradation testing was obtained from an A horizon (top soil) of mixed forest and transferred immediately to the lab. Before the test soil was sieved through a 2 mm sieve and incubated overnight at 20 °C. To obtain soil inoculum 1500 mL of water were added to 1500 g of soil and agitated for 2 hours, then solids were settled and the supernatant was used as a soil derived inoculum. 246 mL of both inocula were used for respective test bottles and yielded cell densities of 10^8 CFU per liter sewage sludge and 10^6 CFU per liter for soil. A concentrated mineral medium was added to result in following composition: 8.5 mg L^{-1} KH_2PO_4, 21.75 mg L^{-1} K_2HPO_4, 22.13 mg L^{-1} $Na_2HPO_4 \cdot 2H_2O$, 1.7 mg L^{-1} NH_4Cl, 27.5 mg L^{-1} $CaCl_2$, 22.5 mg L^{-1}, $MgSO_4 \cdot 7H_2O$ and 0.25 mg L^{-1} $FeCl_3$. Test mixtures were placed in a test bottle made of dark glass equipped with magnetic stirrer and gas-tight closed with manometric cap (Oxitop, WTW). Each test sample was run in triplicate and was accompanied by blank samples (to account for endogenous cellular breathing) and positive controls containing sodium glutamate in the same concentration as the test substance. Sodium hydroxide as a sorbent of carbon dioxide was used. Allylthiourea was added to each bottle as a nitrification inhibitor. The temperature during the test was set at 20 °C and controlled. Decrease in pressure inside the bottle caused by oxygen consumption was measured, recalculated into biological oxygen demand (BOD) and recorded daily for a period of 60 days.

Identification of transformation products

Three samples coming from each column were selected and diluted 1 : 50 with methanol. Subsequently samples were analyzed by electrospray ionization mass spectrometry equipped with an ion trap detector (Brucker-Daltonic GmbH, Germany). Mass spectra for cations were acquired in the positive ion mode in the scan range of m/z^+ 50–400. The ESI source conditions were set according to ref. 29 with a capillary voltage of 2000 V, drying gas flow-rate of 5 L min^{-1}, drying gas temperature at 300 °C and nebulizer at 50 psi.

Conclusions

The major novelty of this work lays in the amendment of soil with sludge and examining both transport and biodegradation in dynamic conditions. We have found that transport of ILs in low organic matter soils will be relatively fast and only slightly hindered in soils amended with organic matter, unless it is present in high amounts (higher than 10%). The biodegradation of the target IL cation in the batch tests was shown to occur for both sludge and indigenous microbial communities. The soil bacterial communities however, were less efficient. Even though sorption on sludge is very high, the amendment of soils with waste sludge will most probably not be an efficient way to hinder transport of ILs into deeper soil layers.

Transformation products were detected in columns containing both soil and soil with sewage sludge. Even though the contact time and oxygen availability were limited, biodegradation still occurred.

One can speculate that in the case of release of [OMIM][Cl] to terrestrial environment due to insufficient removal during wastewater treatment or an accidental spill, this IL might be transported in soils to deeper layers or ground waters as it is fully miscible with water and was only slightly retarded by sorption on soil particles. Nevertheless the degradation in soils most probably will occur, although the rate will be lower that measured in batch biodegradation tests.

Though in batch test the IL cation was degraded by activated sewage sludge faster than by soil microbial community the addition of sewage to the soil did not cause any observable difference (*e.g.* earlier appearance or higher quantities of degradation products). This might have resulted from several limitations imposed by the soil column test. Limited mass transfer of IL to microbial cells, shorter contact time as well as limited amounts of oxygen and lower cell density are expected to decrease the rate of degradation. Though degradation products of IL are generally less hydrophobic than the parent compound, and therefore are expected to have lower affinity for soil, they appear in low concentrations and might additionally have been sorbed preventing their detection.

Taking into account that many imidazolium ILs are not biodegradable within reasonable time frame and that the core is recalcitrant sorption might be the only way to prevent pollution of ground water and is a process that complements biodegradation. We believe this study, once again, shows that application of imidazolium ionic liquids in industrial, large scale processes should be considered carefully and infallible measures assuring zero emissions need to be in place. Other, more environmentally acceptable ILs exist that could be used instead if only technological requirement allow this.

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