Lisiecka, N., Ciesielski, T., Sopata, O., Parus, A., Wozniak-Karczewska, M., Simpson, M., Frankowski, R., Zgola-Grzeskowiak, A., Kloziński, A., Siwinska-Ciesielczyk, K., Klapiszewski, Ł., Niemczak, M., Owsianiak, M., **Heipieper, H.J.**, **Chrzanowski, Ł.** (2023): Sorption of ionic liquids in soil enriched with polystyrene microplastic reveals independent behavior of cations and anions
Chemosphere **341** , art. 139927

https://doi.org/10.1016/j.chemosphere.2023.139927

Sorption of ionic liquids in soil enriched with polystyrene microplastic reveals independent behavior of cations and anions

Natalia Lisiecka[1a], Tomasz Ciesielski[1a], Olga Sopata[1], Anna Parus[1*], Marta Woźniak-Karczewska[1], Maria Simpson[1], Robert Frankowski[1], Agnieszka Zgoła-Grześkowiak[1], Arkadiusz Kloziński[1], Katarzyna Siwińska-Ciesielczyk[1], Łukasz Klapiszewski[1], Michał Niemczak[1], Mikołaj Owsianiak[2] Hermann J. Heipieper[3], Łukasz Chrzanowski[1,3]

[1] Faculty of Chemical Technology, Poznan University of Technology, Berdychowo 4, 60-965 Poznań, Poland

[2] Quantitative Sustainability Assessment Division, Department of Environmental and Resources Engineering, Technical University of Denmark, Produktionstorvet 424, 2800 Kgs. Lyngby, Denmark

[3] Department of Environmental Biotechnology, Helmholtz Centre for Environmental Research – UFZ, Permoserstraße 15, 04318 Leipzig, Germany

[*]Corresponding author: anna.parus@put.poznan.pl

Electronic supplementary information (ESI) available.

[a] both Natalia Lisiecka and Tomasz Ciesielski contributed equally in terms of research and the writing of the manuscript

Keywords: sorption isotherms; cationic surfactants; soil environment; herbicidal ionic liquids; choline.

ABSTRACT

Recently, much attention has been focused on the application of the Ionic Liquids (ILs) with herbicidal activity in agriculture. It has been suggested that through the appropriate selection of cations and anions, one can adjust the properties of ILs, particularly the hydrophobicity, solubility, bioavailability, toxicity. In practical agricultural conditions, it will be beneficial to reduce the mobility of herbicidal anions, such as the commonly applied 2,4-dichlorophenoxyacetic acid [2,4-D] in the soil. Furthermore, microplastics are becoming increasingly prevalent in the soil, potentially stimulating herbicidal sorption. Therefore, we investigated whether cations in ILs influence the mobility of anions in OECD soil supplemented with polystyrene microplastic (PS). For this purpose, we used the 2,4-D based ILs consisting of: a hydrophilic choline cation [Chol][2,4-D] and a hydrophobic choline cation with a C_{12}-chain [C_{12}Chol][2,4-D]. Characterization of selected micropolystyrene was carried out using the BET sorption-desorption isotherm, particle size distribution and changes in soil sorption parameters such as soil sorption capacity and cation exchange capacity. Based on the batch sorption experiment, the effect of microplastic on the sorption of individual cations and anions in soil contaminated with micropolystyrene was evaluated. The results obtained indicate that the introduction of a 1-10 % (w/w) PS resulted in an 18-23 % increase of the soil sorption capacity. However, the sorption of both ILs' cations increased only by 3-5 %. No sorption of the [2,4-D] anion was noted. This suggests that cations and anions forming ILs, behave independently of each other in the environment.

The results indicate the fact that ILs upon introduction into the environment are not a new type of emerging contaminant, but rather a typical mixture of ions. It is worth noting that when analyzing the behavior of ILs in the environment, it is necessary to follow the fate of both cations and anions.

1. INTRODUCTION

The agricultural sector would not survive as an efficient and feasible entity without the invention of plant protection products such as herbicides. Till this day, their worldwide use has raised many discussions related to their negative impact on the environment and human health (Bernardes et al., 2015; Nicolopoulou-Stamati et al., 2016). Therefore, an intense search is currently being conducted to find alternative solutions that are less destructive and more environmentally friendly. Notably, the main adverse effects of herbicides involve their volatility, their high mobility in the soil, the need for additional adjuvants and the unintended acquisition of herbicidal resistance by plants (Arias-Estévez et al., 2008; Curran, 2016). Unfortunately, the improvement of herbicides has slowed down since no new groups of chemicals have been discovered to possess novel mechanisms of interacting with plants (Duke, 2012).

Thus, scientists are investigating how to improve the performance of current herbicides through modifying their chemical compositions. Over the past 15 years, much attention has been focused on a group of compounds called ionic liquids (ILs) (Randviir et al., 2014; Talapin and Shevchenko, 2016). Among severally proposed ideas, the concept of converting herbicides into ILs has emerged, thus creating the novel category of herbicidal ionic liquids (HILs) (Wilms et al., 2020). The majority of HILs are based on an herbicidal anion and a suitable organic cation which, through its characteristics, dictates the properties of the entire ionic pair (Choudhary et al., 2017). The most impactful advantage is the heightened herbicidal activity of HILs compared to the standard commercial formulations of herbicides (Niu et al., 2018; Zhu et al., 2015) their lower-volatility, higher stability and reduced toxicity (Pernak et al., 2020; Piotrowska et al., 2018, 2017), what makes it possible to use lower doses during spraying procedures which supports the framework of green chemistry (Earle and Seddon, 2000; Welton, 2011). Moreover, numerous authors claim that the introduction of a hydrophobic cation translates directly into an increase in the hydrophobicity of the entire IL. This facilitates the possibility to, for example, increase the soil sorption of easily leachable herbicidal anions, such as 2-methyl-4-chlorophenoxyacetic acid (MCPA) or 2,4-dichlorophenoxyacetic acid (2,4-D). Thus, for this to occur, it is common practice to pair herbicidal anions with the appropriately suited hydrophobic cations (Kowalska et al., 2021; Stepnowski et al., 2007).

However, the true behaviour of ILs in the environment remains a large unknown as no one has fully explored their fate in this respect. Therefore, a key issue to investigate is whether the ILs' integral cationic-anionic pair still exists as a whole entity in the environment.

This knowledge is essential to predict how herbicidal ILs will undergo various processes such as sorption and biodegradation. To date, the available publications predominantly focus on studies conducted in aqueous and soil environments for the simplest ILs, consisting of an organic cation and an inorganic anion (Maculewicz et al., 2022; Mrozik et al., 2013, 2012, 2009).

Yet, it should certainly be emphasised that IL interactions in the soil environment are more complex in comparison to those occurring in the aquatic environment. This is attributed to many diverse and intricate factors that can affect the biodegradation rate or sorption effectiveness of various xenobiotics (Fantke, et al., 2017). Moreover, it should be noted that the efficacy of sorption of a particular herbicide in the soil may be dependent, in amongst others features, on the content of organic matter (e.g. humic acids) as well as mineral matter (e.g. iron, aluminium oxides etc.) (Werner et al., 2013).

Furthermore, as of recent, a significant attentiveness has appeared to be directed towards the commonly occurring micro/nanoplastics (MNPs) found in agricultural soil (micro size: 5 mm-100 nm and nano size <100 nm). Such MNPs can distinctly alter the properties and functioning of the soil environment (Galloway et al., 2017; Gangadoo et al., 2020). The creation of such pollutants is manifold and occurs during processes such as abrasion, mulching, the agricultural use of compost and sewage sludge (Yu and Flury, 2021). There are many indicators that suggest that as the variety and mass-scale production of polymers increases, their presence in the natural environment will also rise. From a statistical point of view, approximately 63,000-430,000 t of MNPs enter EU agricultural land from sewage sludge per year (Nizzetto et al., 2016). Additionally, per annum, there has been on average 6 kg/ha of MNPs originating from compost and it has been noted that approx. 72-260 kg/ha of MNPs have risen from various agricultural foils (Bläsing and Amelung, 2018; Nizzetto et al., 2016).

Besides the aforementioned data, it has already been proven that MNPs indeed change the sorption processes of xenobiotics in the soil environment (Fang et al., 2019; Šunta et al., 2020). The evidence of the ability of plastic sorbing herbicides has appeared in scientific research as early as the 1980s. An exemplary case of such studies involved the ability of the herbicide hexazinone to adsorb on polystyrene (Bouchard and Lavy, 1985).

From a scientific standpoint, it will be intriguing to assess how the presence of MNPs influences the sorption process of IL cations and anions, whether the cation and anion, which form an IL, will remain as an integral pair in the soil environment; or whether the cationic-anionic forces of attraction will be overcome, breaking the ionic pair into two separate, mobile entities in the soil.

In our previous studies, we observed that in simple soil systems, the hydrophobic cations become strongly sorbed while the anions retain their mobility (Parus et al., 2023; Woźniak-Karczewska et al., 2022). Yet, could the presence of varying concentrations of MNPs alter the above-noted trends?

Therefore, the purpose of our study was to investigate the effect of polystyrene microplastic on the sorption processes of ILs exhibiting herbicidal activity in an OECD model soil.

A common herbicide known as 2,4-D was used for the study. This anion was individually combined with two cations of different hydrophobicity, namely choline hydrophilic [Chol] and a hydrophobic choline derivative, which was modified by introducing a C_{12} chain [C_{12}Chol].

The analysis of the behavior of the cations and anions, which constitute the IL, in a soil environment that is contaminated with MNP is truly crucial. Such studies will help to understand further whether ILs are a potentially new emerging contaminant.

2. MATERIALS AND METHODS

2.1. Synthesis of ionic liquids displaying herbicidal activity

The synthesis and characteristics of [Chol][2,4-D] and [C_{12}Chol][2,4-D] were previously described by (Praczyk et al., 2012) and (Marcinkowska et al., 2017). Firstly, [2,4-D] was neutralized with appropriately measured stoichiometric amounts of potassium hydroxide in methanol solvent. Secondly, the solvent was evaporated using a rotary vacuum evaporator in order to obtain potassium salts of [2,4-D]. Subsequently, the salts were dried in a vacuum oven at 50 °C for 48 hours.

Next, choline chloride [Chol][Cl] or *N*-dodecylcholine chloride [C_{12}Chol][Cl] (0.01 mol) was dissolved in 10 mL of methanol in a reaction vessel equipped with a mechanical stirrer. Then, a 2% molar excess (10.2 mmol) of potassium salt [2,4-D] was added (previously dissolved in 10 mL of methanol) to initiate ion exchange. After 60 minutes, the mixture was cooled to 0 °C. The precipitated potassium chloride was filtered off and the solvent was evaporated from the filtrate. The obtained products were further purified through the addition of a small portion (10-15 mL) of acetone and subsequently, the undissolved impurities were removed. Then, the solvent was evaporated from filtrates. Finally, the obtained products, namely [Chol][2,4-D] and [C_{12}Chol][2,4-D], were dried at 50 °C for 24 h under reduced pressure. The yields of the reactions were sufficiently large and exceeded > 95 % for both ILs.

2.2. Soil characteristics

The OECD soil (soil prepared in accordance with the guidelines Organization for Economic Co-operation and Development) was purchased from Tigret Ltd. (Warsaw, Poland). The composition and characteristics of the OECD soil have been provided in Table 1.

Table 1. Composition and characteristics of the OECD soil.

Soil composition	Total carbon	pH	Water holding capacity	Cation exchange capacity
70 % air-dried quartz sand, 20 % kaolin clay, 10 % peat.	5 %	6.5 (in H_2O)	40 %	8.76 cmol/kg

Data representing the average of a triplicate soil analysis (standard mean error: ± 5 %, n=3)

2.3. Microplastic preparation

The polystyrene (PS) with the trade name Empera 124L (Brenntag Polska Ltd., Poland) was the utilized microplastic throughout the undertaken research. The PS density (sourced from ISO 1183) was 1.04 g/mL, the tensile stress at yield (according to ISO 527-1.2) was denoted as 50 MPa and the vicat softening temperature (in agreement with ISO 306) was approx. 87 °C (B50). This particular PS in its commercial form constitutes of cylindrical granules with dimensions ranging from 2 to 3 mm. In order to obtain the desired microplastic, PS was ground in dry ice to prevent the plasticization of the polymer as well as to increase the grinding efficiency. The grinding was carried out through the use of an ultra-centrifugal mill (ZM 200, Retsch, Germany) with a vibrating feeder (DR 100, Retsch, Germany). The subsequent rotor speed was set to 10000 rpm and a ring sieve of a mesh size of 0.5 mm was used to enhance the grinding efficiency.

The particle size distribution of microplastics was then measured using a Mastersizer 3000 analyzer (Malvern Instruments Ltd., UK).

2.4. Textural characterization of the PS microplastic

In this section, the surface area (A_{BET}), average pore diameter (S_p) and total pore volume (V_p) of the PS microplastic were determined based on a low-temperature sorption of N_2 at −196 °C. This was achieved through using an ASAP 2020 physisorption analyzer (Micromeritics Instrument Co., Norcross, CA, USA). The Brunauer-Emmett-Teller (BET) model was utilised to calculate the surface area based on adsorptive data for relative pressure (p/p_0) in the range 0.05-0.30. The pore size distribution and the total volume of the pores were estimated from the desorption isotherm based on the Barrett-Joyner-Halenda (BJH) method. This was solved through the use of the Halsey equation. Moreover, prior to measurement, the analyzed sample was degassed under a vacuum at 80 °C for 10 h.

2.5. Determination of the sorption capacity of PS, OECD soil and OECD + PS

The Kappen's method (Jaremko and Kalembasa, 2014; Kappen, 1929) was applied to investigate the potential interaction of the chosen microplastic with the soil matrix. This was employed in order to investigate if there would be an increase in the sorption capacity of OECD soil in the presence of microplastics. Firstly, the sorption capacity of PS at 1, 2, 5 and 10 wt. % (weight percent) was determined. Secondly, the sorption capacity of the pure OECD soil was analysed. Lastly, the final sorption assessment involved the combination of OECD soil with 1, 2, 5 and 10 wt. % PS, respectively. The concentration range that was chosen was based on prior publications, which claimed that the presence of microplastics in agricultural fields can reach values of up to a maximum of 10 %

concentration (de Souza Machado et al., 2019; Fuller and Gautam, 2016; Hüffer et al., 2019). A microplastic with a particle size similar to our PS microplastic was used by Chen et al. (Chen et al., 2021). This size was chosen because microplastics <1 mm in size predominate in soils, as previously reported (Lv et al., 2019; Zhang and Liu, 2018). In addition, the sorption capacity, defined as the sum of the hydrolytic acidity value and the sum of exchangeable alkaline cations, was calculated using formula (1) for each sample:

$$T = H + S \tag{1}$$

where: T – soil sorption capacity [$\mathrm{cmol_{c+}}$/kg], H – sum of the hydrolytic acidity [$\mathrm{cmol_{H+}}$/kg], S - sum of exchangeable base cations [cmol/kg].

2.5.1. *Hydrolytic acidity*

Hydrolytic acidity is defined as the soil acidity that is formulated through the presence of an acidic hydroxyl or carboxyl group (Chestworth, 2008).

The air-dried soil was sieved through a 1 mm mesh sieve. Then 150 mL of 1 mol/L sodium acetate solution was added to 60 g of sieved soil. The suspension was shaken for 1h in a conical flask of about 250 mL on a rotary shaker operating at 230 rpm. The contents were then filtered (0.22 μm PTFE syringe filter). The resulting filtrate was titrated with a 0.1 mol/L sodium hydroxide solution in the presence of phenolphthalein indicator. The hydrolytic acidity values were then calculated from the amount of sodium hydroxide solution consumed using the following formula (2):

$$H = V \cdot c_M \cdot 5 \cdot 1.5 \tag{2}$$

where: H - hydrolytic acidity [$\mathrm{cmol_{H+}}$/kg], V - the volume of NaOH used to neutralize the resulting acid, c_M - NaOH molar concentration [mol/L], 5 - conversion factor for 100 g of soil (since 50 mL of filtrate corresponds to a weight of 20 g of soil), 1.5 - Kappen's coefficient, correction for incomplete displacement of hydrogen and aluminum ions during a single treatment of soil with an ammonium acetate solution.

2.5.2. Exchangeable alkaline cations

Exchangeable alkaline cations are defined by the amount of acidity contributed by free hydrogen ions and acidic cations (e.g. Al^{3+}) that are thus neutralized by a NaOH base (Chestworth, 2008). To 20 g of air-dry soil, 200 mL of 0.1 mol/L hydrochloric acid solution were added. Next, the collected suspension was shaken in a conical flask of approx. 250 mL capacity on a rotary shaker (at 230 rpm) at room temperature for 1 hour and then filtered through a 0.22 μm PTFE syringe filter. The filtrate was titrated with 0.1 mol/L sodium hydroxide solution in the presence of phenolphthalein indicator. Subsequently, the sum of exchangeable alkali cations was calculated from the amount of sodium hydroxide solution used, with the following formula:

$$S = (b - a) \cdot c_M \cdot \frac{200}{40 \cdot \frac{V}{V_c}} \tag{3}$$

where: S - sum of alkaline cations, [$cmol_{c+}/kg$], a - volume [mL] of 0.1 M NaOH consumed in the titration of the analysed sample, b - volume [mL] of 0.1 M NaOH expended during the titration with 0.1 M HCl (the derived average of repetitions), V - volume of extract used for titration, V_c - volume of 0.1 M HCl solution used for the soil extraction, c_M - molar concentration of NaOH solution, $200/(40 \cdot V/V_c)$ - conversion coefficient per 100 g of soil (where the soil to solution ratio is 1:5).

2.6. Sorption of ionic liquids on PS, OECD soil and PS + OECD

The experiments were carried out according to the stipulated OECD (2000) guidelines ("OECD/OCDE 106. Adsorption - Desorption Using a Batch Equilibrium Method.," 2000) for the 2,4-D sodium salt and [Chol][2,4-D] or [C_{12}Chol][2,4-D] combination. Thus, the standard concentration of active substance [2,4-D] for each treatment was equal to 10 mg/L. Firstly, the OECD soil was sterilized using an autoclave for 20 minutes at 121 °C. This procedure was repetitively carried out for three consecutive days. Between sterilizations, the soil was dried at 60 °C in agreement with the procedure described by Shen et al. (Shen et al., 2018).

Therefore, in centrifuge tubes, 5 mL of the corresponding HIL and 1 g of dried sterile OECD soil were mixed with 1, 2, 5 and 10% wt. % PS, respectively. The polypropylene tubes were then shaken on an orbital shaker at 240 rpm at 20 ± 1 °C in the dark (to avoid photodegradation). Samples were collected after 24 hours and centrifuged at 10,000 rpm for 10 minutes. The resulting supernatant was then filtered through a 0.22 μm PTFE syringe filter (Whatman® Puradisc, Sigma Aldrich, UK). In a similar manner, this procedure was also carried out for the OECD soil system, in which 1 g of OECD soil was mixed with 5 mL of the corresponding HIL (without the addition of PS). In addition, treatments in which PS was the only substance were also examined. For such an analysis, each PS sample was supplemented with 5 mL of HIL at a mass of 0.01, 0.02, 0.05 and 0.1 g of PS (these values correspond to chosen concentration range of 1, 2, 5 and 10 wt. % of PS, respectively).

The concentration of cations and anions was determined using the LC-MS/MS equipment. Possible sorption of HILs on the surface of PP centrifuge tubes was also examined. In order to do so, blanks were prepared by shaking a 5 mL solution of the HIL without any soil and microplastic present. Additionally, 1 g of soil with 5 mL of water was also tested, notably, without the analyzed HILs present. All experiments were performed in triplicate. The efficiency of the adsorption process of herbicide cations and anions of ionic liquids in the soil was calculated through the following formula (4):

$$\text{removal }\% = \frac{c_0 - c_e}{c_0} \cdot 100\ \% \qquad (4)$$

where: c_o and c_e are the initial and equilibrium concentrations of the herbicide present in solution (mg/L). Adsorption isotherms were also determined in this experiment. The exact procedure for determination has been described by (Woźniak-Karczewska et al., 2022).

2.7. LC-MS/MS analysis

The LC-MS/MS analysis consisted of the use of UltiMate 3000 RSLC from Dionex (Sunnyvale, CA, USA) alongside the API 4000 QTRAP triple quadrupole mass spectrometer from AB Sciex (Foster City, CA, USA). The samples (with a volume of 5 μL) were injected into a Gemini-NX C18 column (100 mm

× 2.0 mm I.D.; 3 µm) from Phenomenex (Torrance, CA, USA) thermostated at 35 °C. A two-phase gradient elution composed of a 5 mM aqueous solution of ammonium acetate (A) and methanol (B) was used with a flow-rate set to 0.3 mL/min. The mobile phase gradient employed for the determination of the [2,4-D] anion and the [Chol] cation was as follows: 0 min – 50 % B; 1 min – 50 % B; 2 min – 100 % B; 3 min – 100 % B. Likewise, [C_{12}Chol] was determined in a gradient of 0 min – 80 % B; 2 min – 100 % B; 4 min – 100 % B. The effluent from the column was directed to the electrospray ionization source (the Turbo Ion Spray) which has been operated in a negative ion mode for anions and in a positive ion mode for cations. The following settings of the required source parameters were applied: curtain gas 10 psi, nebulizer gas 40 psi, auxiliary gas 45 psi, temperature 450 °C, ion spray voltage +/- 4500 V. Notably, the mass spectrometer working conditions and characteristics of particular ions are listed in Table 2 below.

Table 2. Parameters of the MS detection.

Analyte	**DP (V)**	**Precursor ion [m/z]**	**Product ion [m/z]**	**EP (V)**	**CE (eV)**	**CXP (V)**
[2,4-D]	-45	219.9	161.9	-10	-23	-8
[Chol]	115	104.0	60.0	3	25	10
[C_{12}Chol]	160	257.7	214.1	8	33	13

DP – declustering potential, EP – entrance potential, CE – collision energy, CXP – collision cell exit potential

3. RESULTS AND DISCUSSION

3.1. Determination of the sorption capacity of PS, OECD soil and PS + OECD

Prior to the study, we fully characterised the PS in terms of its particle size, adsorption/desorption isotherms, surface area and pore volume etc. Hence, we will refer to these parameters in the Supplementary Information provided, namely: Figures S1 and S2, Tables S1 and S2.

Assessment of soil sorption capacity and cation exchange capacity (CEC) are among the key parameters for determining soil properties. The introduction of fertilizers, as well as xenobiotics including microplastics, can change soil chemistry, and this can alter both parameters. Hence, there is a need for the analysis of the change in sorption capacity and cation exchange capacity after the introduction of micropolystyrene into soil.

Analysing the sorption capacity of PS, one can see that it increased from 1.35 to 1.78 [cmol/kg] as amount of microplastic present increased (Table 3). A similar observation was made when microplastics were added to the OECD soil.

The introduction of 2 wt. % of PS to the soil resulted in an 18 % (0.81 [cmol/kg]) increase in the sorption capacity in comparison to the pure OECD soil. Moreover, a further increase in the PS content, namely 5 or 10 wt. %, amplified the sorption capacity of the soil by 22 % (1.06 [cmol/kg]) and 23 % (1.11 [cmol/kg]), respectively. Thus, the values of the obtained sorption capacity for the OECD soil containing PS was therefore not equal to the sorption capacities determined for the pure OECD soil sample and the pure PS sample separately. This should potentially result in higher sorption of the analyzed ILs in the soil that is enriched with PS.

Table 3. The sorption capacity determined for PS as well as OECD soil (both with and without PS).

System	Sorption capacity [cmol/kg]
1 % PS	1.35 ± 0.06
2 % PS	1.68 ± 0.05
5 % PS	1.69 ± 0.02
10 % PS	1.78 ± 0.27
OECD + 0 % PS*	3.77 ± 0.09
OECD+ 1 % PS*	3.75 ± 0.11
OECD+ 2 % PS*	4.58 ± 0.11
OECD+ 5 % PS*	4.83 ± 0.07
OECD+ 10 % PS*	4.88 ± 0.02

± standard error of the mean of three independent experiments
*soil OECD with % PS (w/w) addition

Notably, the increases in the soil sorption capacity in the soil with PS present should be attributed to the additional porous structures and reactive surfaces of the microplastic. These elements may influence the interactions (predominantly the non-specific van-der Waals forces) between PS and the soil. Hence, multiple researchers mainly concentrate on the effects of the presence of MNPs on the soil sorption but they do not focus solely on parameters like cation exchange. Instead, many scientific reports predominantly focus on analysing changes in the structure, bulk density or water capacity of soil thereof (Chen et al., 2021; Hu et al., 2020; J. Li et al., 2021).

In our opinion, the studies of the sorption of xenobiotics in soil-microplastic systems are worth to be extended, focusing more on the evaluation of the sorption capacity as well as the cation exchange capacity. The aforementioned two factors both demonstrate certain changes in the potential of the soil sorption complex, i.e. the ability to store ions (mainly cations) through exchange sorption.

3.2. Sorption of herbicidal ionic liquids

3.2.1. Sorption of [Chol] and [C_{12}Chol] cations on PS with its characterisation

The PS microplastic used in our analysis has four noteworthy characteristics: average sized (denoted as d_{50}) equal to 276 µm (Figure 1.), low BET surface area (0.2 m^2/g), low total pore volume (0.001 mL/g) and mean pore diameter of 23.1 nm for each PS granule.

Figure 1. The particle size distributions (particle volume in %) of polystyrene used in the experiments. The obtained microparticle dimensions ranged from 16.4 to 976 µm

Additionally, the attained N_2 adsorption/desorption isotherm for the PS sample is presented in Figure 2 below. The interpretation of the aforementioned parameters, i.e. the porous structure of the PS sample, confirm that the hysteresis loops are in agreement with the relative pressure range of p/p_0=0.48-0.99. Hence, it is visible that the amount of nitrogen adsorbed slowly increases in the relative pressure range p/p_0=0-0.82; above p/p_0=0.82 it rapidly increases to reach a maximum value of 0.7 mL/g at p/p_0=0.99. Hence the analysed PS material can be classified as type II, which is characterized for non-porous or macroporous materials. This type of isotherm indicates an indefinite multi-layer formation after completion of the monolayer and is found in adsorbents with a wide distribution of pore sizes.

Figure 2. N_2 adsorption/desorption isotherms (a) and distribution of pore size (b) of the PS sample.

Notably, the low value presented by the BET surface area for polystyrene materials was also recognized by Sarkar et al. (Sarkar et al., 2021). Their research demonstrated that polystyrene-based microplastics, such as engineered MPs, raw plastic and semi-environmental plastic, are characterized with a BET surface area of 0.379 m^2/g, 0.581 m^2/g and 0.618 m^2/g, respectively. The PS utilized in our analysis classifies as a typical PS micropolymer.

From the obtained data, one can see that the sorption of the [Chol] cation on PS was approx. 3.3 ± 0.4 mg/kg, what this corresponds to 16-18 %, as indicated in Table 4. For the hydrophobic [C_{12}Chol] cation, the sorption was in the range of 19-21 %, which is correlated to approx. 4.1 ± 0.5 mg/kg. Compared to available data, similar trends were also observed in the aqueous environment for the commonly used triazole fungicides hexaconazole, myclobutanil, triadimenol, where the increase in adsorption capacity on 1000 mg/L PS was positively related to their hydrophobicity and was 40 μg/g, 20 μg/g, and 10 μg/g, respectively (Fang et al., 2019). An analogous effect was reported for the sorption of sulfamethoxazole, sulfamethazine and cephalosporin C on naturally aged PS microplastics (Guo and Wang, 2019). Evidently, the sorption capacities of herbicidal ILs on polystyrene microplastics obtained within our studies were indeed in an range of results presented for various organic compounds by other scientists (Gong et al., 2019; S. Li et al., 2021).

Yet, the minor differences between the sorption of the hydrophilic and hydrophobic cation on PS should still be emphasized.

Such a characteristic of PS directly translates into a negligible sorption of the analyzed cations. Notably, 18% of the hydrophilic cation was sorbed ion a 10 % PS sample, while 23% of the hydrophobic cation was sorbed in an analogous system.

Reportedly, the presence of functional groups on the surface of the sorption material also portrays a significant impact during the sorption processes (Gong et al., 2019; Guo and Wang, 2019; Hu et al., 2020; S. Li et al., 2021). In this respect, one can observe that PS is a material poor in functional groups, which means that it is not conducive to the sorption processes. In the assessed PS-xenobiotic system, sorption probably occurs according to the mechanism of π-π, electrostatic and hydrophobic interactions between the analyzed cations and the sorption material, which has also been described by the other authors in their research (Gong et al., 2019; Guo and Wang, 2019; Hu et al., 2020; S. Li et al., 2021). Nevertheless, from our experiments, one can see that the influence of PS is not a determining factor of the cation sorption capacity.

3.2.2. Sorption of [Chol] and [C_{12}Chol] cations on the pure OECD soil, without PS

Notably, the sorption of the [Chol] cation in the pure OECD soil was approx. 44 %, whereas the sorption of the hydrophobic [C_{12}Chol] cation in the OECD soil was 94.8 %, as displayed in Table 4. Thus, the hydrophobic nature of the [C_{12}Chol] cation results in a greater sorption in the soil in comparison to the hydrophilic [Chol] cation. Such a result was indeed expected due to the various reports supporting such a mechanism (Parus et al., 2023). Moreover, recent studies have indicated that hydrophobic cationic surfactants such as [C_{12}Chol] are strongly sorbed in the soil that consists of mineral and organic components (e.g. humic substances) (Bouras et al., 2010; Gamboa and Olea, 2006; Zhan et al., 2013). As reported by Ishiguro et al. (Ishiguro and Koopal, 2016), the transfer of the surfactant tails of dodecyl- and cetylpyridinium chlorides to the hydrophobic components of humic substances is a common mechanism. A key role in the adsorption of cationic surfactants on negatively charged mineral surfaces is dependent on the positive charges of cations and additionally, hydrophobic interactions created by long alkyl chain presence (Li and Gallus, 2007). Moreover, there are also numerous reports on the sorption of cationic surfactants on silicate clays and metal oxides (Ishiguro and Koopal, 2016; Liu et al., 2021). Based on the adsorption studies of dodecyl trimethylammonium and hexadecyl trimethylammonium onto kaolinite, it was confirmed that the chain length of the surfactant substantially influenced the adsorption efficiency (Li and Gallus, 2007). Therefore, the detected high sorption of the hydrophobic cation compared to the low sorption of hydrophilic cation in the soil is indeed consistent with the results obtained in similar studies, where 2,4-D was bound with betaine [Bet] and [C_{12}Bet] (Woźniak-Karczewska et al., 2022). Likewise, in another study, where herbicidal ILs were used, similar trends were observed. This investigation utilised [Chol][Glyph] and [C_{12}Chol][Glyph], where it was noted that 42 – 45 % of the [Chol] cation was adsorbed for OECD and agricultural soils. On the contrary, the hydrophobic [C_{12}Chol] cation was almost quantitively adsorbed in both soil types which is certainly a considerable result.

Hence, it may be concluded that regardless of whether the analyzed herbicidal IL consists of 2,4-D or glyphosate, the efficiency of the cation sorption primarily depends on the hydrophilic or hydrophobic nature of the cation. Moreover, it is independent of anion type (Parus et al., 2023).

3.2.3. Sorption of [Chol] and [C_{12}Chol] cations on OECD soil with PS

The introduction of various amounts of PS (1-10 wt. %) to the OECD soil resulted in the sorption of [Chol] ranging from 44 to 47 % (Table 4). Noticeably, the sorption of the hydrophobic cation [C_{12}Chol] in the pure OECD soil was already high, reaching 94.8 %. Hence, the introduction of PS improved the sorption efficiency by approx. 5 %. Therefore, for both cations, a 3-5 % increase in sorption, in the OECD soil containing PS, was indeed observed. Such an increase in the sorption of the analyzed cations is not a surprising occurrence, since microplastics in the soil act as an additional sorbent (Joo et al., 2021). However, the results indicate that the sorption efficiency is mainly influenced by the soil type. Thus, the addition of a microplastic with a weak porous structure does not result in a statistically large increase in the sorption.

Moreover, the slight increase in the sorption in the soil-microplastic system confirms the assumption that the sorption mechanism, based on the interaction of the xenobiotic with functional groups present in the macro- and micropores of the soil, dictates the sorption efficiency.

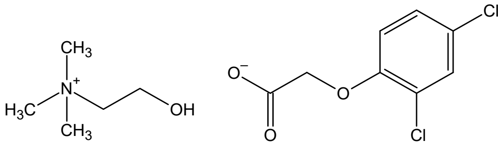
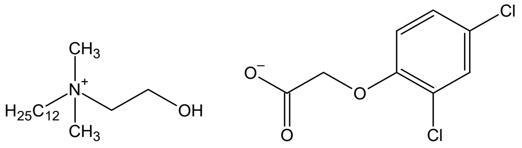
These trends are confirmed by comparative analysis of sorption tests (Table 4) with the results of soil sorption capacity (Table 3). The introduction of micropolystyrene into the soil does not significantly increase the sorption of [Chol] and [C_{12}Chol] cation, because the interaction between micropolystyrene is through π - π and/or electrostatic interactions, which are much weaker than chemical sorption with soil components.

Furthermore, the results obtained by other researchers can also confirm that, for example, the sorption of tetracycline to soil is stronger than that of microplastics. This is attributed to other soil-related interactions such as cation exchange, surface complexation and cation bridging interactions. It was reported that the partition coefficient of tetracycline to soil was 1093 ± 92 L/kg in the concentration range of 0.01-0.1 mg/L (Pan and Chu, 2016). On the contrary, the corresponding coefficient of the selected microplastics (PS, PP and PE) was low, ranging between 160-445 L/kg for higher concentrations (1 mg/L), of course depending on the type of microplastic (Xu et al., 2018).

Another exemplary study, conducted by Hu et al. (Hu et al., 2020), investigated the sorption of 17β-estradiol in the soil with a microplastic such as polystyrene. The results of the experiment showed that the adsorption capacity of the microplastic against 17β-estradiol was stronger than that of soil. We believe this is due to the fact that the researchers conducted this particular study in which the soil was mixed with microplastics in a 2:1 ratio. This significantly differs from real systems. Similarly, Chen et al. (Chen et al., 2021) examined the sorption of triclosan on polyethylene as well as the sorption of polystyrene microplastics on soil particles. The results showed that the sorption potential of the soil was notably lower than that of the microplastic, despite the ratio of soil to microplastic being 1:1. Thus, in order to obtain reliable data, it is crucial to conduct research on the actual amounts of microplastics that occur in agricultural fields. In our assumptions, we took into consideration the worst possible outcome in which the soil was enriched by as much as 10% wt. PS. According to many researchers, such an amount is seen as a significantly high level of microplastic contamination (De Souza Machado et al., 2018; Fuller and Gautam, 2016; Hüffer et al., 2019; Rillig, 2018; Yang et al., 2021). However, we believe that realistically, this contamination could be as low as 1% (Corradini et al., 2019; Katsumi et al., 2021; Scheurer and Bigalke, 2018; Vollertsen and Hansen, 2017; Zhang et al., 2018) (Figure 3). Nonetheless, regardless of the plastic concentration, it was the soil type which was the deciding factor in the sorption process.

Figure 3. Ranges of microplastic concentrations in soil analyzed by different authors

Table 4. Adsorption of cations [Chol] and [C_{12}Chol] as well as [2,4-D] anion in OECD soil, with PS.

 **[Chol][2,4-D]**			 **[C_{12}Chol][2,4-D]**	
System	**Adsorption [%]**			
	[Chol]	**[2,4-D]**	**[C_{12}Chol]**	**[2,4-D]**
1 % PS	16.8 ±0.4	0.0 ± 0.0	20.6 ± 0.5**	0.0 ± 0.0
2 % PS	16.1 ± 0.5	0.0 ± 0.0	18.9 ± 0.6**	0.0 ± 0.0
5 % PS	17.5 ± 0.6	0.0 ± 0.0	18.9 ±0.4**	0.0 ± 0.0
10 % PS	18.1 ± 0.4	0.0 ± 0.0	20.8 ± 0.4**	0.0 ± 0.0
OECD + 0 % PS*	43.8 ± 0.9	0.0 ± 0.0	94.8 ± 1.3**	0.0 ± 0.0
OECD + 1 % PS*	45.7 ± 1.0	0.0 ± 0.0	97.7 ± 1.7**	0.0 ± 0.0
OECD + 2 % PS*	46.7 ± 1.1	0.0 ± 0.0	97.8 ± 1.7**	0.0 ± 0.0
OECD + 5 % PS*	44.7 ± 0.8	0.0 ± 0.0	97.7 ± 1.7**	0.0 ± 0.0
OECD + 10 % PS*	46.9 ± 1.1	0.0 ± 0.0	97.9 ± 1.7**	0.0 ± 0.0
PP falcon	0.0 ± 0.0	0.0 ± 0.0	1.7 ± 0.2	0.0 ± 0.0

*soil OECD with % PS (w/w) addition

** The sorption values were reduced by the sorption on PP falcon, ± standard error of the mean of three independent experiments

3.2.4. Sorption of [2,4-D] anion on PS and OECD soil, (both with and without PS)

From the data, one can discern that the herbicidal anion was practically not sorbed in the analyzed soil sample (Table 4).

Moreover, the heightened mobility of 2,4-D in loam, silt-loam and sandy-loam soil was also discussed previously by other researchers (Brucha et al., 2021; Meftaul et al., 2020; Morillo et al., 2001). In certain studies, the sorption of the [2,4-D] anion at the 10 % level was described for herbicidal ILs with the use of betaine cations in a real agricultural soil (Woźniak-Karczewska et al., 2022). Moreover, in an agricultural soil, 2,4-D is capable of only low sorption due to the presence of specific minerals. In some instances, 2,4-D was even able to sorb, for example, onto quartz (Clausen et al., 2001). Furthermore, due to the presence of COO^- groups, the herbicide has been adsorbed onto the positive sites of an α-Al_2O_3 surface as well as that of calcite (Werner et al., 2013).

At present, there are only a few publications that have investigated the sorption of pesticides on polystyrene microplastics in a soil environment. Predominantly, the effects of microplastics (for example polyethylene beads, polyvinyl chloride, tire fragments) on 2,4-D, glyphosate and atrazine have been deeply analyzed in an aqueous environment (Fatema and Farenhorst, 2022). Certain authors have revealed a weak affinity for microplastics (< 6 %) for herbicides, except for the sorption of glyphosate on PVC (32-36 %) (Fatema and Farenhorst, 2022). This is not a surprising phenomenon, since glyphosate is capable of being sorbed between 30-40 % in the soil (Parus et al., 2023). However, it is worth mentioning that glyphosate is a zwitterion and, through the presence of a positive charge, it will interact with negative charges of soil constituents (Fliss et al., 2021). In Table 5, more information is presented on the sorption of the 2,4-D.

Table 5. [2,4-D] herbicide sorption on different types of soils as well as various microplastics.

2,4-D herbicide sorption	Tested system	Reference
No sorption, lack of integrity of the ion pair in the ionic liquid	OECD soil	This study
Constant low 2,4-D soil sorption (approx. 4-5 mg/kg), regardless of the hydrophobicity of the ionic liquid cation	fine-grained sandy loam type OL	Woźniak-Karczewska et al. (Woźniak-Karczewska et al., 2022)
Low 2,4-D sorption (K_D= 0.66 L/kg)	calcareous soil	Ozbay et al. (Ozbay et al., 2018)
Only 0.5 - 3.5 mg/kg 2,4-D sorption	sandy-loam and loamy-clay soils	Spark et al. (Spark K and Swift R, 2002)
q_{max} values for soils with low carbon content in range of 13-35 mg/kg	loam, silt-loam, clay, sandy-loam soils etc.	Meftaul et al. (Meftaul et al., 2020)
Less than 0.15 µg/L 2,4-D sorption	0.1 g of microplastics (i.e. fiber, polyethylene beads, polyvinyl chloride, and tire fragments)	Fatema et al. (Fatema and Farenhorst, 2022)

The partial sorption of the [Chol] cation and almost quantitative sorption of the [C_{12}Chol] cation did not substantially contribute to the sorption of the anion [2,4-D]. This is solid evidence that neither hydrophilic nor hydrophobic herbicidal IL cations have an effect on the sorption of the [2,4-D] anion. In fact, if the interactions between a cation and an anion in herbicidal ILs were sufficiently strong and formed an ionic pair, a retention effect of the anions should be observed. Similarly, the lack of impact of anions on the total sorption of imidazole-based ILs was examined by Dong et al. (Dong et al., 2018).

Moreover, a study conducted by Stepnowski et al (Mrozik et al., 2013, 2012; Stepnowski et al., 2007) reported that cations were strongly sorbed in the soil, while the simple inorganic anions, such as Cl^- or Br^-, were not analyzed and thus considered insignificant due to soil the properties.

Hence, the generalization that the sorption of the entire IL is dependent solely on the sorption of the cation can be deemed as inaccurate. The omission of the role of even a simple inorganic anion leaves a large gap in the understanding of the fate of ILs in the environment. This is why our research is so important as it shows that ILs, when introduced into the soil environment, act independently. Thus, our research can counter the present belief that ILs act as new, emerging contaminants as suggested in some reports (Oskarsson and Wright, 2019; Wei et al., 2021).

3.3. Sorption isotherms

In order to gain a more complete insight into the behavior of ILs, the analysis of cationic and anionic sorption isotherms was undertaken. Based on the OECD recommendations (Kowalska et al., 2021) as well as the published data, leading studies of the sorption of ILs have used the Freundlich isotherm (Krop et al., 2020). This model has been successfully applied in previous studies of the sorption of xenobiotics on microplastics (Elizalde-Velázquez et al., 2020; Hüffer et al., 2018; Wang et al., 2020) (Figure S1-S2 and Table S1- S2 in ESI). The position of the isotherms on the graphs representing both cations, namely [Chol] and [C_{12}Chol], allows us to conclude that there is no statistical differences in the sorption of both cations in the analyzed systems (both soil OECD and soil OECD with PS) (Figure 4).

Figure 4. Adsorption isotherms for [Chol] (a) and [C_{12}Chol] (b) cations for the OECD + 2 % PS system.

The calculated K_f values are commonly used in order to measure the efficiency of the adsorption process (Ozbay et al., 2018). One can see that there is a direct proportionality between the measured quantities, namely: the higher the K_f value, the higher the sorption of the analyzed xenobiotic (Peruchi et al., 2015). The hydrophilic [Chol] cation was sorbed in a weaker manner in comparison to the hydrophobic [C_{12}Chol] cation. Moreover, the addition of PS to the OECD soil contributed to an increase in K_f values from 3.8 to approx. 4.0-4.4 $mg^{1-1/n} L^{1/n}/g$ for [Chol] cation and from 281 to approx. 319-389 $mg^{1-1/n} L^{1/n}/g$ for [C_{12}Chol] cation. Nevertheless, for both cations, the following trend is visible: the K_f value increases incrementally from PS < OECD soil < OECD+PS soil systems as presented in Figure 5.

Analogously, studies performed by other researchers have also reported an increase in the K_f value in systems enriched with microplastics (Chen et al., 2022; Uber et al., 2019; Wang et al., 2020). For example, the logK_f for triclosan in soil was computed to be 2.20 $(\mu g/g)/(mg/L)^n$, while the addition of PS increased the logK_f to 2.83 $(\mu g/g)/(mg/L)^n$. Furthermore, the hydrophobic [C_{12}Chol] cation can potentially bind in an even stronger manner to the soil when PS is present. A similar trend was also noted for the hydrophilic [Chol] cation, but there were two orders of magnitude differences between the K_f values for the hydrophilic [Chol] cation and the hydrophobic [C_{12}Chol] cation (Figure 5). In other research, similar K_f values were reported for the investigation of the sorption of ILs based on the glyphosate anion, namely [Chol][Glyph] and [C_{12}Chol][Glyph] (Parus et al., 2023), as well as ILs based on the [Chol] cation and the dicamba herbicide in the soil (Parus et al., 2022).

Figure 5. K_f values determined for [Chol] (a) and [C_{12}Chol] (b) cations for PS and OECD soil, both with and without PS. Please note the different scales used on graphs (a) and (b).

It deserves to be mentioned that there are many studies that have been devoted to the sorption of xenobiotics on microplastics in aqueous environments (Fang et al., 2019; Guo et al., 2019; Guo and Wang, 2019; Lan et al., 2021; Liu et al., 2019).

Moreover, one should point out that surface active cations undergo specific interactions due to their amphiphilic structures. Essentially, these surfactants create micelles as well as aggregates that are held together through Van der Waals forces. In such a case, the presence of the anion has a very large influence on the shape of the generated micelle as well as the concentration of the micelles. Thus, this can cause an overriding effect on several interactions with various cells. Furthermore, the changes in the nanostructure (eg. the micelle or its aggregates) are not emphasised enough, since this can potentially lead to invalid observations. Should the nanostructure change, one can claim that the particular structural adjustment is due to the anion’s presence. In reality, it can be attributed to the different behaviour of the cation.

This is attributed to the fact that the IL is not analysed independently, but instead the ionic solution is assessed. It is important to note, that the unique properties of ILs result from the interaction between the cations and anions due to a disruption in the crystallographic structure. This can be especially seen when ILs are a liquid phase below a temperature 100 ºC.

Yet, when water is introduced into such a system, many of the present ions undergo solvation. This is particularly evident in solutions consisting of chlorides, bromides and quaternary ammonium cations. Resultingly, a mixture of anions and cations develops in the aqueous solutions.

It is indeed difficult to describe the toxicity of ILs if such unique interactions between cations and anions do not truly exist. There is a minimal number of scientific reports that have deeply investigated the study of the toxicity of hydrophobic ILs. Unfortunately, it is difficult to formulate an indestructible cation and anion pair, thus such studies are quite complex.

Moreover, hydrophilic ILs yield to dissociation and solvation processes. Only in the case of hydrophobic ILs, is it possible to expect strong interactions between the cations and anions. Yet, such a type of substance would be insoluble in water, hence creating a separate phase. This would therefore behave analogously to the common non-ionic pollutants, such as DDT or dioxins.

The issue of the integrity of ionic pairs can be applied further to the natural environment. The majority of ILs studied by researchers involved the introduction of quaternary ammonium cations with inorganic anions into the natural environment. This automatically means that in aqueous systems, we often witness the behaviour of cationic surface-active compounds or solvated cations, which have been described by previous research regarding the fate of cationic surface-active compounds in a natural setting.

It is very rare to analyse ILs in which the considered cation and anion were both organic substances and were traced simultaneously.

Nevertheless, it should be emphasized that the presence of microplastics in the soil can have a significant impact on the rate of other processes, such as the biodegradation of xenobiotics (Sun et al., 2018).

A notable example that can elucidate these mechanisms further, involves the studies of using ^{13}C herbicidal ILs (Wilms et al., 2020a). The analysis of the aqueous system as well as the soil, indicated that the cation and anion pair are indeed degraded and mineralised independently of each other. Hence, this suggests that in the environment, the interactions between cations and anions cease to exist. Thus, it is difficult to classify ILs as ionic liquids in the natural environment, since they are a mixture of separately acting cations and anions.

Moreover, further tests regarding the sorption were focused on the ability to influence the mobility of an organic anion through pairing it with an appropriate hydrophobic organic cation. The results supported the statement that hydrophobic cations are indeed sorbed in the soil. Simultaneously, the hydrophilic anions do not undergo any particular sorption changes. Likewise, it is necessary to emphasise that the results yielded for the sorption tests show that after ILs dissolve in water, they dissociate into ions which are subsequently solvated (Parus et al., 2023, 2022; Woźniak-Karczewska et al., 2022). There is no tangible proof to believe that such an occurrence is identical in every solvent; for example, in a methanol solvent, one can see a clear quantitative difference between the degree of dissociation and the degree of solvation. Yet, these are undeniably theoretical considerations since using any other solvent but water in the natural environment is completely impractical and unrealistic.

Also, NMR analyses seem to confirm that, in many cases, ILs are more molecular mixtures than actual ion pairs (Parus et al., 2023). The best example is the liquefaction of herbicides (Shamshina et al., 2021). Such studies step by step support the lack of interaction between IL cations and anions once they are introduced in the environment.

Similarly, our studies with polymers indicate that it is difficult to refer to such substances as ionic liquids, since the cations and anions behave entirely independently of each other.

Therefore, there is also a great need for further research on the sorption of xenobiotics in the soil in the presence of microplastics. This must be done in order to gain a better insight on the effects that the addition of microplastics have on the sorption processes.

At the moment, it seems that the definition of the aqueous solution of ionic liquids needs to be redefined or at least clarified, as probably most of these ILs are multicomponent pollutants which are typical of mixed systems, such as municipal wastewater, in which we can easily find a lot of organic cations and anions; certainly, we would not classify them as ionic liquids.

4. CONCLUSIONS

This undertaken research investigated the effect of the polystyrene microplastic on the sorption of two ionic liquids, namely [Chol][2,4-D] and [C_{12}Chol][2,4-D], in an OECD soil. The results presented here highlight the potential ability of polystyrene microplastics to alter the basic properties of the soil's physicochemical environment, which can promote further functional changes in the soil.

The introduction of PS microplastics contributed to an increase in the sorption capacity of the soil complex as well as a 3-5 % increase in the sorption of both cations. Moreover, the sorption analysis revealed that the type of soil has a decisive influence on the sorption efficiency for both [Chol] and [C_{12}Chol] cations.

A key finding in our research is that the [2,4-D] anion did not sorb in the soil system even after the addition of microplastics to the soil. This may indicate that the cations and anions, that together form an ionic liquid, are indeed two separately functioning entities in the soil environment.

Moreover, the cation sorption had no statistical effect on the [2,4-D] anion's sorption. Therefore, the unique interactions between cations and anions, which are essential in the establishing ILs, are no longer relevant in the sorption on negatively charged soil components. This is compelling evidence, that in the soil environment, the choline-based ionic liquids and the [2,4-D] herbicide do not form an ionic pair. Hence, they undergo physicochemical processes as independent cations and anions. It is worth noting that when planning studies using microplastics, the detailed physicochemical characteristics of such potential sorption material should be taken into account, as it is crucial. We certainly hope that the above study will bring to the foreground the need for further scientific research of ILs, additionally raising the issue of the undeniable stability of ionic liquids in the natural environment.

5. ACKNOWLEDGMENTS

This article has been written and developed due to OPUS 21, funded by the National Science Centre in Poland, conferred on the basis of decision DEC-2021/41/B/NZ9/03981. The subsequent grant title is: "Multilevel relationships between the presence of micro/nanoplastics (MNPs) in soil and the amount and availability of water as well as sorption of model xenobiotics in terms of changes in biodegradation kinetics and soil microbial communities". Funds from the Poznan University of Technology for student and doctoral activities are also appreciated.

6. REFERENCES

Arias-Estévez, M., López-Periago, E., Martínez-Carballo, E., Simal-Gándara, J., Mejuto, J.-C., García-Río, L., 2008. The mobility and degradation of pesticides in soils and the pollution of groundwater resources. Agric. Ecosyst. Environ. 123, 247–260. https://doi.org/10.1016/j.agee.2007.07.011

Bernardes, M.F.F., Pazin, M., Pereira, L.C., Dorta, D.J., 2015. Impact of Pesticides on Environmental and Human Health, in: Toxicology Studies - Cells, Drugs and Environment. InTech. https://doi.org/10.5772/59710

Bläsing, M., Amelung, W., 2018. Plastics in soil: Analytical methods and possible sources. Sci. Total Environ. 612, 422–435. https://doi.org/10.1016/j.scitotenv.2017.08.086

Bouchard, D.C., Lavy, T.L., 1985. Hexazinone Adsorption-Desorption Studies with Soil and Organic Adsorbents. J. Environ. Qual. 14, 181–186. https://doi.org/10.2134/jeq1985.00472425001400020006x

Bouras, O., Bollinger, J.-C., Baudu, M., 2010. Effect of humic acids on pentachlorophenol sorption to cetyltrimethylammonium-modified, Fe- and Al-pillared montmorillonites. Appl. Clay Sci. 50, 58–63. https://doi.org/10.1016/j.clay.2010.07.002

Brucha, G., Aldas-Vargas, A., Ross, Z., Peng, P., Atashgahi, S., Smidt, H., Langenhoff, A., Sutton, N.B., 2021. 2,4-Dichlorophenoxyacetic acid degradation in methanogenic mixed cultures obtained from Brazilian Amazonian soil samples. Biodegradation 32, 419–433. https://doi.org/10.1007/s10532-021-09940-3

Chen, X., Gu, X., Bao, L., Ma, S., Mu, Y., 2021. Comparison of adsorption and desorption of triclosan between microplastics and soil particles. Chemosphere 263, 127947. https://doi.org/10.1016/j.chemosphere.2020.127947

Chen, Xian, Liang, J., Bao, L., Gu, X., Zha, S., Chen, Xingming, 2022. Competitive and cooperative sorption between triclosan and methyl triclosan on microplastics and soil. Environ. Res. 212, 113548. https://doi.org/10.1016/j.envres.2022.113548

Chestworth, W. (Ed.), 2008. Encyclopedia of Soil Science, Encycloped. ed. Springer International Publishing, Dordrecht, Netherlands.

Choudhary, H., Pernak, J., Shamshina, J.L., Niemczak, M., Giszter, R., Chrzanowski, Ł., Praczyk, T., Marcinkowska, K., Cojocaru, O.A., Rogers, R.D., 2017. Two Herbicides in a Single Compound: Double Salt Herbicidal Ionic Liquids Exemplified with Glyphosate, Dicamba, and MCPA. ACS Sustain. Chem. Eng. 5, 6261–6273. https://doi.org/10.1021/acssuschemeng.7b01224

Clausen, L., Fabricius, I., Madsen, L., 2001. Adsorption of Pesticides onto Quartz, Calcite, Kaolinite, and α-Alumina. J. Environ. Qual. 30, 846–857. https://doi.org/10.2134/jeq2001.303846x

Corradini, F., Meza, P., Eguiluz, R., Casado, F., Huerta-Lwanga, E., Geissen, V., 2019. Evidence of microplastic accumulation in agricultural soils from sewage sludge disposal. Sci. Total Environ. 671, 411–420. https://doi.org/10.1016/j.scitotenv.2019.03.368

Curran, W.S., 2016. Persistence of herbicides in soil. Crop. Soils 49, 16–21. https://doi.org/10.2134/cs2016-49-0504

de Souza Machado, A.A., Lau, C.W., Kloas, W., Bergmann, J., Bachelier, J.B., Faltin, E., Becker, R., Görlich, A.S., Rillig, M.C., 2019. Microplastics Can Change Soil Properties and Affect Plant Performance. Environ. Sci. Technol. 53, 6044–6052. https://doi.org/10.1021/acs.est.9b01339

De Souza Machado, A.A., Lau, C.W., Till, J., Kloas, W., Lehmann, A., Becker, R., Rillig, M.C., 2018. Impacts of Microplastics on the Soil Biophysical Environment. Environ. Sci. Technol. 52, 9656–9665. https://doi.org/10.1021/acs.est.8b02212

Dong, Z., Wei, L., Xu, S., Sun, J., Shi, X., Qiu, Y., 2018. Transport of imidazolium-based ionic liquids with different anion/cation species in sand/soil columns. Ecotoxicol. Environ. Saf. 147, 480–486. https://doi.org/10.1016/j.ecoenv.2017.09.006

Duke, S.O., 2012. Why have no new herbicide modes of action appeared in recent years? Pest Manag. Sci. 68, 505–512. https://doi.org/10.1002/ps.2333

Earle, M.J., Seddon, K.R., 2000. Ionic liquids. Green solvents for the future. Pure Appl. Chem. 72, 1391–1398. https://doi.org/10.1351/pac200072071391

Elizalde-Velázquez, A., Subbiah, S., Anderson, T.A., Green, M.J., Zhao, X., Cañas-Carrell, J.E., 2020.

Sorption of three common nonsteroidal anti-inflammatory drugs (NSAIDs) to microplastics. Sci. Total Environ. 715, 136974. https://doi.org/10.1016/j.scitotenv.2020.136974

Fang, S., Yu, W., Li, C., Liu, Y., Qiu, J., Kong, F., 2019. Adsorption behavior of three triazole fungicides on polystyrene microplastics. Sci. Total Environ. 691, 1119–1126. https://doi.org/10.1016/j.scitotenv.2019.07.176

Fantke, P. Bijster, M. Guignard, C. Hauschild, M. Huijbregts, M. Jolliet, O. Kounina, A. Magaud, V. Margni, M. McKone, T. Posthuma, L. Rosenbaum, R.K. van de Meent, D. van Zelm, R., 2017. USEtox® 2.0 Documentation.

Fatema, M., Farenhorst, A., 2022. Sorption of pesticides by microplastics, charcoal, ash, and river sediments. J. Soils Sediments 22, 1876–1884. https://doi.org/10.1007/s11368-022-03218-8

Fliss, O., Essalah, K., Ben Fredj, A., 2021. Stabilization of glyphosate zwitterions and conformational/tautomerism mechanism in aqueous solution: insights from ab initio and density functional theory-continuum model calculations. Phys. Chem. Chem. Phys. 23, 26306–26323. https://doi.org/10.1039/D1CP03161A

Fuller, S., Gautam, A., 2016. A Procedure for Measuring Microplastics using Pressurized Fluid Extraction. Environ. Sci. Technol. 50, 5774–5780. https://doi.org/10.1021/acs.est.6b00816

Galloway, T.S., Cole, M., Lewis, C., 2017. Interactions of microplastic debris throughout the marine ecosystem. Nat. Ecol. Evol. 1, 0116. https://doi.org/10.1038/s41559-017-0116

Gamboa, C., Olea, A.F., 2006. Association of cationic surfactants to humic acid. Colloids Surfaces A Physicochem. Eng. Asp. 278, 241–245. https://doi.org/10.1016/j.colsurfa.2005.12.026

Gangadoo, S., Owen, S., Rajapaksha, P., Plaisted, K., Cheeseman, S., Haddara, H., Truong, V.K., Ngo, S.T., Vu, V. V., Cozzolino, D., Elbourne, A., Crawford, R., Latham, K., Chapman, J., 2020. Nano-plastics and their analytical characterisation and fate in the marine environment: From source to sea. Sci. Total Environ. 732, 138792. https://doi.org/10.1016/j.scitotenv.2020.138792

Gong, W., Jiang, M., Han, P., Liang, G., Zhang, T., Liu, G., 2019. Comparative analysis on the sorption kinetics and isotherms of fipronil on nondegradable and biodegradable microplastics. Environ. Pollut. 254, 112927. https://doi.org/10.1016/j.envpol.2019.07.095

Guo, X., Wang, J., 2019. Sorption of antibiotics onto aged microplastics in freshwater and seawater.

Mar. Pollut. Bull. 149, 110511. https://doi.org/10.1016/j.marpolbul.2019.110511

Hu, B., Li, Y., Jiang, L., Chen, X., Wang, L., An, S., Zhang, F., 2020. Influence of microplastics occurrence on the adsorption of 17β-estradiol in soil. J. Hazard. Mater. 400, 123325. https://doi.org/10.1016/j.jhazmat.2020.123325

Hüffer, T., Metzelder, F., Sigmund, G., Slawek, S., Schmidt, T.C., Hofmann, T., 2019. Polyethylene microplastics influence the transport of organic contaminants in soil. Sci. Total Environ. 657, 242–247. https://doi.org/10.1016/j.scitotenv.2018.12.047

Hüffer, T., Weniger, A.-K., Hofmann, T., 2018. Sorption of organic compounds by aged polystyrene microplastic particles. Environ. Pollut. 236, 218–225. https://doi.org/10.1016/j.envpol.2018.01.022

Ishiguro, M., Koopal, L.K., 2016. Surfactant adsorption to soil components and soils. Adv. Colloid Interface Sci. 231, 59–102. https://doi.org/10.1016/j.cis.2016.01.006

Jaremko, D., Kalembasa, D., 2014. A Comparison of Methods for the Determination of Cation Exchange Capacity of Soils. Ecol. Chem. Eng. S 21, 487–498. https://doi.org/10.2478/eces-2014-0036

Joo, S.H., Liang, Y., Kim, M., Byun, J., Choi, H., 2021. Microplastics with adsorbed contaminants: Mechanisms and Treatment. Environ. Challenges 3, 100042. https://doi.org/10.1016/j.envc.2021.100042

Kappen, H., 1929. Die Bodenazidität Nach Agrikulturchemischen Gesichtspunkten Dargestellt. Springer Berlin (Verlag).

Katsumi, N., Kusube, T., Nagao, S., Okochi, H., 2021. Accumulation of microcapsules derived from coated fertilizer in paddy fields. Chemosphere 267, 129185. https://doi.org/10.1016/j.chemosphere.2020.129185

Kowalska, D., Maculewicz, J., Stepnowski, P., Dołżonek, J., 2021. Ionic liquids as environmental hazards – Crucial data in view of future PBT and PMT assessment. J. Hazard. Mater. 403, 123896. https://doi.org/10.1016/j.jhazmat.2020.123896

Krop, H., de Voogt, P., Eschauzier, C., Droge, S., 2020. Sorption of surfactants onto sediment at environmentally relevant concentrations: independent-mode as unifying concept. Environ. Sci. Process. Impacts 22, 1266–1286. https://doi.org/10.1039/C9EM00580C

Li, J., Guo, K., Cao, Y., Wang, S., Song, Y., Zhang, H., 2021. Enhance in mobility of oxytetracycline in a sandy loamy soil caused by the presence of microplastics. Environ. Pollut. 269, 116151. https://doi.org/10.1016/j.envpol.2020.116151

Li, S., Ma, R., Zhu, X., Liu, C., Li, L., Yu, Z., Chen, X., Li, Z., Yang, Y., 2021. Sorption of tetrabromobisphenol A onto microplastics: Behavior, mechanisms, and the effects of sorbent and environmental factors. Ecotoxicol. Environ. Saf. 210, 111842. https://doi.org/10.1016/j.ecoenv.2020.111842

Li, Z., Gallus, L., 2007. Adsorption of dodecyl trimethylammonium and hexadecyl trimethylammonium onto kaolinite — Competitive adsorption and chain length effect. Appl. Clay Sci. 35, 250–257. https://doi.org/10.1016/j.clay.2006.09.004

Liu, Z., Zhao, G., Brewer, M., Lv, Q., Sudhölter, E.J.R., 2021. Comprehensive review on surfactant adsorption on mineral surfaces in chemical enhanced oil recovery. Adv. Colloid Interface Sci. 294, 102467. https://doi.org/10.1016/j.cis.2021.102467

Lv, Weiwei, Zhou, W., Lu, S., Huang, W., Yuan, Q., Tian, M., Lv, Weiguang, He, D., 2019. Microplastic pollution in rice-fish co-culture system: A report of three farmland stations in Shanghai, China. Sci. Total Environ. 652, 1209–1218. https://doi.org/10.1016/j.scitotenv.2018.10.321

Maculewicz, J., Świacka, K., Stepnowski, P., Dołżonek, J., Białk-Bielińska, A., 2022. Ionic liquids as potentially hazardous pollutants: Evidences of their presence in the environment and recent analytical developments. J. Hazard. Mater. 437, 129353. https://doi.org/10.1016/j.jhazmat.2022.129353

Marcinkowska, K., Praczyk, T., Gawlak, M., Niemczak, M., Pernak, J., 2017. Efficacy of herbicidal ionic liquids and choline salt based on 2,4-D. Crop Prot. 98, 85–93. https://doi.org/10.1016/j.cropro.2017.03.011

Meftaul, I.M., Venkateswarlu, K., Dharmarajan, R., Annamalai, P., Megharaj, M., 2020. Movement and Fate of 2,4-D in Urban Soils: A Potential Environmental Health Concern. ACS Omega 5, 13287–13295. https://doi.org/10.1021/acsomega.0c01330

Morillo, E., Pérez-Martínez, J.I., Ginés, J.M., 2001. Leaching of 2,4-D from a soil in the presence of βcyclodextrin: laboratory columns experiments. Chemosphere 44, 1065–1069. https://doi.org/10.1016/S0045-6535(00)00346-5

Mrozik, W., Jungnickel, C., Ciborowski, T., Pitner, W.R., Kumirska, J., Kaczyński, Z., Stepnowski, P., 2009. Predicting mobility of alkylimidazolium ionic liquids in soils. J. Soils Sediments 9, 237–245. https://doi.org/10.1007/s11368-009-0057-1

Mrozik, W., Jungnickel, C., Paszkiewicz, M., Stepnowski, P., 2013. Interaction of Novel Ionic Liquids with Soils. Water, Air, Soil Pollut. 224, 1759. https://doi.org/10.1007/s11270-013-1759-y

Mrozik, W., Kotłowska, A., Kamysz, W., Stepnowski, P., 2012. Sorption of ionic liquids onto soils: Experimental and chemometric studies. Chemosphere 88, 1202–1207. https://doi.org/10.1016/j.chemosphere.2012.03.070

Nicolopoulou-Stamati, P., Maipas, S., Kotampasi, C., Stamatis, P., Hens, L., 2016. Chemical Pesticides and Human Health: The Urgent Need for a New Concept in Agriculture. Front. Public Heal. 4. https://doi.org/10.3389/fpubh.2016.00148

Niu, J., Zhang, Z., Tang, J., Tang, G., Yang, J., Wang, W., Huo, H., Jiang, N., Li, J., Cao, Y., 2018. Dicationic Ionic Liquids of Herbicide 2,4-Dichlorophenoxyacetic Acid with Reduced Negative Effects on Environment. J. Agric. Food Chem. 66, 10362–10368. https://doi.org/10.1021/acs.jafc.8b02584

Nizzetto, L., Futter, M., Langaas, S., 2016. Are Agricultural Soils Dumps for Microplastics of Urban Origin? Environ. Sci. Technol. 50, 10777–10779. https://doi.org/10.1021/acs.est.6b04140

OECD/OCDE 106. Adsorption - Desorption Using a Batch Equilibrium Method., 2000.

Oskarsson, A., Wright, M.C., 2019. Ionic Liquids: New Emerging Pollutants, Similarities with Perfluorinated Alkyl Substances (PFASs). Environ. Sci. Technol. 53, 10539–10541. https://doi.org/10.1021/acs.est.9b04778

Ozbay, B., Akyol, N.H., Akyol, G., Ozbay, I., 2018. Sorption and desorption behaviours of 2,4-D and glyphosate in calcareous soil from Antalya, Turkey. Water Environ. J. 32, 141–148. https://doi.org/10.1111/wej.12311

Pan, M., Chu, L.M., 2016. Adsorption and degradation of five selected antibiotics in agricultural soil. Sci. Total Environ. 545–546, 48–56. https://doi.org/10.1016/j.scitotenv.2015.12.040

Parus, A., Lisiecka, N., Zembrzuska, J., Framski, G., Woźniak-Karczewska, M., Niemczak, M., 2022. Evaluation of the influence of different cations on the mobility and performance of dicamba-based ionic liquids. J. Environ. Chem. Eng. 10, 108397. https://doi.org/10.1016/j.jece.2022.108397

Parus, A., Zdebelak, O., Ciesielski, T., Szumski, R., Woźniak-Karczewska, M., Framski, G., Baranowski, D., Niemczak, M., Zembrzuska, J., Cajthaml, T., Heipieper, H.J., Chrzanowski, Ł., 2023. Can ionic liquids exist in the soil environment? Effect of quaternary ammonium cations on glyphosate sorption, mobility and toxicity in the selected herbicidal ionic liquids. J. Mol. Liq. 370, 120981. https://doi.org/10.1016/j.molliq.2022.120981

Pernak, J., Kaczmarek, D.K., Rzemieniecki, T., Niemczak, M., Chrzanowski, Ł., Praczyk, T., 2020. Dicamba-Based Herbicides: Herbicidal Ionic Liquids versus Commercial Forms. J. Agric. Food Chem. 68, 4588–4594. https://doi.org/10.1021/acs.jafc.0c00632

Peruchi, L.M., Fostier, A.H., Rath, S., 2015. Sorption of norfloxacin in soils: Analytical method, kinetics and Freundlich isotherms. Chemosphere 119, 310–317. https://doi.org/10.1016/j.chemosphere.2014.06.008

Piotrowska, A., Syguda, A., Wyrwas, B., Chrzanowski, Ł., Heipieper, H.J., 2017. Toxicity evaluation of selected ammonium-based ionic liquid forms with MCPP and dicamba moieties on Pseudomonas putida. Chemosphere 167, 114–119. https://doi.org/10.1016/j.chemosphere.2016.09.140

Piotrowska, A., Syguda, A., Wyrwas, B., Chrzanowski, L., Luckenbach, T., Heipieper, H.J., 2018. Effects of ammonium-based ionic liquids and 2,4-dichlorophenol on the phospholipid fatty acid composition of zebrafish embryos. PLoS One 13, e0190779. https://doi.org/10.1371/journal.pone.0190779

Praczyk, T., Kardasz, P., Jakubiak, E., Syguda, A., Materna, K., Pernak, J., 2012. Herbicidal Ionic Liquids with 2,4-D. Weed Sci. 60, 189–192. https://doi.org/10.1614/WS-D-11-00171.1

Randviir, E.P., Brownson, D.A.C., Banks, C.E., 2014. A decade of graphene research: production, applications and outlook. Mater. Today 17, 426–432. https://doi.org/10.1016/j.mattod.2014.06.001

Rillig, M.C., 2018. Microplastic Disguising As Soil Carbon Storage. Environ. Sci. Technol. 52, 6079–

6080. https://doi.org/10.1021/acs.est.8b02338

Sarkar, A.K., Rubin, A.E., Zucker, I., 2021. Engineered Polystyrene-Based Microplastics of High Environmental Relevance. Environ. Sci. Technol. 55, 10491–10501. https://doi.org/10.1021/acs.est.1c02196

Scheurer, M., Bigalke, M., 2018. Microplastics in Swiss Floodplain Soils. Environ. Sci. Technol. 52, 3591–3598. https://doi.org/10.1021/acs.est.7b06003

Shen, G., Zhang, Y., Hu, S., Zhang, H., Yuan, Z., Zhang, W., 2018. Adsorption and degradation of sulfadiazine and sulfamethoxazole in an agricultural soil system under an anaerobic condition: Kinetics and environmental risks. Chemosphere 194, 266–274. https://doi.org/10.1016/j.chemosphere.2017.11.175

Spark K, Swift R, 2002. Effect of soil composition and dissolved organic matter on pesticide sorption. Sci. Total Environ. 298, 147–161. https://doi.org/10.1016/S0048-9697(02)00213-9

Stepnowski, P., Mrozik, W., Nichthauser, J., 2007. Adsorption of Alkylimidazolium and Alkylpyridinium Ionic Liquids onto Natural Soils. Environ. Sci. Technol. 41, 511–516. https://doi.org/10.1021/es062014w

Šunta, U., Prosenc, F., Trebše, P., Bulc, T.G., Kralj, M.B., 2020. Adsorption of acetamiprid, chlorantraniliprole and flubendiamide on different type of microplastics present in alluvial soil. Chemosphere 261, 127762. https://doi.org/10.1016/j.chemosphere.2020.127762

Talapin, D. V., Shevchenko, E. V., 2016. Introduction: Nanoparticle Chemistry. Chem. Rev. 116, 10343–10345. https://doi.org/10.1021/acs.chemrev.6b00566

Uber, T.H., Hüffer, T., Planitz, S., Schmidt, T.C., 2019. Sorption of non-ionic organic compounds by polystyrene in water. Sci. Total Environ. 682, 348–355. https://doi.org/10.1016/j.scitotenv.2019.05.040

Vollertsen, J., Hansen, A.A., 2017. Microplastic in Danish wastewater: Sources, ocurrences and fate. Danish Environ. Prot. Agency 1–39.

Wang, T., Yu, C., Chu, Q., Wang, F., Lan, T., Wang, J., 2020. Adsorption behavior and mechanism of five pesticides on microplastics from agricultural polyethylene films. Chemosphere 244, 125491. https://doi.org/10.1016/j.chemosphere.2019.125491

Wei, P., Pan, X., Chen, C.-Y., Li, H.-Y., Yan, X., Li, C., Chu, Y.-H., Yan, B., 2021. Emerging impacts of ionic liquids on eco-environmental safety and human health. Chem. Soc. Rev. 50, 13609–13627. https://doi.org/10.1039/D1CS00946J

Welton, T., 2011. Ionic liquids in Green Chemistry. Green Chem. 13, 225. https://doi.org/10.1039/c0gc90047h

Werner, D., Garratt, J.A., Pigott, G., 2013. Sorption of 2,4-D and other phenoxy herbicides to soil, organic matter, and minerals. J. Soils Sediments 13, 129–139. https://doi.org/10.1007/s11368-012-0589-7

Wilms, W., Woźniak-Karczewska, M., Syguda, A., Niemczak, M., Ławniczak, Ł., Pernak, J., Rogers, R.D., Chrzanowski, Ł., 2020. Herbicidal Ionic Liquids: A Promising Future for Old Herbicides? Review on Synthesis, Toxicity, Biodegradation, and Efficacy Studies. J. Agric. Food Chem. 68, 10456–10488. https://doi.org/10.1021/acs.jafc.0c02894

Woźniak-Karczewska, M., Parus, A., Ciesielski, T., Trzebny, A., Szumski, R., Wilms, W., Homa, J., Framski, G., Baranowski, D., Frankowski, R., Zgoła-Grześkowiak, A., Niemczak, M., Dabert, M., Táncsics, A., Chrzanowski, Ł., 2022. Effect of Cation Sorption on 2,4-D Mobility of Herbicidal Ionic Liquids in Agricultural Soil Combined with Diversity of the Bacterial Community. ACS Sustain. Chem. Eng. 10, 12559–12568. https://doi.org/10.1021/acssuschemeng.2c02665

Xu, B., Liu, F., Brookes, P.C., Xu, J., 2018. Microplastics play a minor role in tetracycline sorption in the presence of dissolved organic matter. Environ. Pollut. 240, 87–94. https://doi.org/10.1016/j.envpol.2018.04.113

Yang, W., Cheng, P., Adams, C.A., Zhang, S., Sun, Y., Yu, H., Wang, F., 2021. Effects of microplastics on plant growth and arbuscular mycorrhizal fungal communities in a soil spiked with ZnO nanoparticles. Soil Biol. Biochem. 155, 108179. https://doi.org/10.1016/j.soilbio.2021.108179

Yu, Y., Flury, M., 2021. Current understanding of subsurface transport of micro- and nanoplastics in soil. Vadose Zo. J. 20. https://doi.org/10.1002/vzj2.20108

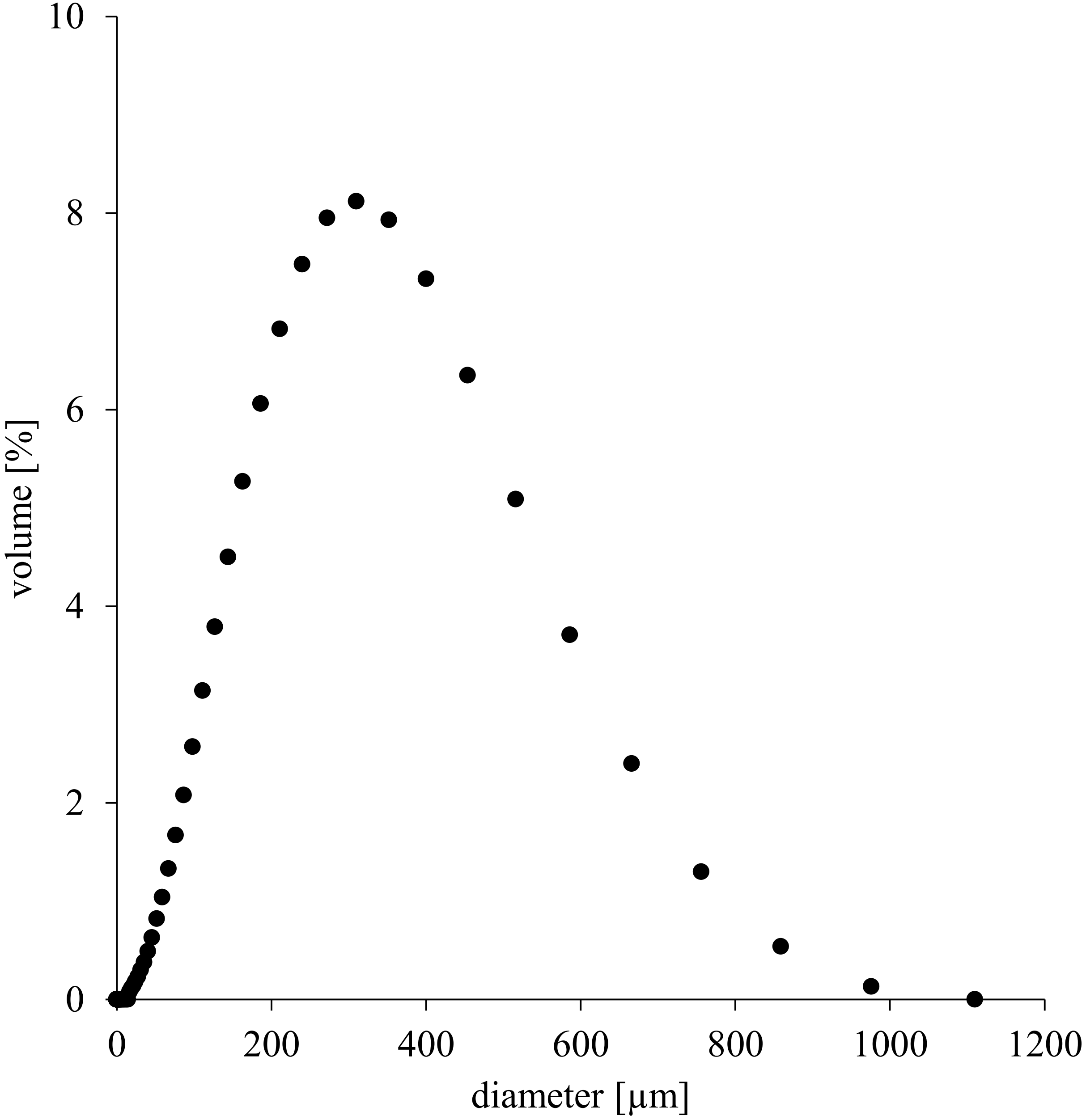
Zhan, Y., Lin, J., Li, J., 2013. Preparation and characterization of surfactant-modified hydroxyapatite/zeolite composite and its adsorption behavior toward humic acid and copper(II). Environ. Sci. Pollut. Res. 20, 2512–2526. https://doi.org/10.1007/s11356-012-1136-1

Zhang, G.S., Liu, Y.F., 2018. The distribution of microplastics in soil aggregate fractions in southwestern China. Sci. Total Environ. 642, 12–20. https://doi.org/10.1016/j.scitotenv.2018.06.004

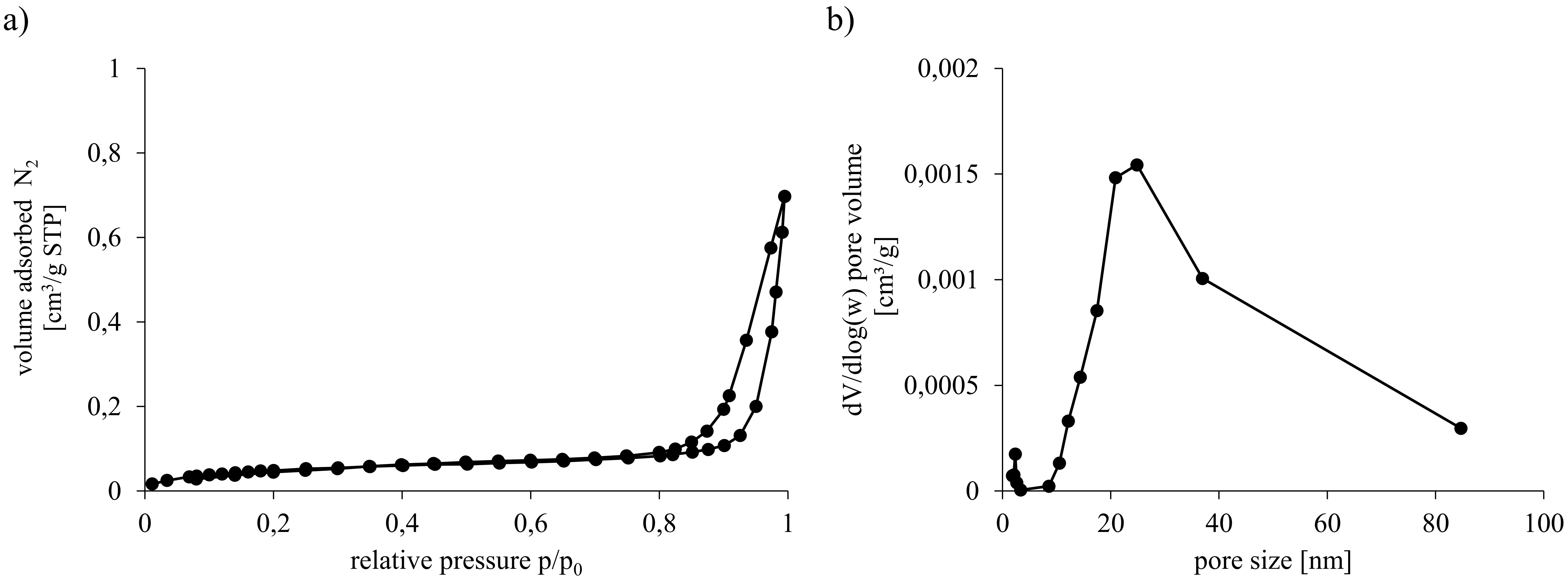
Zhang, S., Yang, X., Gertsen, H., Peters, P., Salánki, T., Geissen, V., 2018. A simple method for the extraction and identification of light density microplastics from soil. Sci. Total Environ. 616–617, 1056–1065. https://doi.org/10.1016/j.scitotenv.2017.10.213

Zhu, J., Ding, G., Liu, Y., Wang, B., Zhang, W., Guo, M., Geng, Q., Cao, Y., 2015. Ionic liquid forms of clopyralid with increased efficacy against weeds and reduced leaching from soils. Chem. Eng. J. 279, 472–477. https://doi.org/10.1016/j.cej.2015.05.025

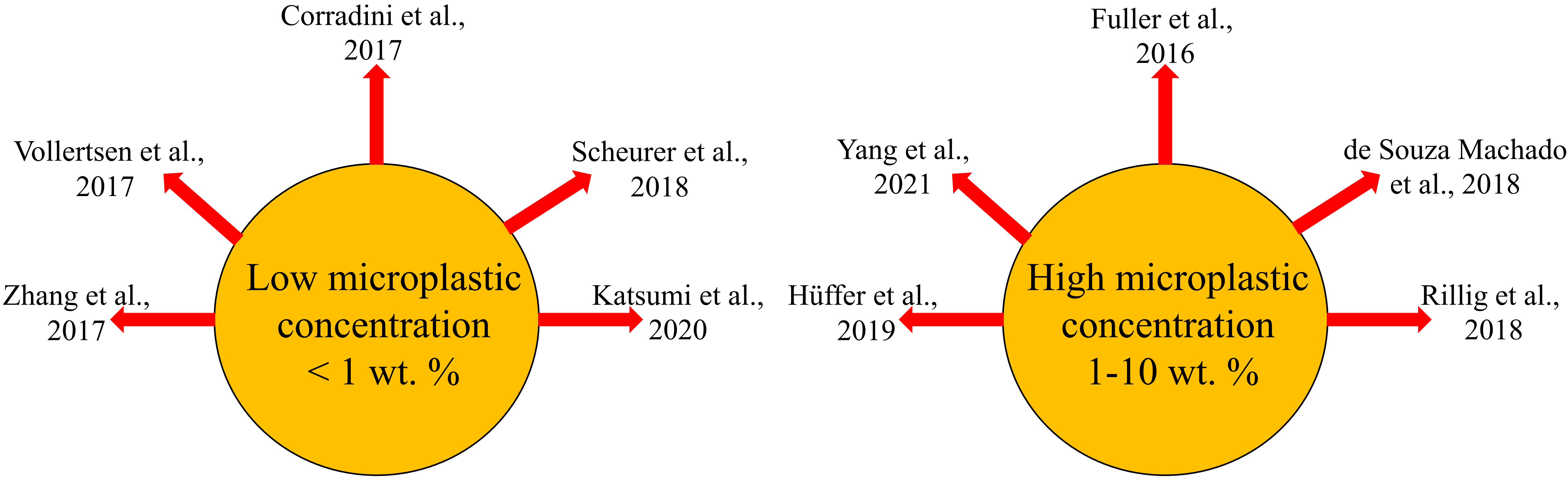
Figure



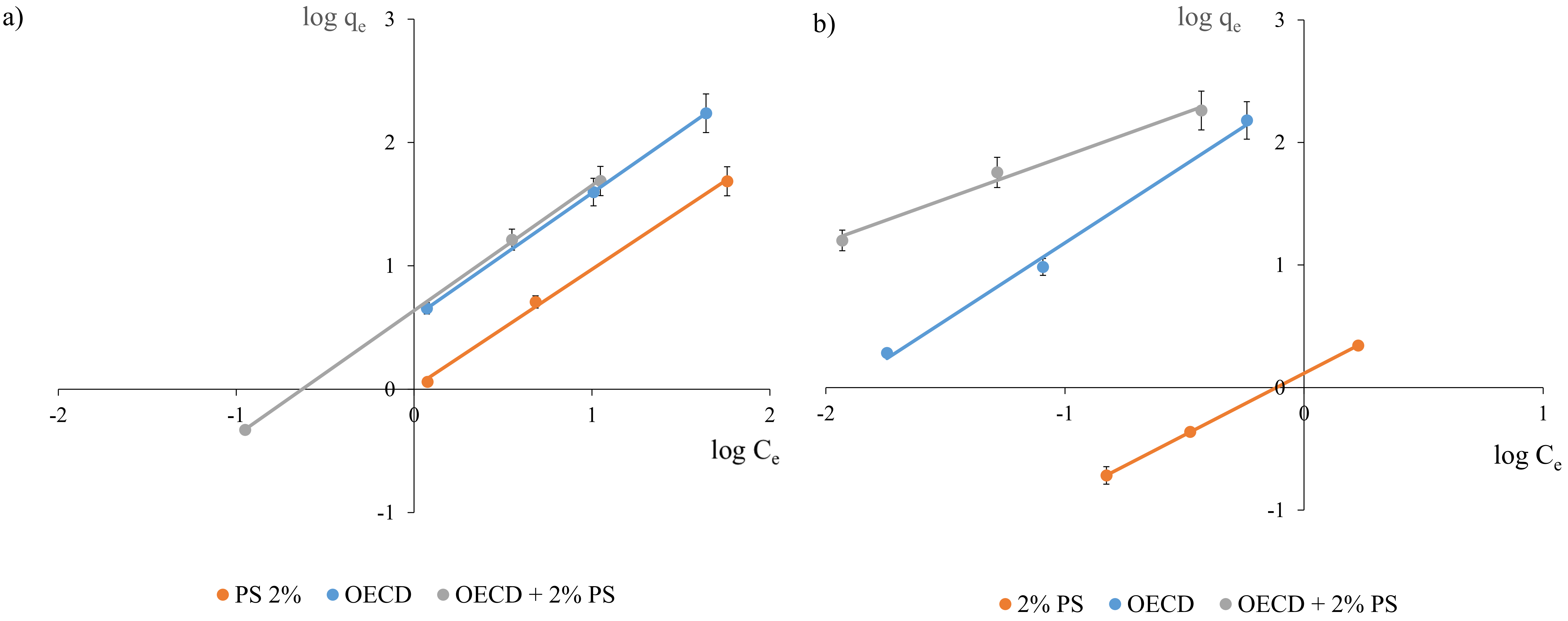
Figure


a)
1
0,8
0,6
0,4
0,2
0
volume adsorbed N_2
[cm³/g STP]
0
0,2
0,4
0,6
0,8
1
relative pressure p/p_0
b)
0,002
0,0015
0,001
0,0005
0
dV/dlog(w) pore volume
[cm³/g]
0
20
40
60
80
100
pore size [nm]

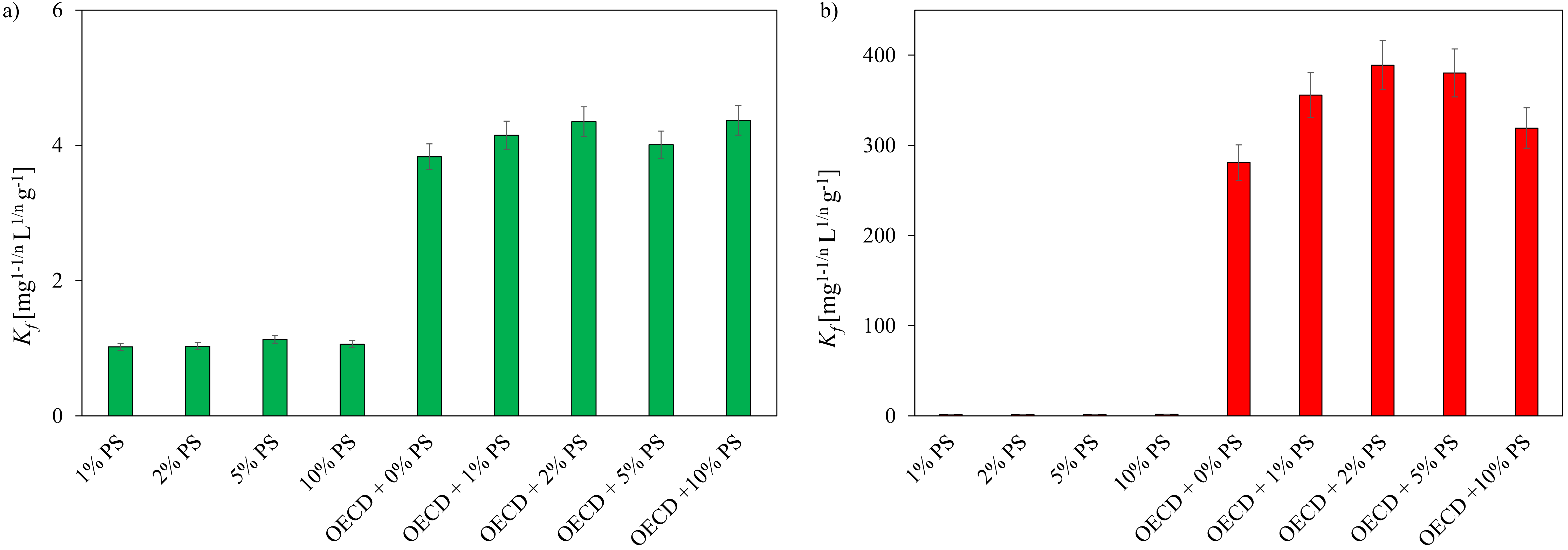
Figure


Low microplastic concentration < 1 wt. %
Corradini et al., 2017
Vollertsen et al., 2017
Scheurer et al., 2018
Zhang et al., 2017
Katsumi et al., 2020
High microplastic concentration 1-10 wt. %
Fuller et al., 2016
Yang et al., 2021
de Souza Machado et al., 2018
Hüffer et al., 2019
Rillig et al., 2018

Figure


a)
log q_e
3
2
1
0
-1
-2
-1
0
1
2
log C_e
● PS 2%
● OECD
● OECD + 2% PS
b)
log q_e
3
2
1
0
-1
-2
-1
0
1
log C_e
● 2% PS
● OECD
● OECD + 2% PS

Figure



a)
K_f [mg$^{1-1/n}$ L$^{1/n}$ g^{-1}]
0
2
4
6
1% PS
2% PS
5% PS
10% PS
OECD + 0% PS
OECD + 1% PS
OECD + 2% PS
OECD + 5% PS
OECD +10% PS
b)
K_f [mg$^{1-1/n}$ L$^{1/n}$ g^{-1}]
0
100
200
300
400
1% PS
2% PS
5% PS
10% PS
OECD + 0% PS
OECD + 1% PS
OECD + 2% PS
OECD + 5% PS
OECD +10% PS