

# Transport parameters of selected neonicotinoids in different aquifer materials using batch sorption tests

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**Abstract:** Contamination of surface and groundwater by neonicotinoids is a global problem and requires comprehensive action by individual countries in order to identify in detail the processes affecting the transport of these pesticides, their properties, and their harmfulness to the environment. The aim of this study was to assess the transport (expressed by sorption parameters) of selected neonicotinoids in the aquatic environment, using batch tests. Tests were carried out for acetamiprid individually and a mixture of five neonicotinoids (acetamiprid, clothianidin, imidacloprid, thiacloprid, and thiamethoxam), for three different aquifer materials and quartz sand. Based on the obtained values of the sorption parameters, the greatest sorption of neonicotinoids was observed on soil with the highest content of organic matter and clay minerals content, while no sorption of these pesticides was observed on quartz sand. In addition, it was noticed that individual neonicotinoids undergo sorption to a different degree — thiacloprid was the most sorbed ( $R$ -value in the range 3.13–26.03), while thiamethoxam was the least ( $R$ -value in the range 1.89–8.41).

**Keywords:** pesticides, neonicotinoids, transport parameters, sorption, batch tests, soil

## INTRODUCTION

Water is a vital natural resource, one crucial for all living organisms and for multiple human activities including domestic uses, agriculture, and industry. However, many contaminants end up in the aquatic environment – groundwater and surface waters, and consequently also in drinking water.

Increasing global attention is being paid to Emerging Contaminants (ECs). The pollution of the water caused by ECs is now a worldwide environmental problem. According to the reports of the US Environmental Protection Agency (EPA) (Ankley et al. 2008) and the authors of numerous publications, ECs pollutants are increasingly detected at

low concentrations ranging from nano- to micrograms per litre in surface and groundwater. Therefore, there is a concern that these compounds may affect organisms living in the aquatic environment and the quality of drinking water (Hladik et al. 2014, Nham et al. 2015, Sultana et al. 2018, Dragon et al. 2019, Sousa et al. 2019).

One of the groups of substances of ECs are pesticides. Pesticides are a broad class of chemicals used to reduce, inhibit, and/or prevent the growth of harmful animals, insects, weeds, invasive plants, and fungi. Pesticides classified according to the target organism include, among others, herbicides, bactericides, fungicides, or zoocides, i.e., insecticides and rodenticides (Fig. 1).

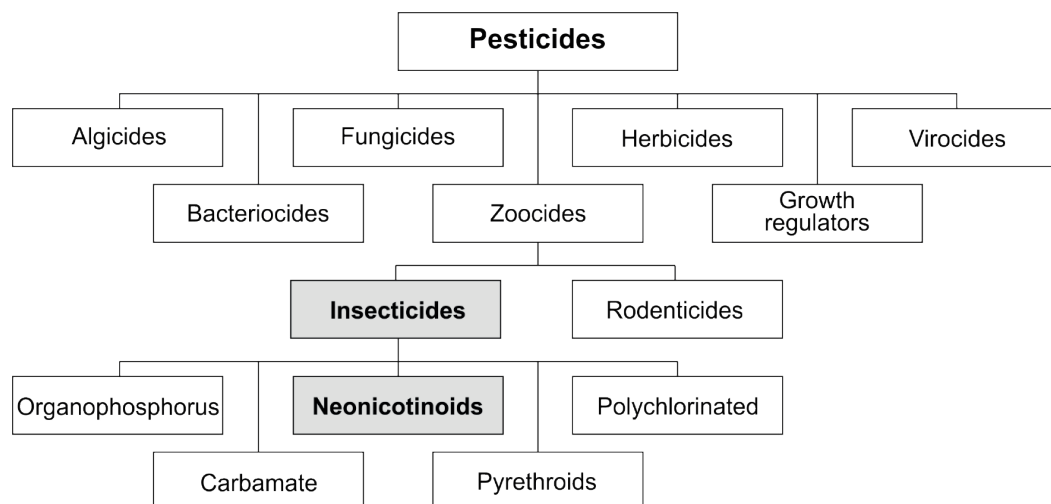


Fig. 1. Types of pesticides by target use group

The main source of pesticides in the environment is agricultural activity (Morrissey et al. 2015, Niu et al. 2020). Pesticides used in agriculture can end up in soil, groundwater, and surface waters. Water pollution caused by the use of pesticides in agriculture is a priority issue of global concern today (Greulich & Alder 2008, Lamers et al. 2011, Moschet et al. 2014, Gonzalez-Rey et al. 2015, Barbosa et al. 2016, Hao et al. 2016, Zheng et al. 2016, Szöcs et al. 2017, Sousa et al. 2018). Among pesticides, the main attention is paid to neonicotinoids, which are one of the most widely used classes of insecticides in agriculture (Fig. 1). Neonicotinoids are neuroactive chemicals with a chemical structure similar to that of nicotine. The best-known insecticides in this class are acetamiprid, clothianidin, imidacloprid, thiacloprid, and thiamethoxam.

The problem of groundwater and surface waters contamination by neonicotinoids is a global issue and requires comprehensive action to identify in detail the processes that affect the migration of these pesticides, their properties, and environmental risk (Morrissey et al. 2015, Q. Zhang et al. 2018, Bonmatin et al. 2019, Pietrzak et al. 2019a, 2020). Obtaining these data can be the basis for taking corrective actions to eliminate the risk and prevent further contamination of the aquatic environment by neonicotinoids.

The purpose of this study is to determine the transport parameters of selected neonicotinoids in

various aquifer materials, using batch tests. These tests are relatively simple and quick to perform, which is why they are still widely used (Wauchope et al. 2002, Cooke et al. 2004, Małecki et al. 2006). They enable one to determine the sorption parameters of the tested substance, i.e., the distribution coefficient for individual sorption isotherms and, as a result, the retardation factor.

Limited information is available in the literature on the sorption parameters of these selected neonicotinoids for various types of soil. On their basis, it can be concluded that thiamethoxam and clothianidin show the lowest sorption capacity (Banerjee et al. 2008, P. Zhang et al. 2015, 2018, Li et al. 2018), higher acetamiprid (Yu et al. 2011, Murano et al. 2018) and imidacloprid (Nemeth-Konda et al. 2002, Oliver et al. 2005, Yazgan et al. 2005, Liu et al. 2006, Papiernik et al. 2006, Leiva et al. 2015, P. Zhang et al. 2018), while thiacloprid is characterized by the highest sorption (Oliver et al. 2005, Kodešová et al. 2011, Rodríguez-Liévana et al. 2013, Li et al. 2017, P. Zhang et al. 2018). However, studies on the sorption properties of neonicotinoids were mainly performed for four of them (clothianidin, imidacloprid, thiacloprid and thiamethoxam), while for acetamiprid the data are negligible. In order to fill the knowledge gaps in acetamiprid sorption, special attention was paid to the transport parameters of acetamiprid individually and acetamiprid present in a mixture of five neonicotinoids.

## MATERIALS AND METHODS

### Chemicals

For batch tests, certified reference materials (CRMs) of the tested neonicotinoids from Dr. Ehrenstorfer (Germany) and Sigma-Aldrich (USA) were bought in powder form. Standard solutions were prepared with acetonitrile. The working solutions were prepared on the day of the experiment as neonicotinoid solutions with appropriate concentrations, from dilution in deionized water (first class purity deionised water) of the previously prepared intermediate working solution (multi-stage CRM dilution). All chemicals and solvents were of the highest purity available from commercial sources and were used without further purification.

The neonicotinoid concentrations in the tested samples were determined using the LC-MS/MS method in the accredited Wessling Poland laboratory in Krakow. LC-MS/MS analyses were performed on an Agilent Infinity 1290 liquid chromatography (USA) coupled to a Sciex QTrap 5500 mass spectrometer (Canada). The method has been validated for experiments following the requirements of the Eurachem guidelines (Ellison & Williams 2012, Magnusson & Örnemark 2014). Detailed results of the method verification were

published in Pietrzak et al. (2019b). The relative expanded uncertainty of the neonicotinoids tested for the enriched deionized water samples ranged from 8.8 to 19.4%, while for the enriched environmental samples it ranged from 25.6 to 30.4% ( $k = 2$ , confidence level 95%).

### Soil sampling and its characteristics

In batch tests, quartz (without silt and clay fraction and organic matter) multi-grained sand prepared in the laboratory (treated as reference material – soil 1) and three natural permeable soils representing an aquifer material with different contents of individual particle size and organic matter (soils 2–4) were used. Soil samples were collected in three locations in southern Poland (Lesser Poland Voivodeship) – Czernichów, Dąbrowa Tarnowska, and Krakow (Fig. 2).

These locations were selected based on the results of field studies conducted for previous research. Soil samples (approx. 30 kg) were collected by shallow drilling (up to 5 m) with the use of a hand-held drilling rig. To ensure the homogeneity of the soils used for the experiments, the collected material was first averaged using the ring and cone method and then reduced using the quartering method (Mucha & Nieć 2012, Campos-M & Campos-C 2017).



Fig. 2. Location of natural soil sampling points for batch tests

For the soils tested, the identification of the particle size distribution was carried out using sieve analysis, following the procedure described in the PN-B-04481:1988 standard. Additionally, the content of organic matter (by roasting at 550°C, following PN-B-04481:1988), organic carbon (thermal method), and the clay minerals that dominate in individual samples (by diffractometric analysis of the clay fraction) were determined. The analysis of the organic carbon content was performed at the Faculty Laboratory of Organic Geochemistry and Environmental Research. AGH The remaining analyses were conducted at the Faculty Laboratory for Phase, Structural, Textural and Geochemical Research – Faculty of Geology, Geophysics and Environmental Protection of the AGH University of Science and Technology in Krakow.

Before each experiment, the soil was dried at 104°C for 24 hours to eliminate the possible activity of soil microorganisms that could reduce the concentration of neonicotinoids tested during the experiments.

### Batch sorption tests

Batch tests were performed to determine the values of the sorption parameters for selected neonicotinoids following the methodology described in OECD (2000). They were carried out for acetamiprid (ACE) individually and a mixture (MIX) of five neonicotinoids (acetamiprid, clothianidin, imidacloprid, thiacloprid, and thiamethoxam) in four soils (soils 1–4).

For each soil, the experiment was similar – 5 g ±0.1 g of dried soil and 25 mL of acetamiprid solution or a mixture of neonicotinoids at six concentration levels (Tab. 1) were added to dark glass vials with a capacity of 40 mL, from Macherey-Nagel, with caps with Teflon washers (PTFE). The soil mass to solution volume ratio was 1 : 5.

The vials were then shaken with 450 rph for 24 hours which allowed the equilibrium conditions to be established. The time to establish the equilibrium, as well as the levels of neonicotinoid concentrations, were assumed based on the analysis of the literature data (Rodríguez-Liébana et al. 2013, Leiva et al. 2015). The experiments were conducted at room temperature (approximately 21°C).

**Table 1**  
Neonicotinoid concentrations in batch tests

Target concentrations [µg/dm <sup>3</sup> ]	Measured concentrations [µg/dm <sup>3</sup> ]*					
	ACE	MIX				
		ACE	CLO	IMD	THI	THX
0.5	0.39	0.39	0.56	0.55	0.43	0.43
1	0.80	0.80	1.10	1.07	0.87	0.88
2	1.60	1.56	2.16	2.15	1.69	1.70
5	3.95	4.12	5.60	5.49	4.11	4.30
10	7.63	7.52	10.63	10.36	8.25	8.47
25	19.00	18.70	27.00	27.30	20.93	20.88

\*The differentiation of the individual concentration values resulted from the concentration of intermediate standards from which the test solutions were prepared (multi-stage CRM dilution).

Explanations: ACE – acetamiprid, CLO – clothianidin, IMD – imidacloprid, THI – thiacloprid, THX – thiamethoxam, MIX – mixture of five neonicotinoids.

The equilibrium concentration of neonicotinoids in the sorption complex (for individual soils) was calculated from the formula based on the mass balance (Małeck et al. 2006):

$$S = (C_0 - C) \cdot \frac{V}{m},$$

where:

- $S$  – concentration of the component in the sorption complex [µg/kg],
- $C_0$  – initial concentration of the component [µg/dm<sup>3</sup>],
- $C$  – final concentration of the component in the solution [µg/dm<sup>3</sup>],
- $V$  – solution volume used for determinations [dm<sup>3</sup>],
- $m$  – dry soil sample mass [g].

The fitting of the appropriate sorption isotherm (Henry's or Freundlich's – Tab. 2) was performed in the PS IMAGO PRO program (with the IBM SPSS Statistics analytical engine), using the linear regression technique. This technique was chosen based on a literature review (Kyzioł-Komosińska & Pająk 2009) and preliminary curve estimation, which gives a better fit for the linear model. The degree of agreement of each isotherm with laboratory data was expressed by the determination coefficient  $r^2$ .

**Table 2**  
Sorption isotherms used in the studies

Sorption model	Formula	Isotherm's type	Retardation factor (R)
Henry's (linear)	$S = K_d \cdot C$		$R = 1 + \frac{\rho_d}{n_e} K_d$
Freundlich's	$S = K_f \cdot C^\eta$		$R = 1 + \frac{\rho_d \cdot C^{\eta-1}}{n_e} K_f$

Explanations:

$K_d, K_f$  – distribution coefficients for Henry's and Freundlich's isotherms [dm<sup>3</sup>/kg],  
 $\eta$  – fit factor for empirical sorption measurements (Freundlich's exponent) [-],  
 $\rho_d$  – bulk density of the soil skeleton [kg/dm<sup>3</sup>],  
 $n_e$  – effective porosity [-].

The obtained values of the distribution coefficient were used to calculate the retardation factor R, using the formulas presented in Table 3. Then, based on the calculated R values the intensity of sorption was classified according to the Osmęda-Ernst & Witczak (1991) (Tab. 3).

**Table 3**  
Sorption intensity classification (Osmęda-Ernst & Witczak 1991)

Sorption intensity	Retardation factor R [-]
Low	1–2
Average	>2–10
Large	>10–100
Very large	>100–1000
Infinite	>1000

Before conducting batch tests, the main factors influencing the uncertainty of the results obtained were identified to include them in the experiments and minimize their impact on the results. The study used dark glass vials with caps with Teflon washers (PTFE) to reduce the possibility of neonicotinoid sorption on the walls of the vial/cap. To verify the correctness of the

experiment methodology, batch tests were performed for soil 1 (quartz sand). As a result, no neonicotinoid sorption was observed on quartz sand or kit components (unpublished preliminary research results). Additionally, to verify the repeatability of the method, the experiment was repeated twice for each concentration level. In further calculations, mean values from two repetitions were used. In the case of the remaining three soils (soil 2–4), control samples were also collected – soil with deionized water, to check whether the soil was originally contaminated with neonicotinoids.

## RESULTS AND DISCUSSION

In batch tests, quartz multi-grained sand prepared in the laboratory (soil 1) and three natural permeable soils representing an aquifer material – medium and loamy sands (soils 2–4) were used. The detailed characteristics of the soil samples – the percentage of particle size distribution, organic matter (OM) and organic carbon (OC) content, pH value, cation exchange capacity (CEC), and main clay minerals are summarized in Table 4.

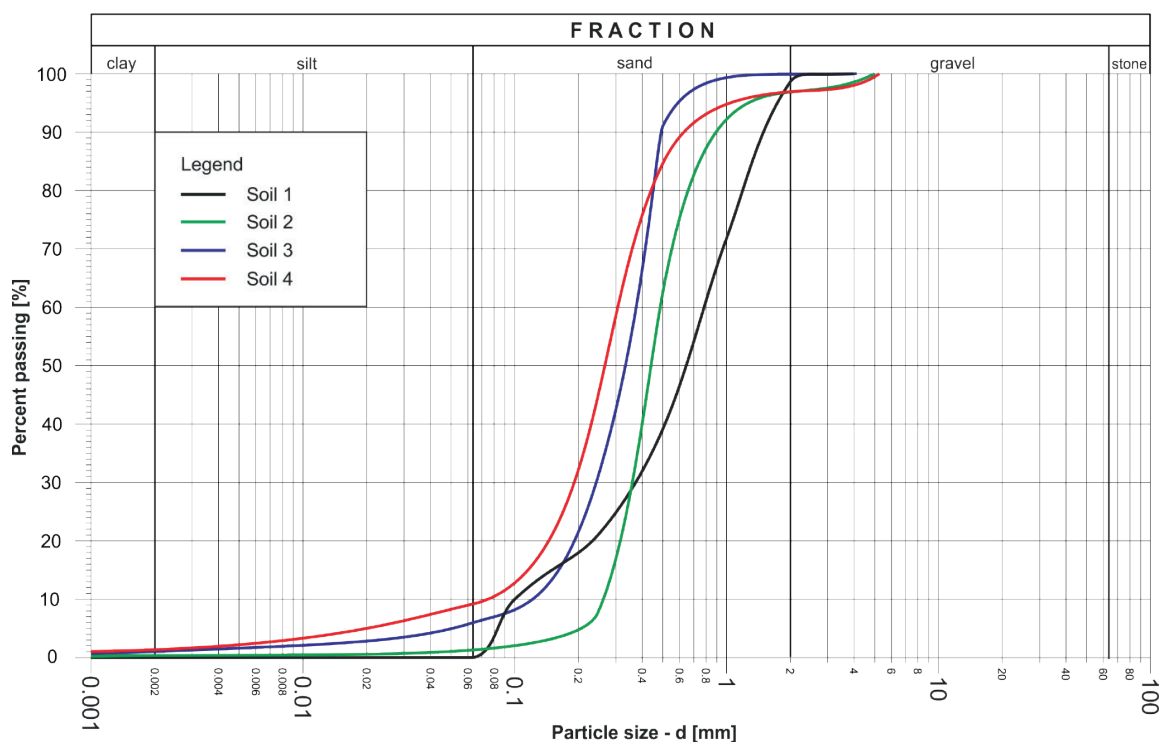
**Table 4**  
Detailed characteristics of the soils used in batch tests

Characteristics	Soil 1	Soil 2	Soil 3	Soil 4
	multi-grained sand	medium sand	loamy sand	loamy sand
Gravel [%]	1.5	3.1	0.2	3.2
Sand [%]	98.5	95.7	93.9	87.6
Silty [%]	0.0	0.9	4.9	7.8
Clay [%]	0.0	0.3	1.0	1.4
OM [%]	0.00	0.21	0.40	1.29
OC [%]	0.00	0.02	0.05	0.49
pH	8.15	8.02	7.09	7.05
CEC [cmol/kg]	0.00	0.28	0.88	2.70
Main clay minerals	–	illite, kaolinite, smectite	kaolinite, smectite, illite	chlorite, vermiculite, illite

Soil 1 was treated as a reference material – without silt and clay fraction and organic matter. Other soils were characterized by different contents of individual particle size (especially clay) and organic matter. Soil 2 has the lowest content of clay and organic matter, while soil 4 has the highest content of these components. The contents of individual

fractions based on the sieve analysis are illustrated in particle-size distribution curves in Figure 3.

The results of batch tests for acetamiprid and a mixture of five neonicotinoids were interpreted using two sorption models – Henry's and Freundlich's. The sorption isotherms obtained for the soils studied (2–4) are shown in Figures 4 and 5.



**Fig. 3.** Particle-size distribution of the soils tested

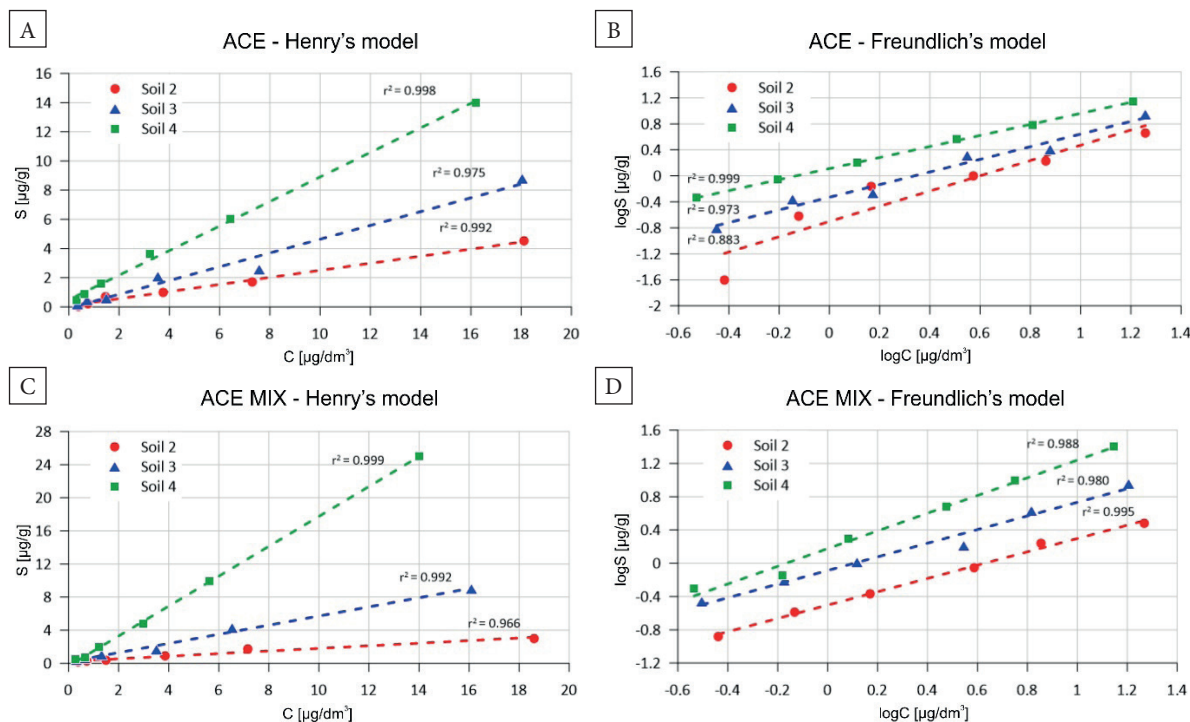


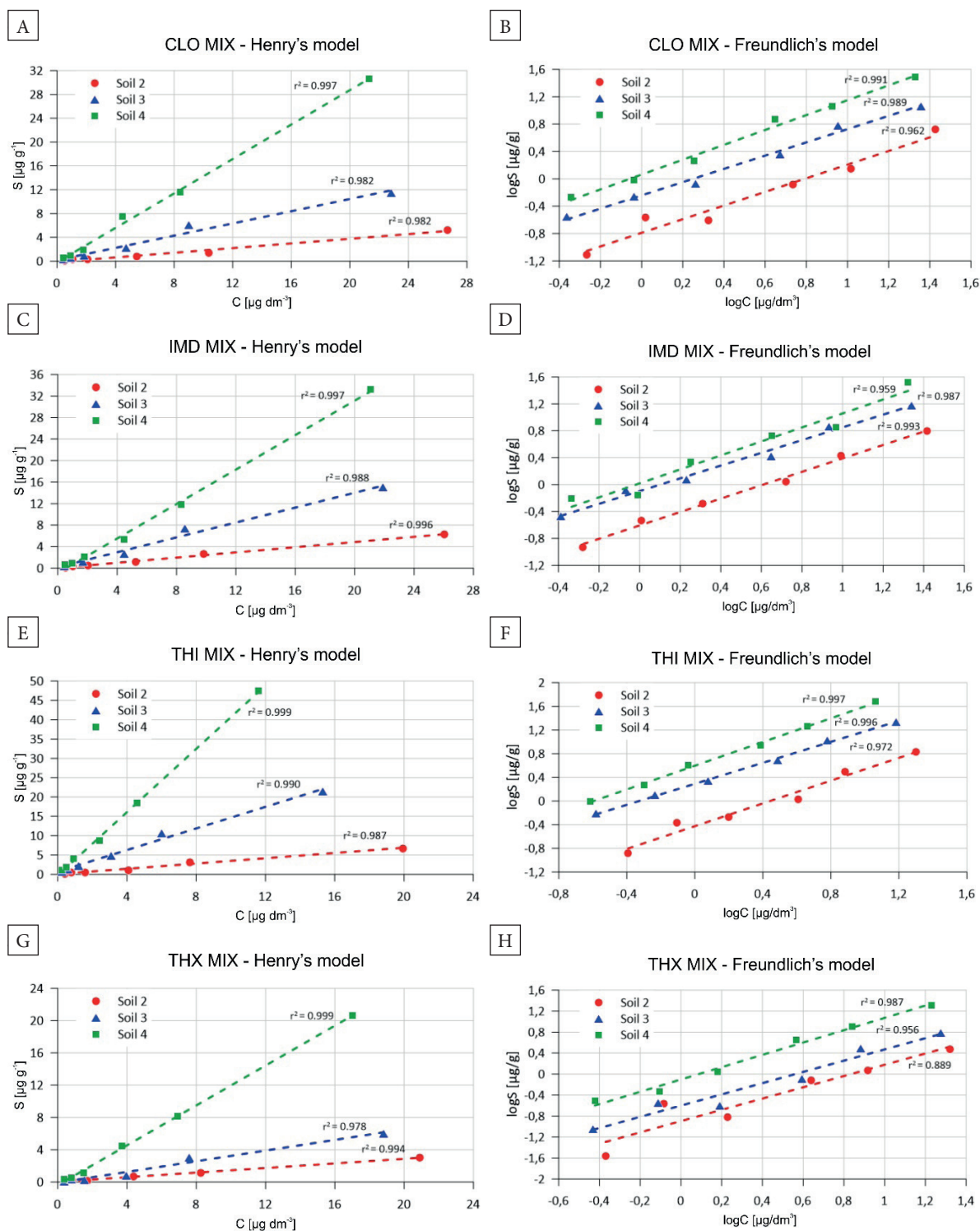
Fig. 4. Neonicotinoid sorption isotherms of acetamidrid individually (a, b) and acetamidrid in the mixture (MIX) (c, d) for the studied soils: 2, 3, 4

The determination coefficient ( $R^2$ ) of the individual sorption models along with the corresponding values of the distribution coefficients

( $K_d$  and  $K_f$ ) and the calculated retardation factors  $R$  are summarized in Table 5.

Table 5  
Parameters of individual sorption models

Soil	Neonicotinoids	Henry's model			Freundlich's model				
		$K_d$ [dm <sup>3</sup> /kg]	$r^2$ [-]	$R$ [-]	$K_f$ [dm <sup>3</sup> /kg]	$\eta$ [-]	$r^2$ [-]	$R$ [-]	
2	ACE	0.249	0.995	2.53	0.198	1.173	0.883	2.65	
	MIX	ACE	0.175	0.968	2.08	0.33	0.779	0.995	2.37
		CLO	0.187	0.986	2.15	0.162	0.997	0.962	2.00
		IMD	0.243	0.998	2.50	0.247	0.996	0.993	2.51
		THI	0.346	0.992	3.13	0.376	0.962	0.972	3.16
		THX	0.144	0.996	1.89	0.127	1.073	0.889	1.90
3	ACE	0.490	0.985	3.87	0.470	0.970	0.973	3.75	
	MIX	ACE	0.569	0.994	4.51	0.819	0.819	0.980	4.73
		CLO	0.525	0.989	4.23	0.573	0.969	0.989	4.32
		IMD	0.704	0.993	5.34	0.801	0.947	0.987	5.44
		THI	1.462	0.992	10.02	1.954	0.887	0.998	10.88
		THX	0.325	0.986	3.00	0.251	1.070	0.956	2.75
4	ACE	0.890	0.995	6.46	1.294	0.850	0.999	7.16	
	MIX	ACE	1.774	0.999	11.94	1.500	1.064	0.988	11.32
		CLO	1.433	0.998	9.84	1.160	1.087	0.991	9.53
		IMD	1.540	0.996	10.50	1.043	1.039	0.959	7.98
		THI	4.058	0.999	26.03	3.952	0.998	0.998	25.44
		THX	1.202	0.998	8.41	0.789	1.173	0.987	7.68



**Fig. 5.** Neonicotinoid sorption isotherms of: clothianidin (a, b), imidacloprid (c, d), thiacloprid (e, f) and thiamethoxam (g, h) in the mixture (MIX) for the studied soils: 2, 3, 4

In most cases, the best fit was achieved for the linear sorption model (Henry's) – the values of the  $R^2$  coefficient were in the range from 0.985 to 0.999. A better fit for the Freundlich's model

was obtained for the acetamiprid tested individually (soil 4,  $r^2 = 0.999$ ) and the acetamiprid in the mixture (soil 2,  $r^2 = 0.995$ ), and also for the thiacloprid (soil 3,  $r^2 = 0.998$ ). However, in many



cases, the fit for the Henry's and Freundlich's models was very similar and equally high ( $r^2$  in the range 0.985–0.999).

The final results of the distribution coefficient were those that corresponded to the sorption models with the best fit (mostly Henry's model). Based on these values, the retardation factors  $R$  for neonicotinoids in the studied soils were calculated (Tab. 5).

The obtained values of the retardation factor of individual neonicotinoids for the studied soils confirmed the observations of other authors (Liu et al. 2006, Banerjee et al. 2008, Leiva et al. 2015, P. Zhang et al. 2015, Li et al. 2018, Murano et al. 2018) that: 1) neonicotinoids sorb primarily on clay minerals and organic matter – the highest sorption was observed for the soil 4 with the highest content of these components, 2) individual neonicotinoids undergo sorption to a different degree – thiacloprid is the most sorbed, and thiamethoxam the least.

No sorption of the neonicotinoids tested was observed on quartz sand (soil 1). This is reflected in the values of the retardation factors which were practically equal to 1 (unpublished data). This relationship is visible both for acetamiprid individually, as well as for the neonicotinoids in the mixture.

In the case of soil 2 (0.3% clay and 0.21% organic matter content), the phenomenon of sorption related to the presence of organic matter and clay minerals was observed in the studied soil. The highest retardation factor value was observed for thiacloprid (3.13), then for imidacloprid (2.50), acetamiprid (individually 2.53 and in a mixture of 2.37), and clothianidin (2.15). The smallest retardation was shown by thiamethoxam, for which the factor  $R$  was 1.89. According to the Osmęda-Ernst & Witczak (1991) sorption intensity classification (Tab. 4), the sorption intensity class for all neonicotinoids for soil 2 is "low".

Soil 3 was characterized by a significant clay (1%) and organic matter (0.4%) content, resulting in correspondingly greater sorption of neonicotinoids on this material. In this case, the highest value of the retardation factor was observed for thiacloprid – 10.88, and the lowest for thiamethoxam – 3.0, while the remaining 3 neonicotinoids are characterized by similar sorption capacity. The migration retardation of these pesticides

was about 2 times lower than for thiacloprid, regardless of the sorption model. Generally, neonicotinoids showed the same retardation order as for soil 2 (thiacloprid → imidacloprid → acetamiprid → clothianidin → thiamethoxam). According to the above classification, the sorption intensity class for the neonicotinoids tested for soil 3 is "average sorption".

Soil 4 contained the highest amount of clay (1.4%) and organic matter (1.29%) among all the tested soils, resulting in the highest sorption of neonicotinoids on this material. Significant discrepancies in the values of the retardation coefficient for individual neonicotinoids were observed. For thiacloprid, it was more than 3 times higher than for thiamethoxam and about 2.5 times higher than for acetamiprid, clothianidin, and imidacloprid.

According to the Osmęda-Ernst & Witczak (1991) classification, the observed sorption intensities can be classified as "average sorption" for acetamiprid (individually), clothianidin, and thiamethoxam. For the remaining neonicotinoids, the sorption intensity is "high".

In the case of soil 2 and 3, the values of the retardation factor for acetamiprid individually and acetamiprid in the mixture were similar, and the differences might stem from the uncertainty of the test methodology, e.g., slight variation of the soil used for higher and lower concentration tests, as well as the uncertainty of sample measurements in the laboratory. Hence, in the case of these soils, the presence of other neonicotinoids does not significantly affect the sorption capacity of acetamiprid, due to the competition between neonicotinoids for sorption sites in the soil. On the other hand, for soil 4, significant discrepancies in the value of the acetamiprid retardation factor were observed, for which the value of this parameter in the mixture was almost twice as high as for a single pesticide – 11.94 and 7.16, respectively.

Analysing the above results, a significant diversification of the sorption parameters depending on the type of soil can be noticed, and in particular on the organic matter and clay minerals content (Fig. 6). The highest sorption of neonicotinoids was observed on soil 4 with the highest organic matter and clay minerals content, while no sorption of these pesticides was observed on quartz sand (soil 1).

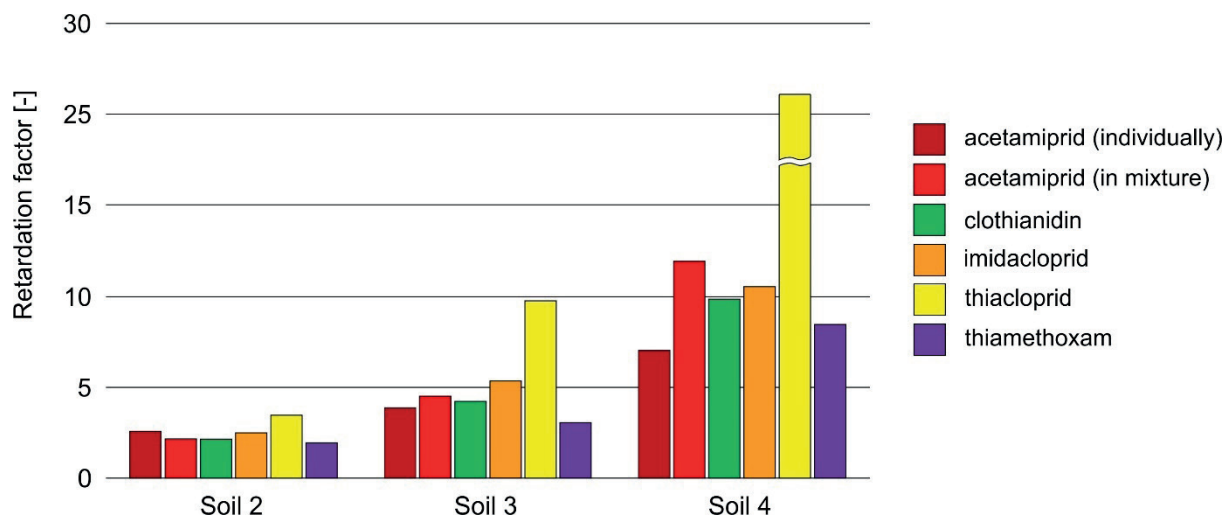


Fig. 6. Values of the retardation factor  $R$  for soils: 2, 3, 4

Oliver et al. (2005), examining three soils with different content of organic carbon and clay minerals, obtained higher values of the  $K_d$  distribution coefficient for imidacloprid and thiacloprid for soils with a higher content of these parameters. The same relationship was observed by Zhang P. et al. (2018) for clothianidin (higher values of distribution coefficients for the Freundlich isotherm) and Banerjee et al. (2008) for thiamethoxam (higher values of distribution coefficients for the Henry's and Freundlich's isotherm). Yu et al. (2011) investigated the amount of acetamiprid sorption on three different natural soils and with 0.5% biochar added, achieving much higher  $K_f$  values in the second case.

Traditionally, the sorption rate of contaminants on the soil is inversely proportional to its solubility in water, which was also observed during the research. Thiamethoxam is characterized by the highest water solubility and thus the lowest sorption (the lowest  $R$  values), while thiacloprid has the lowest water solubility of the tested neonicotinoids and the highest sorption (the highest  $R$  values).

In the case of batch tests, most often only the values of distribution coefficient for selected sorption isotherms are determined. However, rarely the retardation factor  $R$  is also determined, while the calculation of which the effective porosity and the volumetric density of the soil skeleton are additionally taken into account. Due to the above, it was not possible to compare the obtained retardation factors with the results of other studies.

For comparison, the values of distribution coefficients for the Henry's ( $K_d$ ) and Freundlich's ( $K_f$ ) isotherms were used.

For soil 4, the  $K_f$  value for thiacloprid was  $3.95 \text{ dm}^3/\text{kg}$ , which is similar to the studies by Li et al. (2017), where the sorption of thiacloprid on agricultural soil with a similar organic matter (1.23%) and clay content was investigated, obtaining a  $K_f$  value of  $3.26 \text{ dm}^3/\text{kg}$ .

Li et al. (2017), investigated the sorption of imidacloprid on soils from the Zhejiang province with different organic matter content (0.25–4.3%), obtaining  $K_f$  values in the range of  $0.61\text{--}5.09 \text{ dm}^3/\text{kg}$ , in which there is the  $K_f$  value ( $1.04 \text{ dm}^3/\text{kg}$ ) for the soil 4 at organic matter content 1.29%. Furthermore, Li et al. (2017), obtained a similar distribution coefficient, who studied the sorption of imidacloprid on river-water soil (OC content – 0.11%), obtaining  $K_f$  values equal to  $1.01 \text{ dm}^3/\text{kg}$ .

Li et al. (2018) investigated the sorption of clothianidin and thiamethoxam on fine sandy loam (OC content 0.21–0.64%), obtaining  $K_d$  values of  $1.13\text{--}1.94 \text{ dm}^3/\text{kg}$  and  $1.12\text{--}2.03 \text{ dm}^3/\text{kg}$ , respectively. These values are similar to the  $K_d$  values obtained for soil 4 (OC content – 0.49%), which were  $1.43 \text{ dm}^3/\text{kg}$  for clothianidin and  $1.20 \text{ dm}^3/\text{kg}$  for thiamethoxam.

It is difficult to compare the obtained values of the distribution coefficients for soils 2 and 3 because the results of batch tests were found only for agricultural soils, which are characterized

by a significant content of clay minerals and organic matter/organic carbon. The soil studied in the experiment represents the aquifer material, and therefore the proportion of these elements is much lower.

## CONCLUSIONS

The water pollution resulting from the use of various pesticides in agriculture is currently of global interest. Special attention is paid to neonicotinoids, which are one of the most widely used classes of insecticides in agriculture. Due to its high popularity, the problem of contamination of groundwater and surface waters with neonicotinoids quickly appeared in many countries. As data/parameters on the migration and fate of the pesticides in the groundwater environment are often rare and are not yet sufficiently recognized, this study attempts to determine the transport parameters of selected neonicotinoids in various aquifer materials using batch tests. Tests were carried out individually for acetamiprid and for a mixture of five neonicotinoids (acetamiprid, clothianidin, imidacloprid, thiacloprid, and thiamethoxam), for three selected natural soils (soils 2–4 – with different content of silt and clay fractions and organic matter) and quartz sand, treated as reference material (soil 1). The results of the batch tests were interpreted with two sorption models – Henry's and Freundlich's, determining the distribution coefficients  $K_d$ ,  $K_f$ , and the retardation factor  $R$ . Based on the obtained values of the sorption parameters of individual neonicotinoids for the soils studied, it can be concluded that neonicotinoids sorb mainly on clay minerals and organic matter. The greatest sorption of neonicotinoids is observed on soil 4 with the highest content of organic matter and clay minerals content, while no sorption of these pesticides is observed on quartz sand (soil 1). In addition, it was noticed that individual neonicotinoids undergo sorption to a different degree — thiacloprid was the most sorbed ( $R$  value in the range 3.13–26.03), while thiamethoxam was the least ( $R$  value in the range 1.89–8.41).

In order to fill the knowledge gaps in acetamiprid sorption, special attention was paid to the transport parameters of acetamiprid individually

and acetamiprid present in a mixture of five neonicotinoids. The results shows that the presence of other neonicotinoids does not significantly affect the sorption capacity of acetamiprid, due to the competition between neonicotinoids for sorption sites in the soil.

The results of batch tests can be further used in modelling the migration of pollutants in the groundwater environment using various programs (Pietrzak 2021).

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