Title: Behaviour of neonicotinoids in contrasting soils

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Behaviour of neonicotinoids in contrasting soils

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Highlights

- All the study neonicotinoids had low affinity for soil with low SOC.

- Thiametoxam and thiacloprid were the least and most adsorbed neonicotinoids in soil.

- Thiacloprid has low tendency to migrate through soil

- Thiametoxam and thiacloprid were retained faster in soil rich in organic matter.

- Thiametoxam reached equilibrium faster than thiacloprid in soil with poor SOC

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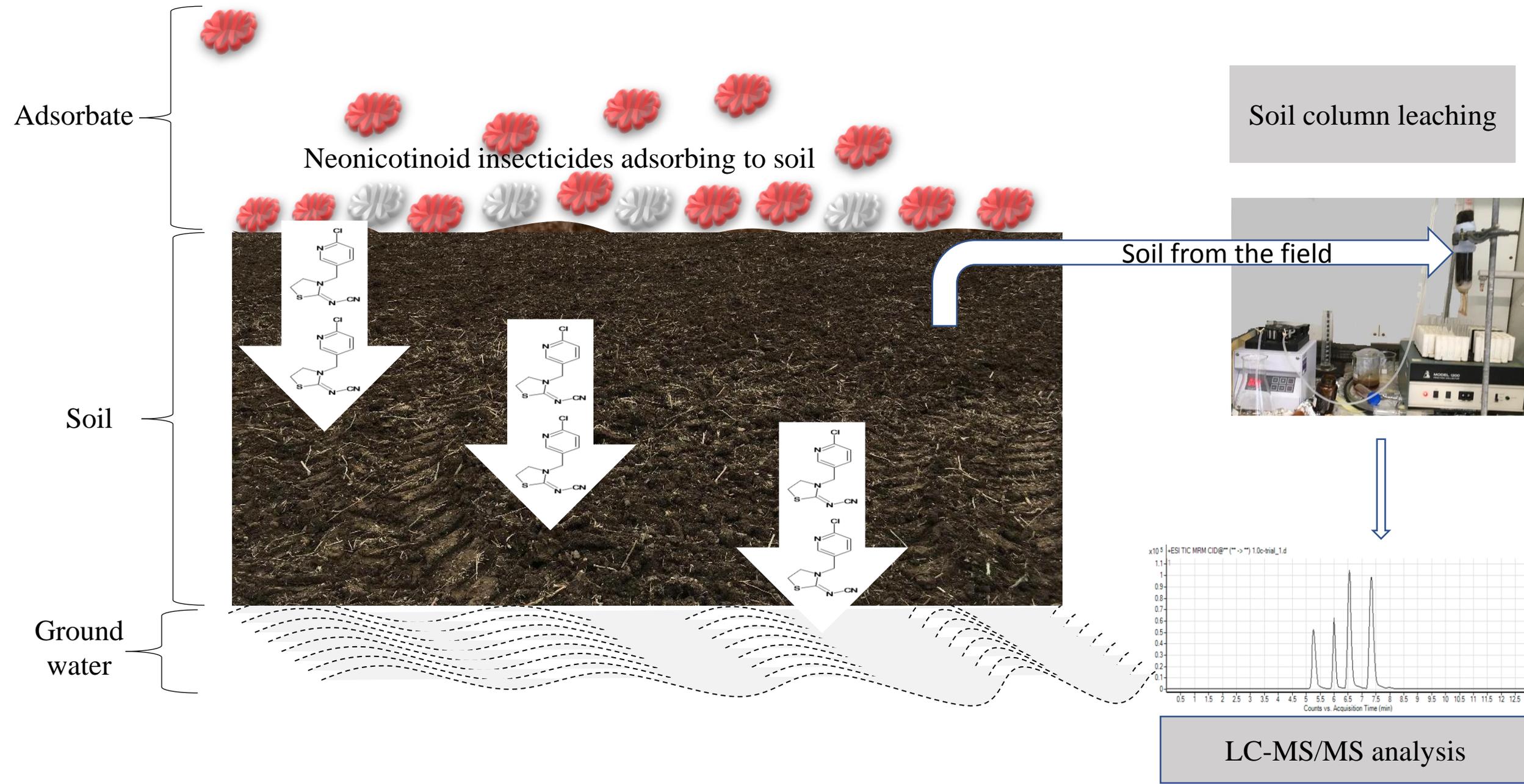Adeniyi K. Aseperi[a*], Rosa Busquets[a], Peter S. Hooda[b], Philip C.W. Cheung[c], James Barker[a]

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Abstract

Neonicotinoids are widely used to control insect pests in agriculture. Their presence in the environment can affect the health of non-target insects and aquatic animals. The behaviour of four neonicotinoids, namely imidacloprid, acetamiprid, thiacloprid and thiamethoxam, has been investigated in soils with contrasting characteristics to understand their migration in soil and risk. Among the study neonicotinoids, thiametoxam and thiachloprid were found to be the least and most uptaken neocotionoids by all the soils, respectively (up to 186 time greater adsorption of thiacloprid), and their uptake was affected by the content of organic matter in the soil. Leaching studies in columns confirmed that thiamethoxam leached out of the soils readily, pointing out to a relatively high risk of ground water contamination with possible ecological impact when thiametoxam is used in soils with low organic matter. In soil column studies, the soil with the lowest organic matter presents the greatest residue of neonicotinoids in the sub-surface ($\leq$5cm). In contrast the soil richer in organic matter presented most of the contamination deeper down in the column; a factor to be considered in the remediation from soil.

1. Introduction

The use of neonicotinoid insecticides has been increasing in the last two decades ever since the first neonicotinoid imidacloprid was commercialised in 1991 (Mörtl *et al.*, 2016). Neonicotinoids are authorised for use in over 120 countries and are applied to more than 290 crops (Jeschke *et al*., 2011, Main *et al.,* 2015). They have a unique mode of action at the nicotinic acetylcholine receptor in the central nervous system of insects (Li *et al.,* 2018) and also disrupt the tyroid endocrine system of lizards (Wang et al., 2020) and cause metabolism disorders and oxidative stress in mice (Yan et al., 2020). The low application rate, selective toxicity and pronounced residual activity of neonicotinoids (Kurwadkar *et al.*, 2013, Radolinski *et al.,* 2018) have promoted their wider application range from agricultural, horticultural and veterinary to domestic use. According to the UK's Food and Environment Research Agency (FERA, 2018), about 120 t of neonicotinoids were applied to over 2 million hectares of farmland in Britain in year 2012 – 2016. In December 2013, the European Union introduced a moratorium on the use of imidacloprid, thiamethoxam and clothianidin in bee-attractive crops however they could still be used in crops such as winter-sown cereals or sugar beets, and these uses could imply new entrance of neonicotinoids in the environment. In 2018, the European Food Safety Authority banned the use of these same neonicotinoids in the European Union, except for their use in greenhouses, as a result of the evidence of toxicity available (EFSA, 2018)Only about 5% of the neonicotinoid active ingredient applied through seed coating is taken up by crop plants and the rest may will be transferred to the soil (Wood and Goulson, 2017). The possibility of accumulation and transport of neonicotinoids in the environment has been highlighted contemporarily: in the United States, at least one neonicotinoid was detected in 63% of 48 freshwater streams surveyed (Hladik & Kolpin, 2015). In Sydney (Australia), 93% of river samples tested contained two or more

neonicotinoids in the range 0.06 - 4.5 μg/L (Sánchez-Bayo & Hyne, 2014). In the Guangzhou section of the Pearl river (China), acetamiprid, thiamethoxam, imidacloprid and clothianidin were detected 100% of the times while thiacloprid was detected with a frequency of 93% with total concentration of the 5 neocotinoids 93-321 ng/L. The equivalent total concentration in soil was 0.40-2.59 ng/g soil (dry weight), with detection frequencies ≥78% and imidacloprid was never detected (Yi et al., 2019). Jones *et al.* (2014) found that the concentration of neonicotinoids (clothianidin > imidacloprid > thiamethoxam) in arable soils ranged from 0.02 - 13.6 μg/kg soil, from eighteen sites widely spread out in England, after the application of seed treatment in the preceding years. In the EU, extensive sampling carried out in nectar from winter-sown rapeseed oil flowers from 291 fields in France during the moratorium (2014-2018) led to the detection of the 3 restricted neonicotinoids, with frequent detection of imidacloprid (at levels up to 45 ppb) and with no sign of declining levels but large variability between years. The spread of imidacloprid in soil from other crops that were not in the vicinity, through dust drift or transport through contaminated run-off was suggested as a hypothetical cause (Wintermantet et al., 2020). A study of sorption of commonly used pesticides, including imidacloprid, in agricultural soils all of low organic content found a lack of correlation between the amount of insecticides adsorbed and the soil organic carbon (Fernández-Bayo *et al.*,2008)). Hence, alternative sorption mechanisms may come into play.

Herein, we aim to understand the behaviour of widely used neonicotinoids in soil to inform future remediation strategies and help to interpret possible causes of contamination of crops even in cases were the used of neonicotinoid has been banned. The four neonicotinoids focussed on in this research are: acetamiprid, imidacloprid, thiacloprid and thiamethoxam. The modes of distribution of pesticides in the soil-water phase are of fundamental importance to any ecological impact analysis of pesticides. To date, there is still very little information on

the sorption of neonicotinoids relative to other insecticides (Boivin, *et al.,* 2005; Anderson *et al.*, 2015).

2.0 Materials and methods

2.1 Chemicals and materials

Stock solutions (~1000 µg/g) of each neonicotinoid were prepared in water − methanol (50:50). The neonicotinoids studied and their purities were: acetamiprid (ACE, 99.9 %), imidacloprid (IMI, 99.9 %), thiacloprid (THA, 99.9 % purity) and thiamethoxam (THX, 99.6 % purity), all obtained from Sigma-Aldrich, Dorset, UK. Their structure, IUPAC name and physicochemical properties are reported in Supporting Information Table S1. Diluted intermediate solutions of 15, 5.0 and 1.0 µg/g were prepared in water and subsequent calibration standard solutions ranging from 0.001 − 1.0 µg/g were also prepared in water; these contained 2-chloroaniline at 0.6 µg/g as internal standard. Liquid Chromatography-Mass spectrometry (LC-MS) grade methanol from Honeywell Riedel-de Häen (Germany); LC-MS grade water from VWR Chemicals (France) and LC-MS grade formic acid from Fisher Chemical (Czech Republic) were used for the quantification of neonicotinoids with LC-MS. Ultrapure water was used for the adsorption and leaching experiments. All prepared standards and samples were wrapped with aluminium foil throughout the study to prevent photolytic degradation of neonicotinoids and the standards were refrigerated at $4^{°}$C until analysis. All samples were filtered through 0.22 µm PTFE filter (Millex, Millipore, UK) or X50 sterile 0.22 µm Durapore PVDF filters (when volumes were <0.3 ml) prior to their injection.

2.2 Sampling and pre-treatment of soils

Topsoil samples from three randomly selected spots, ~100 cm apart, in each selected five locations in the UK were collected to 20 cm deep using a hand trowel. The samples were

independently mixed to form a composite sample for each location and then labelled, as shown in Table 1.

The soils were air-dried in a fume hood in the laboratory for 4 days in the dark with the removal of plant debris/stones before gentle grinding using a pestle and mortar to ensure sample uniformity. Soil particles (< 2 mm diameter) were thoroughly mixed, stored and sealed in sample polythene bags prior to their use in experiments.

2.3 Soil characterisation

Soil pH values were determined in soil-water suspensions of weight ratio 1:2.5. After shaking with a rotary shaker for 2 h and allowed to stand for 15 minutes, the pH was measured using a previously calibrated pH meter. Soil organic carbon (SOC) was determined using the Walkley-Black procedure (ISRIC, 2002). Soil particle sizes were determined by the hydrometer method. Cation exchange capacity (CEC) was determined using 1M sodium acetate solution to saturate the soil exchange sites with Na^+ ions at pH 7. The sodium ions were displaced with quaternary ammonium ions (from ammonium acetate solution). Sodium content was then determined by inductively coupled plasma atomic emission spectrometer (ICP-AES) (Jobin-Yvon ultima, 2C, France). The soil pH, SOC, CEC and soil particles sizes, listed above, were all determined as outlined in ISRIC (2002).

2.4 Adsorption, sorption isotherm and time dependent kinetics of neonicotinoids in soil

Initial batch adsorption experiments were performed in the five different soils to assess the effects of pesticides' concentration on adsorption capacities of the soils with varying SOC. 20 ml of the individual pesticides, at two extreme concentrations of 2.5 μg/g and 25 μg/g in aqueous solution, were mixed with 4 g of soil in 50 ml polypropylene centrifuge tubes. The centrifuge tube were shaken in an orbital shaker set to operate at 100 rpm and at 25 °C for 48

hours (OECD, 2000). The supernatants were centrifuged (2264 x g for 10 min at 22 °C), filtered through 0.22 µm PTFE filters, prior to addition of the internal standard. The amount of pesticides adsorbed, expressed as per unit mass of soil, was determined from the difference between the amount of pesticide found in the supernatant of each sample after incubation and the control solutions where soil was absent. Each experiment was carried out in triplicate.

The sorption equilibrium isotherm of the most and least adsorbed neonicotinoids on four out of the five soils were performed at relatively low concentrations levels. ST soil was excluded from the experiment because it was not within the south east of England. 2 g of soil to 10 ml of pesticides solution at 0.10; 0.25; 0.50; 0.75; 1.0; 1.25; and 1.50 µg/g were incubated in a 15 ml centrifuge tube in an orbital shaker set to operate at 100 rpm and at 25 °C for 48 h. The above steps on supernatants, as previously described, were followed accordingly prior to analysis.

Following the adsorption capacities and sorption isotherm earlier assessed, the time dependent sorption kinetics of the most and least adsorbed neonicotinoids with the most and least adsorbing soils samples were assessed. Soil (4g) were incubated with solution of the individual pesticides (20 ml at 2.5 µg/g) in polypropylene 50 ml centrifuge tube in an orbital shaker set to operate at 100 rpm and at 25 °C. Aliquots were taken at 5, 15, 30 min, and at 1, 6, 12, 24, 48, and 72 h. The volume the pesticide-soil solution was kept > 90%, after taking aliquot sample of the supernatant for analysis, throughout the experiment; to minimise alteration in the equilibria. The supernatants were centrifuged and analysed as described above.

2.5 Column leaching experiments

A fraction of soil (< 2 mm) was packed, at 15 cm high, into a flash chromatography glass column (4 cm i.d. and 50 cm height) by addition of successive layers of soil to establish a

uniform bulk density of about 1.1 g/ml. Generally, soils with bulk density greater than 1.6 g/ml (McKenzie *et al.*, 2004) are known to restrict root growth and soils with bulk density lower than 1.5 g/ml are generally desired for optimum movement of air and water through the soil (Hunt and Gilkes, 1992). Glass wool was placed at the bottom of the column to avoid soil loss. The unspiked soil was pre-wetted with one pore volume of water (188 ml) in order to displace air trapped in the soil pores. Thereafter, the excess water in the soil column was left to drain off by gravity overnight. The glass columns, after draining excess water, were covered with aluminium foil to avoid photolytic degradation of the pesticides during the leaching period. A single 1 ml pulse application of 1000 µg/g of the standard neonicotinoid solution was evenly applied at the top layer of the soil column to obtain a homogenous distribution of the pesticides. To avoid disturbance of the soil surface by water droplets, a minimum of 10 cm water-head was constantly maintained while dropping water through the peristaltic pump at 0.8 ml/min. The soil column was, thereafter, drained using a liquid to solid ratio of 2 L/kg dry matter according to the ISO guideline on soil quality (ISO/TS 21268-1, 2007). The leachates were collected in glass tubes at a pre-set time of 1 hour using a "fraction collector". The collected leachates were mixed with methanol (60:40 methanol/ aqueous leachate) to precipitate macromolecules from the sample. The methanol-leachate solution was centrifuged at 2264 x g for 10 min at 22 °C and the supernatant was filtered through 0.22 µm PTFE filters prior to their injection into LC-MS/MS.

After soil column leaching experiment was completed, the soil from the column was divided into three sections (top, 0-5 cm; middle, 5-10 cm; and base, 10-15 cm) and air-dried in the dark until constant weight was attained. The air-dried soil was finely ground with a pestle and mortar and the pesticides residual determined by extraction, clean-up and analysis with LC-MS/MS.

2.6 Determination of neonicotinoids

Extraction and clean-up of neonicotinoids from soil

Neonicotinoids were extracted from soil by sonicating 1.5 g of the soil (air-dried) in 15 ml methanol for 15 min after previously allowing to stand for 24 hr in the dark. The mixture was centrifuged (2264 x g for 10 min) and the supernatant was freeze-dried. The dried residue was reconstituted in 0.75 ml of methanol: water (55:45) with an internal standard at a concentration of 0.6 µg/g. The reconstituted sample was filtered with 0.22 µm PTFE filter prior to injection in LCMS. This extraction process was adapted from Rodríguez-Liébana *et al.* (2018), and it was carried out in triplicate.

Quantification of neonicotinoids

The analysis of all the study compounds was carried out by liquid chromatography-tandem mass spectrometry (LC-MS/MS) (Agilent LC-1260 Infinity and Agilent MS-6340 Triple Quad, UK). The analytical column used was a Waters Atlantis® (UK) C_{18} (5 µm, 150 mm x 2.1 mm) protect4d with a C_{18} guard column (5 mm x 2.1 mm) from Waters Atlantis® (UK). The optimal separation conditions in the LC-MS/MS were 0.27 ml/min; 10 µL injection volume; column temperature 40°C; mobile phase was methanol (solvent A) and 0.1 % formic acid in water (solvent B) under a gradient condition of 0 – 2 min, 10 % solvent A in B, 2 - 6 min, 10-50 % solvent A, 6 – 9 min, 50 % solvent A, and return to initial conditions in 4 min with 5 min post run delay to equilibrate the column. The ionisation source used was electrospray (ESI) operating in positive mode. The acquisition of the four study compounds in Multiple Reaction Monitoring (MRM) is shown in Table 2 with their corresponding collision energies (CEs) and quantitation/confirmation ions. A capillary voltage ±4000 V, octapole RF 600 V; octapole DC 5 V; Lens 1 DC 4.2 V; Lens 2 DC -6.2 V; Lens 2 DC EF Off -6 V; skimmer 15 V; chamber current of 0.12 µA, nebuliser gas (N_2) at 50 psi., gas temperature 325°C and drying gas (N_2) flow of 12 L/min were used for mass spectrometry.

The quality parameters limit of detection (LOD), limit of quantification (LOQ) were estimated at a signal-to-noise ratio of 3 and 10, respectively. Repeatability and reproducibility were assessed with standard at 0.001 µg/g concentration from the injection of the mentioned standards on 6 repeated analyses during the same day; and 2 analyses on 3 non-consecutive days, respectively. Quality controls at a concentration of 0.5 µg/g was run every 6 samples for the LC-MS/MS analysis.

For the determination of the extraction efficiency of the extraction method applied to the soils after the column leaching experiment, a recovery assessment of the analysis of neonicotinoids was conducted in the soils. About 1.5 g of soils (BR and TH) were spiked in triplicate with 0.75 ml aqueous solution of 1 µg/g of the pesticides (thiacloprid and thiamethoxam) individually and allowed to stand in darkness for 24 hours. Thereafter, the extraction procedure as described.

The effect of the soil matrix on the study compounds in the sample leachates was assessed. The signal of neonicotinoids in a standard mixture was compared with the signal when in the presence of soil extract purified through the proposed clean-up. Different percentages of methanol in the reconstituting solvent were assayed to find conditions with minimum ion suppression. To achieve this, a known standard, 0.1 ml of 1.0 µg/g of neonicotinoid, was added to 0.9 ml of ultrapure water as the control and varying percentages, 20, 30, or 40 %, of the mixture was made up to 1 ml with respective percentages, 80, 70 and 60 % of methanol. The mixture was centrifuged (2264 g for 10 min at 20 °C) and the supernatant was decanted and pass through a 0.22 µm PTFE filter prior to their injection to LC-MS. The procedure above was, thereafter, repeated with drained water, taken from the first pore volume form the soil column without contamination, instead of ultrapure water as earlier stated and the results were compared with that of spiking with ultrapure water.

2.7 Statistical analysis

The effect of the amount of soil organic carbon (% SOC) on the adsorption of neonicotinoids was evaluated with a t-correlation test. Two-way analysis of variance (ANOVA), without replicates, was performed to analyse the effect of the different soils and type of neonicotinoids in the soil uptake of the pesticides using Excel 2016 software (Microsoft, US). Significant differences (t-test) in the average adsorption capacities of all the pesticides, within all the soils, were tested at 95 % confidence.

3.0 Results and discussion

To determine the sorption behaviours of acetamiprid (, imidacloprid, thiacloprid and thiamethoxam in soils with different physicochemical properties, methodology for their analysis was established and validated. The eeffect of sorption as a function of organic matter content for four relevant neonicotinoid insecticides was investigated at different contamination levels. Finally, the lixiviation of the least and most sorbed neonicotinoids and adsorbing soil types were studied to understand their mobility and potential ecological risks when applied to soils with divergent uses.

3.1 Method validation

The validation of LC-MS/MS method for the analysis of the study neonicotinoids followed the European Union SANTE/11813/2017 guidelines (European Union, 2018). The calibration curves of the standards, at 7 levels of aqueous concentrations, presented regression coefficients $R^2 > 0.9994$. The total ion chromatogram of the four compounds analysed with the LC-MS/MS at a concentration of 1µg/L is shown in Figure 1. The LOD and LOQ for all the compounds were 0.10 - 0.23 and 0.34 - 0.78 µg/L in standards, respectively. The repeatability and reproducibility for the study compounds assessed at 1 µg/L were 4.6 – 9.5 and 6.6 – 16.6 % respectively (Table 2). Blank soil was obtained from a field with no history of farming activities or pesticides application due to lack of certified reference material. The

recovery was assessed with spiked blank soil at 1 µg/g. Recovery test indicated a mean extraction efficiency of 82 % (with a range of 72.2 - 86.1 % across neonicotinoids) which is considered acceptable according to the European Union SANTE/11813/2017 guidelines.

It is well accepted that electrospray ion source is prone to the effect of the matrix on the signal of the analytes and for that reason the matrix effect in the analysis was assessed..The matrix effect of the BR purified blank sample matrix on thiamethoxam, reconstituted with 60:40 methanol and water prior injection, , caused 2.2 % ion suppression and an enhancement on thiacloprid's signal of 10.3% in the LC-MS/MS. In contrast, the analysis of purified blank extracts from TH soil , reconstituted in 60:40 methanol/ water led to 27.4 % enhancement of thiamethoxam signal and 10.1 % suppression of thiacloprid. The assessed suppressions and enhancement of the ionisation were used to correct quantification of neonicotinoids in column leachates from the BR and TH soils. 3.2 Pesticides-soil adsorption evaluation

Organic carbon content of soil, and to a lesser extent the soil textural composition, temperature, pH, cation exchanged capacity, bulk density, nanoparticles in pesticides formulation, have been reported to influence the sorption of neonicotinoids (Kurwadkar *et al.*, 2014; Das *et al*. 2015; Gao *et al.*, 2016, Martins *et al.*, 2018, Kah *et al*., 2018). However, the presence of dissolved organic carbon may compete with neonicotinoids on binding sites with soil organic carbon (Anderson *et al.* 2015); consequently increasing their mobility and persistence in the environment.

To investigate the distribution potential of the studied insecticides in soils, physicochemical properties of the selected soils were determined (see Table 1). In this work, two concentration levels of pesticides were added to soil; these were at higher levels than those found in the environment (Jess *et al*., 2018). The reason for the choice of these concentrations was to simulate a worst-case scenario where farmerswould apply pesticides at about 30 − 40 %

higher concentrations than the recommended level (Selvarajah & Thiruchelvam, 2007 and Garthwaite *et al*., 2016).

Neonicotinoid adsorption in 5 contrasting soils (Figure 2) presented adsorption capacities range 0.17 - 11.26 µg/g and 0.19 - 115.33 µg/g when incubated with aqueous solutions containing 2.5 and 25 µg/g of each individual neonicotinoids respectively, using a 1:5 soil/water dose (Supporting information S2). The most adsorbed compound was thiacloprid with adsorption capacities ranging 5.93 - 10.77 and 31.93 - 115.33 µg/g at the low and high contamination levels assayed respectively. In contrast, the least adsorbed insecticide, thiamethoxam, presented adsorption capacities ranging from 0.17 – 9.3 µg/g at low and 1.33 – 31.58 µg/g at a high contamination level (Supporting information S2, 1.1 - 1.5). All the study neonicotinoids showed lower affinity for the BR soil, with the lowest % SOC, and the highest for the TH with highest % SOC.

The 2-way ANOVA results showed a significant effect of the soil on the uptake of each of the five pesticides at the two different concentrations (high, $p = 0.002$ and low, $p = 1.5 \cdot 10^{-5)}$) assayed at $\alpha = 0.05$. The results of the adsorption study showed that the pesticides interacted significantly different with the soils (Supporting information S3). This suggests that the soil organic carbon content may play a part in the pesticide-sorption relationship. The clay content of the soils, was relatively the constant (23.4 ± 2.5 %). The pH ranges of the soil depict neutral to strongly alkaline environment and may play a role in the soil structure. Therefore, the relationship between % SOC and the pesticide adsorption capacities were assessed, and these showed a lack of correlation with the insecticides, except for imidacloprid and thiamethoxam, following a t correlation test (p 0.05) (Supporting information S3).

The adsorption capacities of the neonicotinoids in all the soils studied, displayed in Figure 2, were in agreement with the trend of their individual log K_{ow} values (Table S1). Therefore,

soil adsorption of thiamethoxam, with a high solubility in water (4100 mg/L), did not appear to be influenced by soil organic content, and may be competing with minerals and dissolved organic compounds for binding sites on soils (Jin *et al.,* 2016; Zhang *et al.,* 2018). This attribute is important in understanding the role and effect of soil amendment with dissolved organic compounds to cause their build up in the environment (Spark & Swift, 2002). The high soil adsorption capacity of thiacloprid (one of the most adsorbed insecticides, see Figure 2) may not only be due to its moderate solubility in water (180 mg/L), but also to a favourable log K_{ow} value of 1.26, and the presence of chloro-substituted pyridine and thiazole rings in its structure which can participate in van der Waals attractive forces with soil components (Table S1).

Soils with contrasting SOC levels (i.e. 12.5 % for TH and 0.8% for BR soil) could help to establish the role of SOC on the mobility of neonicotinoids. The sorption kinetics, isotherms and leaching THA and THX (most applied pesticides in UK since 2012 (FERA 2018)) were further assessed to study their behaviour and potential to spread in the environment.

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3.3 Sorption kinetics and isotherms

The time dependent sorption behaviours of thiacloprid and thiamethoxam were observed over a period of 72 h in soil TH and BR with contrasting values of SOC (see Table 1). These soils represent the witnessed 0 – 300 g/kg range organic carbon content distributed across England and Wales (Bellamy *et. al.* 2005). In the BR soil, thiamethoxam attained equilibrium faster than thiacloprid *i.e.,* at 6 h vs 24 h (sorption profile with time shown in Figure 3). It is interesting to note that sorption of both insecticides in the TH soil was rapid: within the first 15 minutes, about 79-82 % adsorption was achieved. Thereafter, no changes were observed in sorption profile as time passed, denoting the attainment of equilibrium in the same soil with

higher % SOC. The organic carbon content of the soil may also be responsible for enhanced sorption, such as reported for imidacloprid and diuron (Fernández-Bayo, *et al.* 2008) and dinotefuran, imidacloprid and thiamethoxam (Kurwadkar, *et al.* 2013). This sorption behaviour correlates well with the log K_{ow} and solubility (Table S1) of the tested insecticides.

Four kinetic models; hyperbolic, pseudo-second order rate equations, Elovich and Weber-Morris models were applied to gain a further insight into their sorption phenomena. Interpretations of the parameters of the applied sorption kinetic models are given in the Supporting information S4.

3.3.1 Pseudo-second order (PSO) and hyperbolic model

Thiacloprid presents higher q_{max} values on both soils than thiamethoxam (Table 3). The significant role of SOC in the sorption of pesticides has been propounded by Liyanage *et al.,* (2006) and the results obtained in the present study concur with their findings. The values of the kinetic rate constant (k) for the two pesticides were similar in both soils, with the values of the TH-soil more than double those of the BR-Soil (Table 3). Among all the models, the linearised form of pseudo-second order (PSO) kinetic reaction model gave the best fitting with R^2 in the range 0.990 - 1.00, for both pesticides on both soils (Figure 4). The values of q_{max} obtained with the pseudo-second order model (see Table 3) were similar to the values in hyperbolic model, but with better regression coefficients. Similar results were obtained by Fernández-Bayo *et al.* (2008), with other pesticides, imidacloprid and diuron, when tested on different soils.

3.3.2 Elovich equation

For the two pesticides (thiacloprid and thiamethoxam) in both soils, there was a poor correlation between the determined coefficients of the Elovich equation (Table 3) and the

values of R^2 fell in the range 0.219 - 0.890. Also, the amount of sorbates at the end of the initial rapid phase (at 6 h), compared to that at the end of 24 h, were observed to be higher in thiacloprid for both soils compared to thiamethoxam (Table 3). Although the Elovich equation did not appear to be a perfect fit for linearity, the results were congruent with the two-phase principle of sorption mechanism proposed by the Elovich model. The values of 1/Y were lower in the soils with higher soil organic content, indicating that sorption equilibria of insecticides were probably attained within the first 6 hours of application. However, this result was dissimilar to that of Fernández-Bayo *et al*., (2008), who examined soils with similar SOC levels, implying that other factors may be controlling the sorption process such as clay content. In our work, the clay contents were similar across the soils examined (Table 1).

3.3.3 Weber-Morris model

With the Weber-Morris model, it is known that linearity is observed when intra-particle diffusion is involved in the adsorption process (Supporting information S4). Usually, a linear graph is obtained when sorbed quantity (µg/g) of pesticides at time t (q_t) is plotted against the square root of time ($t^{1/2}$), on condition that intra-particle diffusion is the dominant rate-controlling mechanism (Yakout & Elsherif, 2010). Intra-particle diffusion is known to be one of the significant rate-determining steps in sorption. For the two soils, the results obtained show poor linearity with both pesticides and the intercept fails to go pass through the origin in each case. The recorded values of R^2 for the equation was between 0.04 and 0.72.

Thermal diffusion of molecular and ionic species in water, governed by Fick's Law, is present in any aquatic system. In this work, the lack of linearity observed when the Weber-Morris equation was applied suggests that Fickian diffusion in the bulk aqueous phase may be accompanied by other attenuations to the overall rate of mass transfer. The nature and

thickness of the nominally stagnant liquid film at the solid-liquid interface, often referred to as the boundary layer, may contribute to the pesticides' thermal diffusion properties. The strength of Van der Waals forces between the pesticide moiety and the surface of a soil particle also plays an important part in all sorption processes. In terms of interpretation, the higher the value of the intercept C, the greater the thickness of the boundary layer (Kannan & Sundaram, 2001). Calculated values of the intercept C (with units of µg/g), listed in Table 3, for both pesticides were significantly higher than the corresponding values of *k* (the intraparticle diffusion rate constant). This indicates some degree of boundary layer control which implies that intra-particle diffusion is not only the rate controlling step.

3.3.4 Langmuir model

The Langmuir model, as represented with this equation, $q_e = (Q_o K_L C_e)/(1+K_L C_e)$, assumes only a monolayer is formed and no further deposit of adsorbate on sorbed adsorbate molecules except on free adsorbent surface only. However, the transformed linear equation, to obtain the Langmuir parameters is, $1/q_e = 1/Q_o + 1/(Q_o K_L C_e)$ where q_e is adsorption capacity (µg/g of soil), Q_o is the maximum monolayer coverage capacity (µg/g), K_L is Langmuir isotherm constant (L/g), C_e is the equilibrium conc. of adsorbate (µg/g) and Co is initial concentration.

Also, the Langmuir equilibrium parameter, R_L, was computed as follows: $R_L = 1/[1+(1+K_L C_o)]$. This indicates the adsorption nature to be either unfavourable if $R_L > 1$, linear if $R_L = 1$, favourable if $0 < R_L < 1$ and irreversible if $R_L = 0$. The values of Q_o and K_L were both derived from the slope and intercept of the plot of $1/q_e$ against $1/C_e$ while the regression coefficient, R^2, was obtained from the regression equation of the plot (Table 4).

The Langmuir equilibrium parameter, R_L, was generally low ranging from $0.20 - 0.48$ for both neonicotinoids on all the soils tested. According to Langmuir description, favourable if 0

$< R_L < 1$, adsorption of the thiacloprid and thiamethoxam on all the soils with contrasting characteristic, is likely. However, the values seem to be very low and may suggest low adsorption intensities or not adequately represented by the model; although thiacloprid, with the highest value of R_L (Table 4), was adsorbed most (Qo = 1.84 µg/g) in the TH soil, with the most %SOC.

3.3.5 Freundlich model

Adsorption data were fitted to the Freundlich adsorption equation, $Q_e = K_f * Ce^{1/n}$, which was transformed into its linear form by taking log of both sides of the equation and represented as: Log Q_e = Log K_f + 1/n C_e, where Qe is adsorption capacity (µg/g) and C_e is the equilibrium conc. of adsorbate (µg/g). The constant K_f is an approximate indicator of adsorption capacity, while 1/n is a function of the strength of adsorption in the adsorption process. If n = 1 then the partition between the two phases are independent of the concentration, while normal adsorption and cooperative adsorption are 1/n < 1 and 1/n > 1 respectively.

The Freundlich values of 1/n for the thiacloprid and thiamethoxam on the soils tested were found to be < 1 (Table 4); this indicates that the sorption of both neonicotinoids is favourable. However, only thiamethoxam on BR soil showed 1/n value of 1.32, indicating cooperative adsorption type, according to Freundlich model, where adsorbates react with other adsorbates to synergistically enhance their adsorption (Liu, 2015). This behaviour may be influenced by the reactive nitro-functional group of thiamethoxam, which needs to be further investigated. Similarly, in the same BR soil, the value of 1/n for thiacloprid was reported to be 0.93, relatively close to thiamethoxam behaviour. The thiamethoxam experimental data obtained from three of the soils, except in TH (soil with the most % SOC), were well described by the Freundlich equation with $R^2 \geq 0.931$. However, the R^2 response from thiamethoxamon similar soils were lower, in the range 0.748 – 0.968.

From the results of the adsorption isotherm (Table 4), both Langmuir and Freundlich fitted well into the adsorption of both pesticides on BR soil with high values of coefficient of determination, R^2, (0.872 – 0.995). There is, therefore, evidence that these compounds may be adsorbed by soil and removed from the aqueous environment. However, the extent of removal would be influenced by the surface chemistry of the adsorbent. This is an area to be investigated further.

3.4 Leaching evaluation

Neonicotinoids are considered to be moderate to high leachers as a result of their high solubility in water (Gupta *et al*., 2008, Bonmatin *et al.*, 2014). Morevoer, their low affinity for soil mineral matrix promotes their leaching via advection or bulk flow during the partial equilibrium condition created by rain storm (Radolinski *et al.,* 2018). Several studies have been carried out on the sorption and leaching of neonicotinoids in soils across many countries such as China (Zhang *et al.*, 2018, Han *et al.*, 2019, US (Papiernik *et al.*, 2006), Spain (Rodríguez-Liébana *et al., 2018)*, Austria (Kah *et al.*, 2018) but these studies were focused on imidacloprid and thiamethoxam and knowledge is needed from the ubiquitous thiacloprid (Yi et al., 2019)..

The breakthrough curves for leaching of the two insecticides, most and least adsorbed, through soil with the least and most %SOC are shown in Figure 5. The elution of thiamethoxam from the column with BR-soil was at approximately 0.16 bed volume (bv) and 0.29 bv was recorded for thiacloprid. Similar elution order was observed in TH-soil, with 0.75 bv and 14.0 bv for thiamethoxam and THA respectively. Therefore, leaching from the soil poorer in organic carbon took place easily, with potential environmental consequences in terms of the migration of these pesticides.

Both thiacloprid and thiamethoxam presented very limited interaction with the BR soil. Specifically, the thiacloprid band in the BR-soil was broader when compared to hiamethoxam (see Figure 5), and this indicates that thiacloprid has somewhat more affinity with the BR soil than thiamethoxam. The asymmetrical curve of the two pesticides, particularly in BR soil, with a longer extended tail in thiamethoxam curves, may be due to the existence of more than one mechanism involved in the retention, or limited interactions with the soil, as reported by Rodríguez-Liébana *et al*. (2018). When the mobility of both insecticides was assessed on a second soil, characterised as being high in organic carbon, the elution was delayed but the same elution order was observed. The bands were broader in this soil which may indicate a range of unspecific interactions with the soil, and overloading of the active sites of the soil taking part in the adsorption process (Figure 5). The gaussian nature of the thiamethoxam in the TH soil indicates similar interaction of the neonicotinoid molecules migrating through the column with the soil. However, under similar column study condition, a diminished non-symmetrical elution profile was observed with thiacloprid pesticide in TH soil indicating a stronger affinity for the soil high in %SOC. This results evidence that thiacloprid has low tendency to migrate through soil, and therefore other reasons than its soil migration from neighbouring fields could be behind its occurrence in crops where the pesticide has not been applied.

The amount of pesticides recovered from the BR-soil column were 0.09 and 0.71 %, respectively for thiamethoxam and thiacloprid of the amount initially applied. Similarly, in the TH-soil column, 0.69 % for THX and 29.8 % for thiacloprid were recovered after the column leaching is concluded. The analysis of residues of the pesticides present in the soil after the column leaching study showed that the amount of thiamethoxam that had eluted from TH-soil was five times greater than thiacloprid and it was almost twice in BR soil. This

implies that thiamethoxam has the capacity to migrate and the soil characteristics may not mitigate its migration.

The longer times of abode of thiacloprid in the soils (especially with high % SOC) may result in greater exposure to soil faunas due to corresponding longer contact times (Cláudia *et al.,* 2017). The fate of these two insecticides (thiacloprid and thiamethoxam) in the soils with contrasting organic contents correlates well with the GUS leaching index and their solubilities (Table S1). With the smallest value of CEC (Table 1), the BR-soil environment is also strongly alkaline (see Table 1), hinting the existence of high levels of exchangeable cations. Therefore, with greater tendency for clay to disperse and produce poor soil structure, a hydrophilic pesticide like THX, in this environment, leaches through the soil with very limited interaction with the substrate.

In the present work, it has been demonstrated that thiamethoxam is leached out of soil readily due to its relatively lower affinity for organic materials, and a high risk of ground water contamination is to be expected as a result of its application. For instance, the herbicide atrazine (with solubility 34.7 mg/L and $\log_{10} K_{ow}$ 2.7) is frequently detected in European surface water at levels of 5 - 25 ng/L (Hillebrand *et al.* 2014; Criquet *et al.*, 2017 and Poulier *et al.* 2014) despite its use being banned in Europe since 2004.

Insecticide residues were retained in both soil columns with BR-soil harbouring less residues after leaching, compared to TH soil, see Table 5. Interestingly, most residues of the insecticides were extracted from the upper layer in the BR-soil column, with least amount from the lower layer; this informs remediation strategies for this type of soil when contaminated with the study neonicotinoids. In the TH-soil column, more residues were extracted from the middle and lower layers than the upper part of the column. It is likely that the high level of binding organic matter in TH soil, washed down during continuous flow of

water, may be responsible for the differential adsorption behaviour of the insecticides in the soil column operating under gravity.

The leaching of thiamethoxam in BR-soil with 0.8 % SOC gave similar results to that obtained by Gupta, *et. al.* (2008), with 0.5 % SOC soil and recovering about 66-79 % of applied thiamethoxam from leachate, with no residue detected in soil, after draining with 2.5 litres of water. The inability of thiamethoxam to bind strongly with soil, high in %SOC, may be due to its ionised form through the protonated nitrogen and nitro group; meaning it stays in the aqueous solution instead. This property may be responsible for its ease of leaching which leads to enhanced mobility, with potential pollution consequences for both ground water and run-off.

Although these pesticides are highly mobile, some neonicotinoids have been reported to persist in the environment with their residue being detected in plants years after their application (Wood & Goulson, 2017; Jiang *et al.*, 2018). Therefore, this positions thiacloprid and their metabolites, with stronger affinities for the binding organic carbon content of the soil, to be a risk to the health of soil faunas.

4.0 Conclusions

Thiamethoxam was the least adsorbed insecticide in all soils, and it is one of the most widely-used neonicotinoids in the UK. The implication is that it has the greatest potential to contaminate ground water, especially when used in a soil type with relatively low organic carbon. In contrast, thiacloprid, the most adsorbed insecticide, is expected to be more retained in soils with high organic carbon content.

Adsorption to soil is favourable for the studied neonicotinoids and the results were well described by Freundlich isotherm. However, sorption is strongly influenced by soil types and

nature of the pesticides. Adsorption kinetics of neonicotinoids on soils with different organic content are well represented by a pseudo second order kinetic model (R^2 >0.999); though kinetic rate of sorption of the insecticides appeared to be higher in soil rich in organic matter.

In flow through experiments, the soil type high in organic carbon content prolonged the elution of the pesticides, four times more with thiamethoxam and forty-eight times more with thiacloprid. This has two implications: (i) if not degraded, thiacloprid will be rapidly available in the soil environment; (ii) soil faunas may be damaged. Thiamethoxam and thiacloprid tend to leave greater residues in the first half of the soil column with the least adsorbing soil rich in silt (BR). In contrast, a soil rich in organic matter (TH) presented most residues deep down in the soil column. This has implications in the bioavailability of the neonicotinoids by plants and soil organisms.

Acknowledgement

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Figure captions

Figure 1. Total ion chromatogram of the four compounds; thiamethoxam (THX); imidacloprid (IMI); acetamiprid (ACE); thiacloprid (THA) analysed with LC-MS/MS at 1µg/L

Figure 2. Assessment of the amounts of neonicotinoids sorbed in soils. Study carried out at soil: solution ratio of 1:5 at two levels of pesticide contamination: 2.5 µg/g (A) and 25 µg/g (B). Results given as average (n=3) ± SD.

Figure 3. Percentage of the amount of thiamethoxam and thiacloprid sorbed to soils (TH and BR) when 4 g of the soil samples were incubated with 20 ml of 2.5 µg/g pesticides aqueous solution at different time intervals 0 – 72 h.

Figure 4. The linear form of pseudo second-order equation of the uptake of thiacloprid in soil BR (A) and TH (B) and thiamethoxam in soil BR (C) and TH (D) at different contact times.

Figure 5. Breakthrough curves corresponding to the leaching of thiacloprid (THA) and thiamethoxam (THX) in 2 equivalent soil columns (4 cm i.d. and 15 cm height) where the neonicotinoids were spiked onto soils (1 ml of 1000 µg/g of pesticide were added to 192 g of soil which was deposited on a layer on the top of the column) where soils had 0.8 and 12.5 % SOC (BR and TH). 1 Bed volume (bv.) = 175 ml.

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Figure 5
Click here to download Figure: Figure 5.pptx
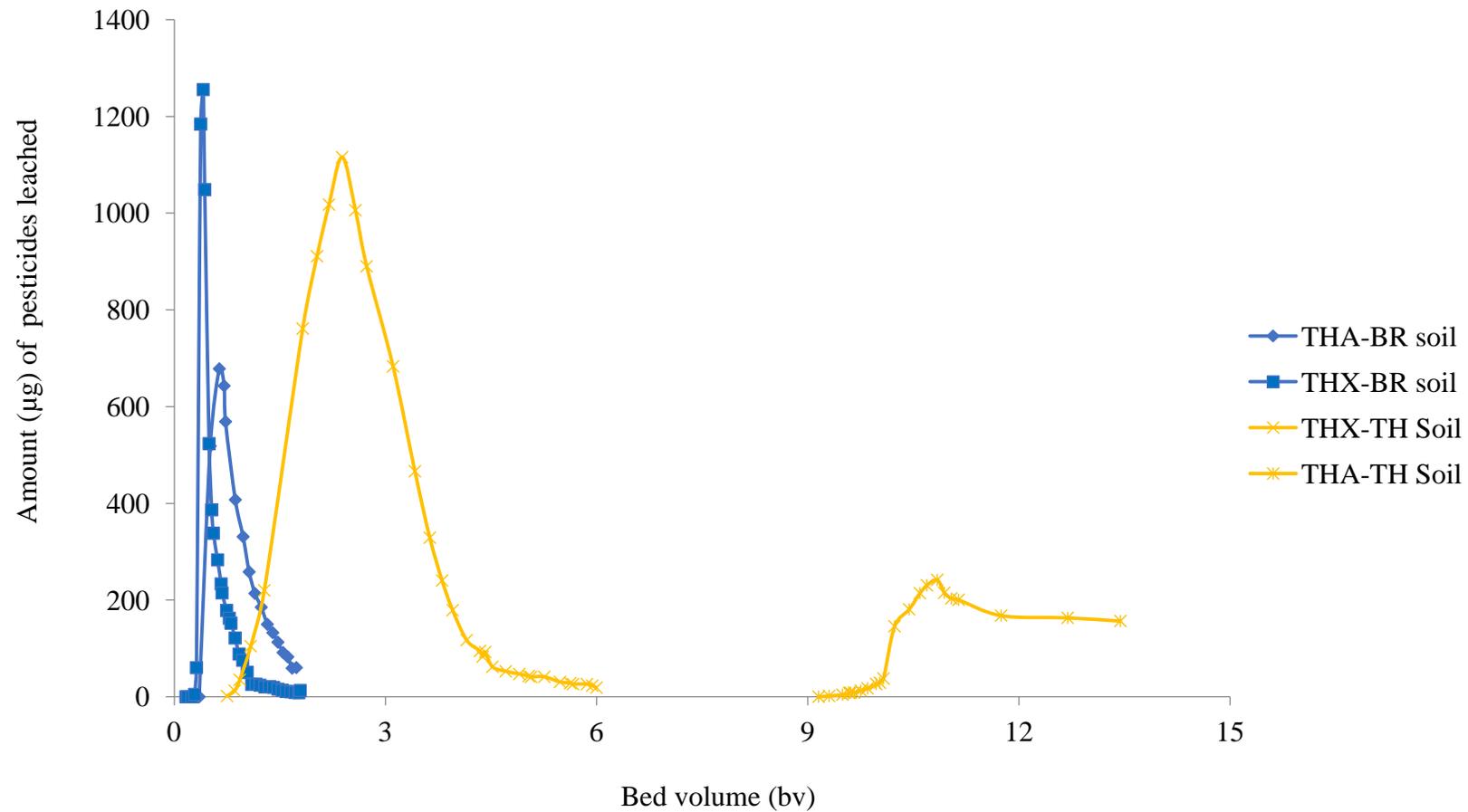
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Table 1. Soil characteristics of five soils from different locations in the UK. The characterisation of the soils was carried out as described in ISRIC (2002).

Soil sampling locations	Location (UK)	Latitude – Longitude	Land use	sand-silt-clay, %	SOC, %	pH (water)	CEC, cmol/kg
BR	Brighton (East Sussex)	50.849133, 0.118022	Golf course	31.9 - 45.3 - 22.8	0.8	8.8	1.4
EY	Eynsford (Kent)	51.374549, 0.213009	Farmland	45.1 - 31.5 - 23.4	2.6	8.3	5.6
TLW	Tolworth (Surrey)	51.372305, 0.276660	Farmland	46.1 - 26.5 - 27.4	3.2	7.3	10.8
ST	Stornoway (Western Isles, Scotland)	58.205537, 6.353212	Domestic garden	77.9 - 1.5 - 21.3	9.2	7.1	14.1
TH	Thornton Heath (Surrey)	51.397848, -0.097930	Domestic garden	41.0 - 37.6 - 21.4	12.5	7.1	21

Table 2. Detection conditions including MRM transitions for quantitation/confirmation for each compound studied with their corresponding collision energies (CEs) and instrumental quality parameters are included. Repetitivity and reproducibility were assessed at 1µg/L.

Compound	Q1 (m/z)	Q3 (m/z)	CE, (eV)	MRM transition	LOD (µg/L)	LOQ (µg/L)	Repe-titivity (%)	Repro-ducibility (%)
Acetamiprid	223	126	20	Quantitation	0.11	0.38	9.5	11.7
	223	90	20	Confirmation				
Imidacloprid	256	209	45	Quantitation	0.23	0.78	7.8	13.3
	256	175	47	Confirmation				
Thiacloprid	253	126	40	Quantitation	0.10	0.34	4.6	6.6
	253	90	40	Confirmation				
Thiamethoxam	292	211	32	Quantitation	0.20	0.68	7.2	16.6
	292	181	45	Confirmation				

Dwell time: 0.01s

Table 3. Sorption kinetics of thiacloprid and thiamethoxam on two soils with contrasting organic carbon obtained from four models

Soil	Thiacloprid												Thiamethoxam											
	Hyperbolic model		Pseudo-second-order reaction			Elovich			W-M			Hyperbolic model		Pseudosecond-order reaction			Elovich			W-M		
	q_{max}[a]	R^2	q_{max}	K[b] x 10^{-3}	R^2	%[c]	$1/Y$	R^2	C[d]	K[e]	R^2	q_{max}	R^2	q_{max}	K x 10^{-3}	R^2	%	$1/Y$	R^2	C	K	R^2
BR	5.08	0.467	5.49	7.88	0.999	88	0.25	0.890	4.32	0.180	0.717	3.66	0.762	3.78	7.05	0.999	66	0.16	0.666	3.10	0.100	0.408
TH	10.27	0.984	10.18	18.53	1	99	0.03	0.616	10.18	0.008	0.354	0.51	0.06	0.52	19.09	1	96	0.003	0.219	0.50	0.003	0.217

[a]q_{max} unit in µg/g; K[b] unit in g/µg/min; %[c] Percent sorbed during the initial phase (6 h) with respect to the sorbed amount at 24 h; C[d] units in g/µg; K[e] unit in (µg/g/min$^{1/2}$)

Table 4. Sorption isotherm of thiamethoxam and thiacloprid on four soils with contrasting organic carbon obtained from two models (Freundlich and Langmuir adsorption isotherm)

THX

	TLW						EY						BR						TH					
	Freundlich			Langmuir			Freundlich			Langmuir			Freundlich			Langmuir			Freundlich			Langmuir		
K_f	$1/n$	R^2	Q_o	$R_L{}^a$	R^2	K_f	$1/n$	R^2	Q_o	$R_L{}^a$	R^2	K_f	$1/n$	R^2	Q_o	$R_L{}^a$	R^2	K_f	$1/n$	R^2	Q_o	$R_L{}^a$	R^2
7.32	0.43	0.803	1.16	0.31	0.797	7.32	0.43	0.748	1.16	0.31	0.71	7.51	1.32	0.968	1.14	0.41	1	5.16	0.13	0.01	1.4	0.2	0.39

THA

	TLW						EY						BR						TH					
	Freundlich			Langmuir			Freundlich			Langmuir			Freundlich			Langmuir			Freundlich			Langmuir		
K_f	$1/n$	R^2	Q_o	$R_L{}^a$	R^2	K_f	$1/n$	R^2	Q_o	$R_L{}^a$	R^2	K_f	$1/n$	R^2	Q_o	$R_L{}^a$	R^2	K_f	$1/n$	R^2	Q_o	$R_L{}^a$	R^2
1	0.58	0.976	0.86	0.31	0.934	1	0.5	0.979	0.86	0.29	0.94	11.35	0.93	0.931	0.95	0.36	0.87	3.5	0.23	0.28	1.84	0.48	0.03

Table 5
Click here to download Table: Table 5 new.docx

Table 5. Amount of thiamethoxam and thiacloprid retained in different sections of the soil column after leaching. Results given as average (n=3) µg neonicotinoid/g soil ± SD.

Soil	Thiacloprid			Thiamethoxam		
	Upper layer [a] (µg /g)	Middle [b] (µg /g)	Lower layer [c] (µg /g)	Upper layer [a] (µg /g)	Middle [b] (µg /g)	Lower layer [c] (µg /g)
BR	10.34 ± 0.91	6.95 ± 0.78	4.59 ± 0.29	1.21 ± 0.23	1.01 ± 0.26	0.57 ± 0.06
TH	26.36 ± 1.56	85.62 ± 38.79	83.87 ± 15.67	6.55 ± 0.26	9.58 ± 0.45	7.79 ± 0.81

[a] 0-5 cm; [b] 5-12 cm; [c] 12-20 cm

Supplementary material

Behaviour of neonicotinoids in contrasting soils

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Table S1. Chemical structure and physicochemical properties of the four pesticides studied. [a,b]

Pesticides	IUPAC name	Solubility in water (mg/L) at 20°C	log K_{ow}	K_{oc}	GUS leaching potential index (Leachability rating)
Acetamiprid	((E)-N1-[(6-chloro-3-pyridyl) methyl]-N2-cyano-N1-methyl acetamidine)	2,950	0.8	200	0.82 (low)
Imidacloprid	1-[(6-Chloro-3-pyridinyl) methyl]-4,5-dihydro-N-nitro-1H-imidazol-2-amine	610	0.57[a]	156-960	3.76 (high)
Thiacloprid	[3-[(6-chloro-3-pyridinyl) methyl]-2-thiazolidinylidene] cyanimide	180	1.26	261-870	1.44 (low)
Thiamethoxam	3-(2-Chloro-5-thiazolylmethyl) tetrahydro-5-methyl-N-nitro-4H-1,3,5-oxadiazin-4-imine	4,100	0.13[a]	33-117	4.69 (high)
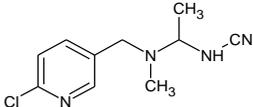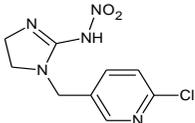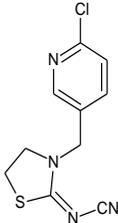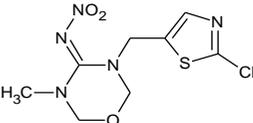
S2. Results of the individual pesticide adsorbed on the 5 soils at two different concentration levels

Table S2.1 Acetamiprid adsorption capacity, K_d and K_{oc} in 5 different soils assayed at low and high concentrations of insecticide: 2.5 µg/g and 25 µg/g. All values are given as mean $\pm$ SD

Soil type	Insecticide conc. (µg/g)	Adsorption capacity (µg/g soil)	K_d	K_{oc}
EY	Low	5.40 ± 0.39	5.37 ± 0.77	204.00 ± 29.32
	High	50.75 ± 1.74	6.89 ± 0.55	261.39 ± 20.98
BR	Low	1.21 ± 0.31	0.66 ± 0.19	80.37 ± 23.63
	High	0.13 ± 4.53	0.02 ± 0.26	1.99 ± 31.54
TH	Low	6.70 ± 0.16	8.89 ± 0.59	71.42 ± 4.75
	High	52.42 ± 2.45	7.47 ± 0.90	60.04 ± 7.22
TLW	Low	5.42 ± 0.12	5.36 ± 0.25	166.43 ± 7.70
	High	31.71 ± 2.10	2.84 ± 0.29	88.14 ± 9.00
ST	Low	4.42 ± 0.08	3.66 ± 0.11	39.96 ± 1.24
	High	37.94 ± 2.07	3.82 ± 0.36	41.75 ± 3.93

Table S2.2. Dinotefuran adsorption capacity, K_d and K_{oc} in 5 different soils assayed at low and high concentrations of insecticide: 2.5 µg/g and 25 µg/g. All values are given as mean $\pm$ SD.

Soil type	Insecticide conc. (μg/g)	Adsorption capacity (μg/g soil)	K_d	K_{oc}
EY	Low	1.52 ± 0.13	0.51 ± 0.05	19.37 ± 1.84
	High	46.64 ± 6.11	1.88 ± 0.33	71.17 ± 12.48
BR	Low	3.29 ± 0.36	1.26 ± 0.17	152.99 ± 20.45
	High	31.65 ± 6.23	1.14 ± 0.28	138.63 ± 34.13
TH	Low	3.66 ± 2.03	1.55 ± 1.14	12.48 ± 9.19
	High	34.41 ± 11.73	1.29 ± 0.56	10.32 ± 4.53
TLW	Low	3.24 ± 3.00	1.425 ± 1.30	44.224 ± 40.31
	High	40.84 ± 7.28	1.573 ± 0.36	48.831 ± 11.09
ST	Low	5.28 ± 0.28	2.37 ± 0.19	25.86 ± 2.02
	High	47.17 ± 3.25	1.90 ± 0.18	20.71 ± 1.95

Table S2.3. Imidacloprid adsorption capacity, K_d and K_{oc} in 5 different soils assayed at low and high concentrations of insecticide: 2.5 µg/g and 25 µg/g. All values are given as mean $\pm$ SD.

Soil type	Insecticide conc. (µg/g)	Adsorption capacity (µg/g soil)	K_d	K_{oc}
EY	Low	6.49 ± 0.25	5.46 ± 0.45	207.31 ± 16.88
	High	56.53 ± 1.79	3.73 ± 0.21	141.49 ± 7.88
BR	Low	1.07 ± 0.67	0.48 ± 0.32	58.90 ± 38.43
	High	43.57 ± 4.82	2.47 ± 0.41	300.51 ± 50.45
TH	Low	4.69 ± 0.71	3.07 ± 0.70	24.63 ± 5.65
	High	114.37 ± 0.95	31.74 ± 1.99	254.97 ± 15.96
TLW	Low	7.99 ± 0.81	9.25 ± 2.36	287.21 ± 73.27
	High	66.99 ± 2.23	5.13 ± 0.35	159.10 ± 10.91
ST	Low	11.26 ± 0.48	53.98 ± 24.73	589.41 ± 269.97
	High	91.83 ± 1.79	11.33 ± 0.72	123.75 ± 7.84

Table S2.4. Thiacloprid adsorption capacity, K_d and K_{oc} in 5 different soils assayed at low and high concentrations of insecticide: 2.5 µg/g and 25 µg/g. All values are given as mean $\pm$ SD.

Soil type	Insecticide conc. (µg/g)	Adsorption capacity (µg/g soil)	K_d	K_{oc}
EY	Low	11.65 ± 0.00	26.58 ± 0.034	1008.84 ± 1.29
	High	93.47 ± 0.16	13.98 ± 0.09	530.81 ± 3.50
BR	Low	6.77 ± 0.02	4.78 ± 0.03	582.69 ± 3.59
	High	29.08 ± 9.09	1.51 ± 0.60	184.47 ± 73.75
TH	Low	11.67 ± 0.03	26.88 ± 0.47	215.99 ± 3.81
	High	110.50 ± 0.47	33.69 ± 1.10	270.65 ± 8.83
TLW	Low	10.97 ± 0.12	19.12 ± 0.96	593.41 ± 29.87
	High	91.85 ± 2.79	13.16 ± 1.45	408.43 ± 44.89
ST	Low	11.46 ± 0.19	24.14 ± 2.31	263.60 ± 25.26
	High	104.41 ± 2.03	23.35 ± 2.56	254.94 ± 28.15

Table 2.5. Thiamethoxam adsorption capacity, K_d and K_{oc} in 5 different soils assayed at low and high concentrations of insecticide: 2.5 µg/g and 25 µg/g. All values are given as mean ± SD.

Soil type	Insecticide conc. (µg/g)	Adsorption capacity (µg/g soil)	K_d	K_{oc}
EY	Low	0.98 ± 0.42	0.36 ± 0.17	13.52 ± 6.31
	High	8.55 ± 3.61	0.27 ± 0.12	10.27 ± 4.65
BR	Low	0.17 ± 0.10	0.06 ± 0.04	6.95 ± 4.30
	High	1.43 ± 1.66	0.04 ± 0.05	5.23 ± 6.08
TH	Low	9.35 ± 0.51	15.29 ± 3.58	122.86 ± 28.75
	High	25.37 ± 1.48	1.09 ± 0.08	8.74 ± 0.62
TLW	Low	0.55 ± 0.16	0.19 ± 0.06	5.99 ± 1.83
	High	6.13 ± 4.11	0.19 ± 0.13	5.95 ± 4.15
ST	Low	0.85 ± 0.46	0.18 ± 0.11	2.01 ± 1.15
	High	33.87 ± 0.73	0.78 ± 0.02	8.55 ± 0.24

S3. Assessment of uptake of the study neonicotinoids by the study soils.

The results of treating the study soils with neonicotinoids and corresponding adsorption capacities are reported in Table 6a.

Table S3.1 Adsorption capacities (µg neonicotinoid/g soil) assayed at low concentration of neonicotinoids (2.5µg/g), n=3.

Soil	ACE (µg/g)	DIN (µg/g)	THA (µg/g)	IMI (µg/g)	THX (µg/g)
EY	6.43	1.15	10.48	6.49	0.97
BR	1.44	2.49	5.93	1.07	0.17
TH	7.96	2.77	10.47	4.69	9.32
TLW	6.44	2.45	9.84	7.99	0.55
ST	5.26	4.00	10.30	11.26	0.84

Table S3.2. ANOVA table (two-way without replication) from the study of the adsorption of neonicotinoids at low concentration (2.5µg/g).

Summary	*Count*	*Sum*	*Average*	*Variance*
EY	5	25.52137	5.104274	16.3075
BR	5	11.10397	2.220794	4.986834
TH	5	35.21621	7.043242	10.38982
TLW	5	27.27627	5.455255	14.91125
ST	5	31.66334	6.332669	19.19192
ACE	5	27.53117	5.506234	6.080391
DIN	5	12.87168	2.574336	1.027477
THA	5	47.00989	9.401978	3.842231
IMI	5	31.51001	6.302001	14.36374
THX	5	11.85842	2.371684	15.1887

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit.
Rows	68.12793	4	17.03198	2.902697	0.05549	3.006917
Columns	169.267	4	42.31676	7.211886	0.00161	3.006917
Error	93.88224	16	5.86764			
Total	331.2772	24				

Table S3.3 Adsorption capacities (µg neonicotinoid/g soil) assayed at high concentration of neonicotinoids (25µg/g)

Soil	ACE	DIN	THA	IMI	THX
EY	76.64	35.97	96.77	56.53	7.97
BR	0.20	24.41	31.93	43.57	1.33
TH	79.16	26.53	115.33	114.37	23.66
TLW	47.89	31.49	96.02	66.99	5.72
ST	57.30	36.38	110.04	91.83	31.58

Table S3.4. ANOVA table (two-way without replication) from the study of the adsorption of neonicotinoids at high concentration (25µg/g)

Summary	Count	Sum	Average	Variance
EY	5	273.8796	54.77593	1197.147
BR	5	101.4356	20.28712	364.4383
TH	5	359.0571	71.81141	2032.09
TLW	5	248.1161	49.62321	1178.357
ST	5	327.1271	65.42543	1185.659
ACE	5	261.1877	52.23754	1018.298
DIN	5	154.7822	30.95645	29.31851
THA	5	450.0923	90.01847	1124.351
IMI	5	373.2898	74.65795	806.4269
THX	5	70.26347	14.05269	166.9517

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit.
Rows	7955.281	4	1988.82	6.878606	0.002024	3.006917
Columns	19204.66	4	4801.166	16.60549	1.5E-5	3.006917
Error	4626.101	16	289.1313			
Total	31786.04	24				

S4. Sorption kinetic models

- *Hyperbolic Model:* The linear form (Eq. 1) of this model provides useful sorption parameters values that can be adjusted to the experimental data

$$\frac{1}{q_t} = \left(\frac{B}{q_{max}} x \; \frac{1}{t}\right) + \frac{1}{q_{max}} \qquad \text{Eq. (1)}$$

Where, q_t is the sorbed quantity (μg/g) at time t (h), q_{max} (μg/g) is the maximum sorbed amount, t (h) is the pesticides solution-soil contact time, and B is an empirical constant.

- *Pseudosecond-Order Kinetic Reaction Model:* The application of this model is with the assumption that the sorption capacity could be proportional to the number of active sites on the adsorbent, as reflected in Eq. 2 below.

$$\frac{dq}{dt} = \; k(q_{max} - q_t)^2 \qquad \text{Eq. (2)}$$

q_{max} and q_t were as defined in the hyperbolic model above and k is the reaction-rate constant (μg g^{-1}min^{-1}).

The following linear equation was obtained after separating the variables, integrating with appropriate boundary condition and rearranging the terms.

$$\frac{t}{q_t} = \frac{1}{k \; q_{max}} + \frac{t}{q_{max}} \qquad \text{Eq. (3)}$$

- *Elovich Equation:* This equation describes second order kinetics with the assumption that the actual solid contact surface is energetically heterogeneous. However, the equation fails to propose any definite mechanism for adsorbent-adsorbate. Also, the equation reflects two phase of adsorption kinetics; a fast initial reaction due to pesticides movement to the most accessible part of the sorbent, and slower reaction phase due to in and out pesticides' diffusion from the sorbent microspores. The linear form of this equation is given below by:

$$q = \frac{1}{Y} ln(X * Y) + \frac{1}{Y} ln\ t \qquad\qquad\qquad \text{Eq. (4)}$$

where q is the sorbed quantity ($\mu g\ g^{-1}$) at time t, X and Y are constants as obtained from the experiments.

- *Weber-Morris Model (Intraparticle diffusion):* This equation (Eq. 5) considers a varying degree of proportionality of the sorption processes with $t^{1/2}$ and this is given *by:*

$$q = k\ t^{1/2} + C \qquad\qquad\qquad \text{Eq. (5)}$$

Also, q is the sorbed quantity ($\mu g\ g^{-1}$) of pesticides at time t, C is the intercept ($\mu g\ g^{-1}$) as shown in the equation (Eq. 5) and k is the intraparticle diffusion rate constant ($\mu g\ g^{-1}$).