

Differences in Neonicotinoid and Metabolite Sorption to Activated Carbon Are Driven by Alterations to the Insecticidal Pharmacophore

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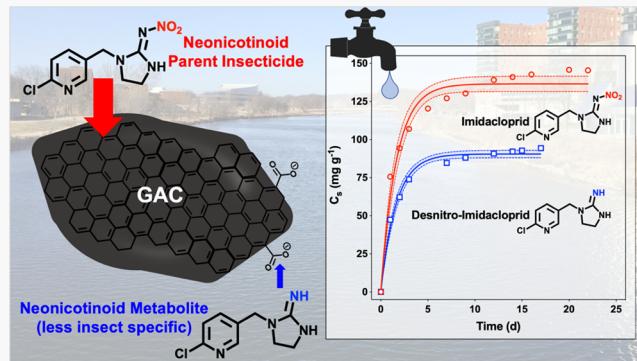
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ABSTRACT: Widespread application of neonicotinoids has led to their proliferation in waters. Despite low neonicotinoid hydrophobicity, our prior studies implicated granular activated carbon (GAC) in neonicotinoid removal. Based on known receptor binding characteristics, we hypothesized that the insecticidal pharmacophore influences neonicotinoid sorption. Our objectives were to illuminate drivers of neonicotinoid sorption for parent neonicotinoids (imidacloprid, clothianidin, thiamethoxam, and thiacloprid) and pharmacophore-altered metabolites (desnitro-imidacloprid and imidacloprid urea) to GAC, powdered activated carbon, and carbon nanotubes (CNTs). Neonicotinoid sorption to GAC was extensive and largely irreversible, with significantly greater sorption of imidacloprid than desnitro-imidacloprid. Imidacloprid and imidacloprid urea (electronegative pharmacophores) sorbed most extensively to nonfunctionalized CNTs, whereas desnitro-imidacloprid (positive pharmacophore) sorbed most to COOH-CNTs, indicating the importance of charge interactions and/or hydrogen bonding between the pharmacophore and carbon surface. Water chemistry parameters (temperature, alkalinity, ionic strength, and humic acid) inhibited overall neonicotinoid sorption, suggesting that pharmacophore-driven sorption in real waters may be diminished. Analysis of a full-scale drinking water treatment plant GAC filter influent, effluent, and spent GAC attributes neonicotinoid/metabolite removal to GAC under real-world conditions for the first time. Our results demonstrate that the neonicotinoid pharmacophore not only confers insecticide selectivity but also impacts sorption behavior, leading to less effective removal of metabolites by GAC filters in water treatment.



INTRODUCTION

Neonicotinoids are the most widely used insecticides in the world, with applications in urban landscaping, pet treatments, forestry, and agriculture.^{1–4} Due to the highly polar, water soluble nature of neonicotinoids⁵ ($\log K_{ow}$: –0.13 to 1.26) and their limited sorption to soil (up to $\sim 1 \mu\text{g g}^{-1}$),^{6–9} neonicotinoids are readily transported with water from their site of application. For instance, the most commonly used neonicotinoids, imidacloprid, clothianidin, and thiamethoxam, have been detected in groundwater, surface water, and drinking water at concentrations ranging from $<1 \text{ ng L}^{-1}$ to $>100 \mu\text{g L}^{-1}$.^{4,10–13} The prolific use and transport of neonicotinoids has negatively impacted non-target organisms, including declines in pollinator populations, inhibited behaviors/reproduction among aquatic insects, and impaired flight/reproduction among granivorous birds.¹

Neonicotinoids transformed in the environment can yield metabolites with slightly altered structures that are substantially more mammalian-toxic.^{14–18} Neonicotinoid insect selectivity is largely conferred by an electronegative nitro- or cyano-pharmacophore that exploits specific structural differences

between the insect and mammalian nicotinic acetylcholine receptors (nAChR).^{14,15,17,18} The pharmacophore can be altered via biotic and abiotic pathways (e.g., microbial metabolism, photolysis), resulting in desnitro-/descyano-metabolites with a more positive charge distribution (as is well established in the literature) that enables favorable interaction with the mammalian nAChR.^{14,15,17–19} Selective receptor binding is subsequently reversed from insects to mammals for some neonicotinoid metabolites (e.g., desnitro-imidacloprid is $>300\times$ more toxic toward mammals than imidacloprid based on half-maximum inhibitory concentrations [IC_{50}]).^{14,15,17,18} In the limited number of studies conducted thus far, neonicotinoid metabolites are detected at lower concentrations than the parent insecticides in the environ-

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ment,^{13,20,21} but the enhanced mammalian toxicity and lack of current data demands further investigation. Thus, understanding the fate of neonicotinoid metabolites with altered pharmacophores is critical.

We recently reported the first detection of neonicotinoids in finished drinking water ($0.24\text{--}33.5\text{ ng L}^{-1}$)^{13,20} and, subsequently, two metabolites (imidacloprid urea and desnitro-imidacloprid, $0.03\text{--}0.29\text{ ng L}^{-1}$)²⁰ present in source and finished drinking water at two drinking water treatment plants (DWTP) in Iowa City, Iowa, USA.²⁰ Neonicotinoids in finished drinking water were almost completely removed from the DWTP using granular activated carbon (GAC), whereas virtually no removal occurred in the conventional DWTP without activated carbon treatment, thus implicating GAC filtration as a significant removal process.¹³ Even with activated carbon treatment, the more mammalian-toxic metabolite desnitro-imidacloprid was still detected in finished water above the lower limit of detection (LLD), while the parent compound imidacloprid was completely removed, suggesting differences in sorption between the parent and pharmacophore-altered metabolite.²⁰ Thus, understanding underlying sorption mechanisms for parent insecticides and metabolites is imperative. Imidacloprid, clothianidin, and thiacloprid are known to sorb to biochar ($0.25\text{--}7.1\text{ mg g}^{-1}$), with greater sorption to chars with greater aromaticity and surface area.^{22,24} Similarly, GAC and powdered activated carbon (PAC) can adsorb imidacloprid (up to 110 mg g^{-1} PAC).^{13,25,26} Nevertheless, little is known regarding the efficacy of carbonaceous sorbent materials (e.g., activated carbon) for removing neonicotinoid metabolites from drinking water or environmental conditions that may impact removal.

Although sorption is often driven by hydrophobic interactions and physical entrapment, sorption of polar organic compounds to activated carbon can also be attributed to specific surface interactions, such as hydrogen bonding, ion exchange, and $\pi\text{-}\pi$ interactions.^{27,29} Experiments using calcium-containing clay surfaces suggested hydrogen bonding as a possible sorption mechanism for the hydrogen bond acceptors imidacloprid and imidacloprid urea, an interaction that may also be relevant to black carbon.^{29,30} In contrast, the amine/imine functional group of desnitro-imidacloprid is a hydrogen bond donor, which could alter its sorption propensity. Electrostatic differences between neonicotinoids and their metabolites may also impact sorption to black carbon. Following the loss of the electronegative pharmacophore (nitro-/cyano), neonicotinoid metabolites gain a more positive functional group that may subsequently impact sorption to activated carbon via cation coordination (cation bridging)^{28,31} or $\pi\text{-}\pi/\pi^+\text{-}\pi$ interactions.^{29,30,32} These potential impacts on sorption may be further complicated by water chemistry (e.g., water hardness/alkalinity, dissolved organic carbon, pH, and temperature) due to sorption site blocking,^{33–35} charge shielding,^{36–40} or competition.^{9,41,42} Thus, alteration of the neonicotinoid pharmacophore not only changes organism receptor binding^{15,18,43} and reactivity with chlorine²⁰ (as we previously demonstrated) but may also impact sorption in natural and engineered systems.

Therefore, the objectives of this study were to (1) establish sorption parameters with GAC, PAC, non-functionalized and functionalized carbon nanotubes, and probe drivers of sorption for the three most commonly used neonicotinoids (imidacloprid, clothianidin, and thiamethoxam), a representative cyano-neonicotinoid (thiacloprid), and two pharmacophore-altered

metabolites (desnitro-imidacloprid and imidacloprid urea); and (2) determine the impact of drinking water chemistry on the sorption of a neonicotinoid (imidacloprid) and its structurally altered metabolite (desnitro-imidacloprid) to commercially available GAC, including analysis of water and spent carbon from the GAC filter at a full-scale DWTP to assess neonicotinoid removal in a real-world treatment scenario. This research provides critical insights into differences in sorption propensity and probable mechanisms for neonicotinoids following alteration of the insecticidal pharmacophore, with implications for fate of target-specific pesticides and their metabolites, water treatment technologies, and human exposure.

MATERIALS AND METHODS

Chemicals. Neonicotinoids used in bench experiments were purchased at a purity of $\geq 95\%$: imidacloprid, clothianidin, thiamethoxam, thiacloprid, imidacloprid urea, and desnitro-imidacloprid hydrobromide. Analytical standards (imidacloprid, clothianidin, thiamethoxam, thiacloprid, and desnitro-imidacloprid hydrochloride) were of Pestanal-grade. Neonicotinoid isotopically labeled standards were imidacloprid- d_4 and thiamethoxam- d_3 . Solvents used for chromatography (water, acetonitrile, and formic acid) were of Optima LCMS (liquid chromatography mass spectrometry) grade. Solvents used for desorption experiments and solid phase extraction (acetone, acetonitrile, dichloromethane, hexanes, and methanol) were, at a minimum, ACS grade. Chemicals are fully described in the Supporting Information.

Sorbents. Established, commercially available sorbents (GAC and PAC) were used to represent those in a DWTP, while more uniform, idealized, carbon sorbents (carbon nanotubes) were used to better understand neonicotinoid uptake on activated carbon. Calgon Filtrasorb-200 granular activated carbon (F-200 GAC, $670\text{ m}^2\text{ g}^{-1}$ Table S.1) was used in isotherm and sorption kinetics experiments. Powdered activated carbon obtained from the University of Iowa water treatment plant (Cabot Hydrodarco B PAC, $400\text{ m}^2\text{ g}^{-1}$, Table S.1) was used in isotherm and sorption kinetics experiments. This PAC was chosen for analysis rather than a powdered form of the F-200 GAC to assess neonicotinoid sorption to a commercially available sorbent in use at the University of Iowa DWTP where we previously studied neonicotinoid removal from drinking water.^{13,20} Non-functionalized multiwalled carbon nanotubes (CNTs, $190\text{ m}^2\text{ g}^{-1}$), carboxylic acid-functionalized, and amine-functionalized multiwalled CNTs were used in isotherm experiments to probe sorption mechanisms (Table S.1).⁴⁴ Carboxylated CNTs ($120\text{ m}^2\text{ g}^{-1}$) were chosen as an analog for activated carbon with predominantly negative surface charge at pH 7 based on reports of pK_a values for surface carboxyl groups ($pK_a < 5$).⁴⁵ Amine-functionalized CNTs ($220\text{ m}^2\text{ g}^{-1}$) were chosen to compare effects of functional groups expected to have a more neutral charge in aqueous suspensions at pH 7 based on existing characterization⁴⁶ and application in metal cation uptake.⁴⁷ According to the vendor, carboxylic acid-functionalized MW-CNTs had a $-\text{COOH}$ content of 4–5%, while amine-functionalized MW-CNTs had a $-\text{NH}_2$ content of 5.5–8.5% (with NH , $\text{O}=\text{C}-\text{NH}_2$, and $\text{C}=\text{N}$ functionalities). BET surface area was measured for each of these sorbents and provided in Table S.1 with further sorbent information.

Activated Carbon Isotherms. Isotherms were used to determine the capacity for GAC to adsorb neonicotinoids

(imidacloprid, clothianidin, thiamethoxam, and thiacloprid) and two imidacloprid metabolites (imidacloprid urea and desnitro-imidacloprid). Isotherms were generated in light-sensitive amber or foil-covered glass vials (to avoid photodegradation) containing 100 mM phosphate buffer (to control against pH changes associated with activated carbon) and 50 mM sodium azide (to inhibit microbial growth).⁴⁸ At 25 °C, batch solutions containing individual neonicotinoids or neonicotinoid metabolites (not mixtures) at equivalent initial concentrations ranging from 10 to 60 mg L⁻¹ were combined with 0.3 g L⁻¹ Calgon F-200 GAC, alongside controls (without GAC). Isotherms were mixed on an end-over-end rotator at 25 rpm until pseudo-steady state (achieved within 16 days, Figure S.1). Pseudo-steady state or “equilibrium” sorbed concentration (C_s , mg g⁻¹) and aqueous concentration (C_w , mg L⁻¹) were fit using the Langmuir sorption model (eq 1) with 95% confidence intervals:

Langmuir model:

$$C_s = \frac{Q_m K_L C_w}{1 + (K_L C_w)} \quad (1)$$

where Q_m is the maximum mass of neonicotinoid that can be adsorbed per gram of GAC (mg g⁻¹) and K_L is the Langmuir constant (L mg⁻¹). The Langmuir model was used because it was assumed neonicotinoid molecules adsorbed via specific interactions with surface functional groups, leading to a finite number of available sorption sites on the carbon surface. Isotherms for imidacloprid and desnitro-imidacloprid (10–60 mg L⁻¹) were also generated with powdered activated carbon (PAC, 0.3 g L⁻¹) obtained from the University of Iowa DWTP (at pH 7) as described above.

The reversibility of neonicotinoid sorption to GAC was tested for imidacloprid, desnitro-imidacloprid, and thiacloprid. At 16 days, sorption isotherms reached pseudo-steady state and the 30 mg of GAC was filtered from the buffer solutions containing aqueous neonicotinoid and placed in light-sensitive amber or foil-covered glass vials (to avoid photodegradation) containing 100 mM phosphate buffer (100 mL, equivalent to isotherm volume used; 0.3 g L⁻¹ neonicotinoid-bound GAC) without any neonicotinoid added to the solution. Following rotation on an end-over-end rotator for 7 days at 25 rpm (Figure S.1), there was no sign of microbial growth and aqueous samples were analyzed to determine the mass of neonicotinoid desorbed from the surface (see Supporting Information Method Details).

Specific neonicotinoid-black carbon surface interactions were probed using carbon nanotubes. Isotherm parameters were determined for imidacloprid, desnitro-imidacloprid, and imidacloprid urea using non-functionalized carbon nanotubes (nF-CNTs), carboxylic acid-functionalized CNTs (COOH-CNTs), and amine-functionalized CNTs (NH₂-CNTs). Imidacloprid and metabolites (5–200 μM) in 5 mM phosphate buffer were mixed with 0.05 g L⁻¹ CNTs in suspension (see the Supporting Information for details). Each vial was well mixed (reached equilibrium within 1 h) and left in the dark to settle CNTs overnight before sampling and analysis using the Langmuir model.

Water Chemistry and Sorption Kinetics. Batch kinetics experiments assessed the impacts of water chemistry parameters on the sorption of imidacloprid and desnitro-imidacloprid (pharmacophore intact and altered, respectively). Experiments were conducted at two initial neonicotinoid concentrations, 50

mg L⁻¹ (used in 20–25 day experiments to determine impacts on sorption capacity) and 10 μg L⁻¹ (used in 24 h experiments to determine impacts on sorption kinetics at a more environmentally relevant concentration). These experiments (at both concentrations) were mixed in duplicate with 0.3 g L⁻¹ Calgon F-200 GAC alongside controls without GAC at 25 rpm on an end-over-end rotator in light-sensitive amber or foil-covered glass vials (to prevent photodegradation). Water chemistry conditions included ionic strength (500 mM NaCl in 1 mM buffer), humic acid (5 ppm Aldrich humic acid in 1 mM buffer), CaCO₃ (45 ppm in 1 mM buffer), excess buffer concentration (100 mM buffer), and temperature (1 mM buffer at 4 °C, only assessed for 10 μg L⁻¹ kinetics). 1 mM Buffer at 25 °C was used as a control to assess the impact of each water chemistry condition on neonicotinoid sorption. Experiments were conducted at two pH conditions: in phosphate buffer (pH 7) and borate buffer (pH 9.2; borate has an optimal buffering capacity ~pH 9). A 45 ppm CaCO₃ system adjusted to pH 11 with 1 M NaOH was also used to probe the effects of the carbonate anion on 10 μg L⁻¹ sorption kinetics. Sorption (at 50 mg L⁻¹) was also evaluated in filtered (0.7 μm PES) Iowa River water and University of Iowa tap water as outlined above. Solutions containing 10 μg L⁻¹ were sampled at eight predetermined time points over 24 h and analyzed by pseudo-first-order decay. For solutions containing 50 mg L⁻¹ imidacloprid or desnitro-imidacloprid (sampled over 20–25 days), the relative concentrations over time were used to determine the sorbed concentration of neonicotinoid and were analyzed using a first-order rate model based off the Langmuir one-site kinetic model⁴⁹ (eq 2):

Modified Langmuir kinetic model:

$$C_{s,t} = C_{s,eq}(1 - e^{-k_{ad} \times t}) \quad (2)$$

where, $C_{s,t}$ is the concentration of neonicotinoid adsorbed at time t (mg g⁻¹), $C_{s,eq}$ is the maximum concentration of neonicotinoid adsorbed at pseudo-steady state, k_{ad} is the adsorption rate constant (d⁻¹), and t is time (d). The full Langmuir one-site kinetic model (provided in equation S.1) was simplified assuming the desorption rate constant to be negligible based on sorption reversibility data (see the Supporting Information), simplifying the model to a pseudo-first-order sorption model.⁴⁹

Drinking Water Treatment Plant Experiments. Water samples (1 L) were collected at the GAC filter inlet (influent) and outlet (effluent) to assess whether the GAC filter at a full-scale DWTP in Iowa City, IA (USA) is capable of removing neonicotinoids from source water, as we previously postulated.^{13,20} Water samples were collected in acid-washed amber glass bottles at the Iowa City DWTP at the inlet and outlet of GAC filter 5, extracted by solid phase extraction (SPE), and analyzed in the manner previously published;^{13,20} details are further described in the Supporting Information (Figure S.2).

GAC that had been used in a filter for 5 years at the Iowa City DWTP (spent GAC) was obtained to determine if neonicotinoids and metabolites would desorb from the field GAC material. Spent GAC (0.2 g) was mixed with solvents of varied polarity, individually (4 mL in pH 7 buffer $n = 6$, pH 9 buffer $n = 6$, methanol $n = 6$, acetone $n = 6$, acetonitrile $n = 6$, dichloromethane $n = 6$, and hexane $n = 3$), for 6 days at 25 rpm on an end-over-end rotator. Solvent was removed and evaporated under nitrogen (except buffered solutions) and reconstituted in 1 mL of acetonitrile:water (50:50 v/v) for

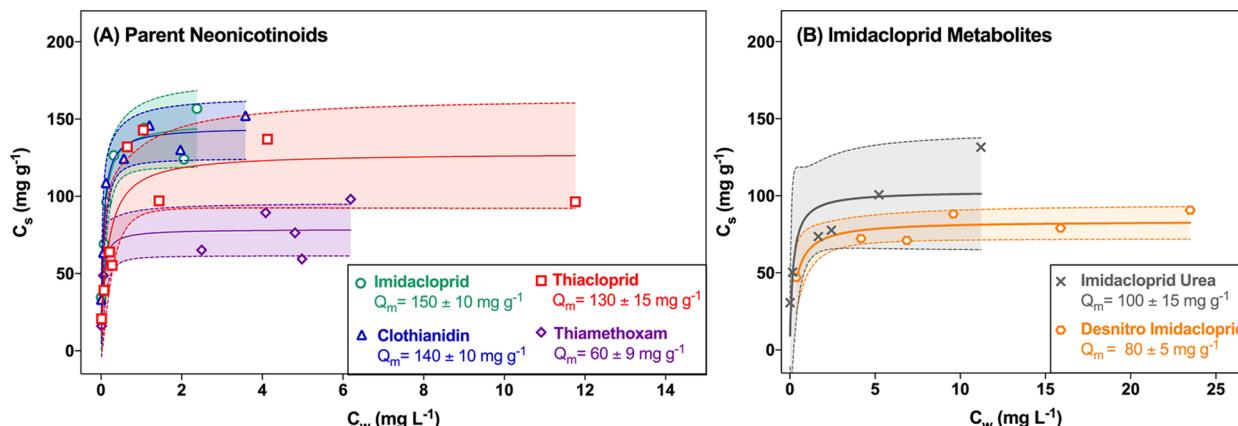


Figure 1. (A) GAC sorption isotherms for the nitro-neonicotinoids imidacloprid (circles), clothianidin (triangles), thiamethoxam (diamonds), and the cyano-neonicotinoid thiacloprid (squares). (B) GAC sorption isotherms for the imidacloprid metabolites imidacloprid urea (crosses) and desnitro-imidacloprid (hexagons). Isotherms are fit with the Langmuir sorption model and plotted with 95% confidence intervals.

analysis. To verify desorption of neonicotinoids, spent GAC was also analyzed by the USGS lab in Sacramento, California (USA) where the GAC was extracted with dichloromethane, acetone, acetonitrile, and methanol (see *Supporting Information Method Details*).

Analytical Methods. Solid Phase Extraction. Neonicotinoids and neonicotinoid metabolites were extracted from water samples following previously published methods with appropriate controls (see the *Supporting Information*).²⁰ Neonicotinoid and neonicotinoid metabolite recoveries were previously reported and are presented in **Table S.3**. Standard error of the regression was used to account for error in determining the concentration of field samples that underwent extraction and enrichment via SPE (see the *Supporting Information*).^{13,20}

Quantification via LC-MS/MS. All samples (except for 50 mg L⁻¹ sorption kinetics) were quantified using an Agilent 1260 Infinity liquid chromatograph with an Agilent 6460 triple quadrupole mass spectrometer (LC-MS/MS) with electrospray ionization in positive ionization multiple reaction monitoring mode (MRM) (**Tables S.4 and S.5**) similar to our previous methods.^{13,20} The chromatography column was an Agilent Zorbax eclipse plus C18 column (4.6 mm × 150 mm × 5 μm) with a Zorbax eclipse plus C18 guard column (4.6 mm × 12.5 mm × 5 μm). An injection volume of 20 μL was loaded onto the column preheated to 50 °C. The mobile phases contained 0.1% formic acid in (A) water (77.5%) and (B) acetonitrile (22.5%) with a flow rate of 0.8 mL min⁻¹. Lower limits of detection (LLD) were previously reported²⁰ and are provided in the *Supporting Information* (**Table S.6**).

Quantification via LC-DAD. Sorption kinetics samples (50 mg L⁻¹) were analyzed using an Agilent 1260 Infinity liquid chromatograph with an Agilent 1260 diode array detector (LC-DAD) and separated using the same column and solvent mixture as above (see details in **Table S.7**).

Quality Assurance and Statistical Analysis. Amber or foil-covered glass serum vials were used in bench experiments to minimize photolysis or evaporative losses. All isotherms where sodium azide was added to control for microbial growth were conducted alongside no-black carbon controls containing sodium azide (where no loss due to azide was observed for any of the neonicotinoids). All samples were spiked with imidacloprid-*d*₄ to account for instrumental variability upon analysis. Samples not immediately analyzed were stored at -20

°C until analysis was performed. Concentrated samples (analytes in the ppm range) were diluted 10-fold using Optima grade LCMS water prior to analysis on any instrument to work within the linear calibration range.

Matched-pairs experimental design was used whenever possible to maximize statistical power. Two-tailed *t*-tests or ANOVA ($\alpha = 0.05$) with Tukey post-hoc tests determined if two data sets or three or more data sets, respectively, were significantly different. ANOVA assumptions (i.e., parametric tests) were verified via the Shapiro-Wilk normality test. All isotherm and kinetics data sets passed normality tests at a significance level of $\alpha = 0.05$. Comparisons of specific best fit values (e.g., sorption capacity, Langmuir constant, and rate constant) were conducted via extra sum-of-least-squares *F*-tests ($\alpha = 0.05$). All statistical analyses were conducted at a 95% confidence level using Graphpad Prism 8 software (La Jolla, CA).

RESULTS AND DISCUSSION

Neonicotinoid Sorption Isotherms with Carbonaceous Materials. Despite low hydrophobicity, neonicotinoids demonstrated extensive sorption to carbonaceous materials. The capacity for GAC (F-200) to sorb neonicotinoids and imidacloprid metabolites ranged between 60 and 150 mg g⁻¹ (BET surface area: 670 m² g⁻¹, **Table S.1**) with Langmuir constants of 3.1–35 L mg⁻¹ (**Figure 1** and **Table S.9**). These sorption capacities are comparable to those for other pesticides with some similar structural properties^{50,51} (e.g., 2,4-D sorption capacity: 126–181 mg g⁻¹ GAC) and water solubilities^{52–54} (e.g., amitrole log $K_{ow} = -0.97$; sorption capacity: 30–45 mg g⁻¹ GAC). GAC had the greatest capacity to sorb imidacloprid and clothianidin followed by thiacloprid, imidacloprid urea, desnitro-imidacloprid, and thiamethoxam. Reversibility experiments with three representative neonicotinoids—imidacloprid (nitro-neonicotinoid), thiacloprid (cyano-neonicotinoid), and desnitro-imidacloprid (pharmacophore-altered metabolite)—revealed that no significant ($p > 0.05$) desorption occurred (**Figures S.5**). These results indicate that, although sorption to GAC likely undergoes monolayer uptake, limited reversibility suggests that neonicotinoids undergo Langmuir-like sorption.^{49,55} Similarly, nF-CNTs extensively sorbed neonicotinoids (sorption capacities of 25–135 mg g⁻¹, Langmuir constants of 0.06–0.67 L mg⁻¹; BET surface area: 190 m² g⁻¹, **Table S.1**),⁴⁴ with the greatest capacity to sorb thiacloprid and imidacloprid

followed by clothianidin, thiamethoxam, imidacloprid urea, and desnitro-imidacloprid. The trends in neonicotinoid uptake for GAC and nF-CNTs were consistent with those observed previously with biochar^{21,22} and soils,^{6,8,56} wherein thiacloprid and imidacloprid had the greatest capacity and thiamethoxam the least.^{6,8,9,56} Imidacloprid and thiacloprid sorption capacities were not significantly different from one another for either GAC or nF-CNTs ($p > 0.05$), suggesting that differences between the nitro- (imidacloprid) vs cyano- (thiacloprid) functional group did not materially impact sorption for these otherwise structurally similar molecules. Further information regarding statistical analysis of comparisons in sorption parameters are provided in Tables S.10–S.12.

The surface area normalized sorption capacities of GAC and PAC (pH 7) were nearly identical for both imidacloprid (0.22 vs 0.23 mg m⁻², respectively) and desnitro-imidacloprid (0.13 vs 0.11 mg m⁻², respectively), indicating that differences in observed sorption capacity between the two sorbents were predominately driven by differences in surface area (Figure 2).

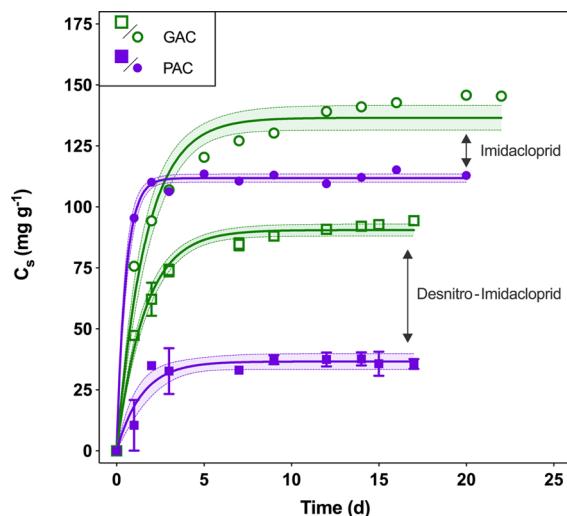


Figure 2. Sorption kinetics of imidacloprid (circles) and desnitro-imidacloprid (squares) to GAC (open green) and PAC (solid purple), illustrating the impact of the altered insecticidal pharmacophore on sorption. Isotherms are fit with the Langmuir one-site sorption model and plotted with 95% confidence intervals. Error bars represent the error associated with duplicate samples taken at each time point. Error bars not visible are present but smaller than the data point symbol. The slopes of sorbed concentrations of imidacloprid and desnitro-imidacloprid (C_s) from day 13 to the end of each GAC and PAC sorption experiments were not significantly different from zero ($p > 0.05$). Although incremental increases may still occur for additional weeks or months,^{57–60} the null slopes indicate that sorption was at pseudo-steady state.

Alternatively, the surface area normalized sorption capacities for the parent neonicotinoids and imidacloprid urea were higher with nF-CNTs than GAC (0.34–0.70 mg m⁻²; $p = 0.0597$ imidacloprid, $p < 0.0001$ other nitro-neonicotinoids, $p = 0.0001$ thiacloprid, $p = 0.0266$ imidacloprid urea); however, desnitro-imidacloprid was not different (0.13 mg m⁻², $p = 0.8565$). The 2.2- to 4.6-fold increase in the surface area normalized nF-CNTs capacity to sorb parent neonicotinoids and imidacloprid urea suggests a strong affinity for $\pi-\pi/\pi^+-\pi$ interactions between the neonicotinoid and electronegative pharmacophore and the aromatic graphitic structure of nF-CNTs.^{29,32,61} GAC surfaces can be expected to and have more functional groups

than nF-CNTs that may inhibit the electronegative nitro-/cyano-/carbonyl group to interact with the heterogeneous surfaces.²⁹

Differences in Sorption Driven by the Altered Neonicotinoid Pharmacophore. Differences in sorption capacity between imidacloprid and desnitro-imidacloprid illustrate the impact of the pharmacophore with an altered charge distribution. The sorption capacity of desnitro-imidacloprid was significantly less than that for imidacloprid for GAC and PAC ($p = 0.0045$ and $p = 0.0323$, respectively; Figures 1 and 2 and Tables S.10 and S.14) and nF-CNTs ($p = 0.0345$; Figure 3 and Table S.12). In contrast, the GAC and nF-CNT sorption capacities for imidacloprid and imidacloprid urea were not significantly different ($p = 0.3364$ and 0.1084, respectively), which is likely because imidacloprid urea contains a carbonyl group that holds a partial-negative charge (albeit less than the nitro group of imidacloprid), retaining the potential for some electrostatic and/or specific binding interactions (Figure 1 and Tables S.10 and S.12). Unlike imidacloprid and imidacloprid urea, desnitro-imidacloprid has a more positive charge distribution¹⁴ (due to the amine group), which may explain why significantly less desnitro-imidacloprid is adsorbed to nF-CNTs compared to imidacloprid urea ($p = 0.0017$; Figure 3 and Table S.12). Based on previously published pK_a and point-of-zero-charge values for the specific GAC used in this study,^{62,63} localized charges of largely basic functional groups on the GAC surface are expected to interact more favorably with imidacloprid than desnitro-imidacloprid (at pH 7, imidacloprid is not protonated on the imidazole ring and thus would not be positively charged).¹⁴

Functionalizing the CNT surface with carboxylic acid moieties diminished the CNTs capacity to sorb imidacloprid and imidacloprid urea (which have an electronegative charge distribution) but increased sorption of desnitro-imidacloprid (which has a more positive charge distribution), demonstrating the importance of charge effects on neonicotinoid sorption (Figure 3, Figure S.7, and Table S.16). The imidacloprid sorption capacity was significantly less (32%; $p = 0.0026$) for COOH-CNTs than nF-CNTs (Figure 3A and Table S.16), while imidacloprid urea sorption to CNTs was not significantly affected by COOH functionalization (11% lower capacity, $p = 0.5813$; Figure 3B and Table S.16). In contrast, COOH-CNTs sorbed significantly more desnitro-imidacloprid (57% greater capacity) when compared to nF-CNTs ($p = 0.0084$; Figure 3C and Table S.16). At circumneutral pH (pH 7), the surface carboxylic acid moieties are largely dissociated ($pK_a < 5$) and act as a negatively charged hydrogen bond acceptor. Imidacloprid and imidacloprid urea contain electronegative, hydrogen bond-accepting functional groups (e.g., the nitro-pharmacophore) that may be repelled by $-COO^-$, thereby decreasing the COOH-CNT sorption capacity compared to that of the nF-CNTs. In contrast, desnitro-imidacloprid is a hydrogen bond donor with a more positive functional group (compared to imidacloprid and imidacloprid urea) and may more favorably interact with the $-COO^-$, thereby increasing COOH-CNT uptake of desnitro-imidacloprid compared to nF-CNTs.

Amine functionalization of CNTs decreased desnitro-imidacloprid sorption but did not significantly impact the sorption capacity for imidacloprid or imidacloprid urea (Figure 3). Sorption capacity for imidacloprid and imidacloprid urea (Figure 3 and Table S.16) were slightly, but not significantly, diminished between NH₂-CNTs and nF-CNTs (19%, $p =$

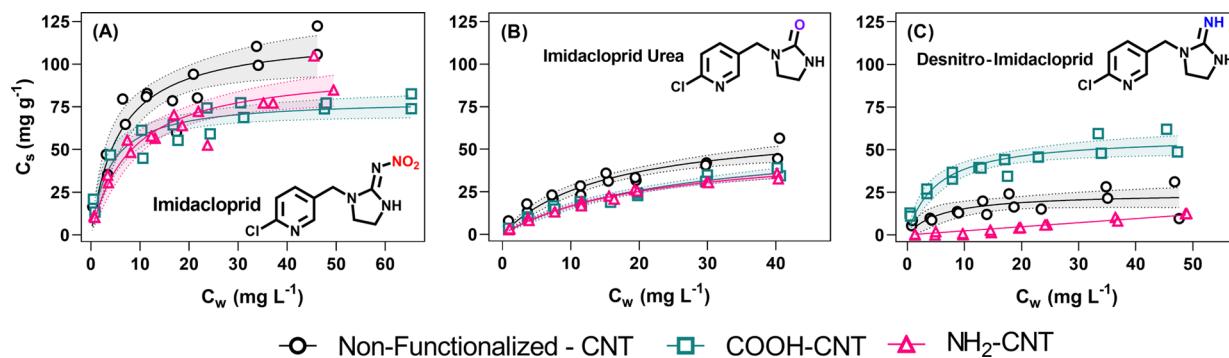


Figure 3. Sorption isotherms (pH 7) for imidacloprid (A) and its metabolites desnitro-imidacloprid (B) and imidacloprid urea (C). Isotherms depict neonicotinoid sorption to non-functionalized CNTs (black circles), COOH-functionalized CNTs (teal squares), and NH₂-functionalized CNTs (pink triangles). The sorption capacities for the electronegative imidacloprid and imidacloprid urea followed similar patterns where surface functionalization decreased CNT sorption capacity. In contrast, the more positively charged desnitro-imidacloprid was highly sensitive to surface functionalization with significantly greater sorption to COOH-CNTs and significantly less to NH₂-CNTs compared to nF-CNTs. These results highlight the impacts of the neonicotinoid insecticidal pharmacophore alteration on the sorption of neonicotinoids to black carbon.

Table 1. Measured Sorption Capacities and Kinetics of Imidacloprid and Desnitro-Imidacloprid Sorption to GAC in Buffer Systems with Altered Water Chemistry Variables^{a,b}

Buffer System	Imidacloprid					Desnitro-Imidacloprid				
	Sorption Capacity (mg g⁻¹ ± SE; C ₀ = 50 mg L⁻¹)		Sorption Rate (h⁻¹ ± SE; C ₀ = 10 µg L⁻¹)			Sorption Capacity (mg g⁻¹ ± SE; C ₀ = 50 mg L⁻¹)		Sorption Rate (h⁻¹ ± SE; C ₀ = 10 µg L⁻¹)		
	pH=7	pH=9.2	pH=7	pH=9.2	pH=11	pH=7	pH=9.2	pH=7	pH=9.2	pH=11
Control 1 mM buffer (µ = 5 mM)	145±3.0	150±2.1	0.09±0.01	0.11±0.01	-----	90±2.4	90±2.8	0.15±0.01	0.15±0.02	-----
Buffer Concentration 100 mM buffer (µ = 500 mM)	144±2.7	112±6.1 ^v	0.07±0.01	0.24±0.07 ^Δ	-----	93±4.5	64±2.9 ^v	0.13±3.0×10 ⁻³	0.16±0.01 ^Δ	-----
Ionic Strength 1 mM buffer + 0.5 M NaCl (µ = 500 mM)	141±3.7	141±3.1 ^v	0.10±0.02	0.07±0.02	-----	91.0±3.4	110±2.8 ^Δ	0.14±0.01	0.14±4.0×10 ⁻³	-----
Alkalinity/Hardness 1 mM buffer + 45 ppm CaCO ₃	146±1.9	129±6.1 ^v	0.11±0.01	0.09±0.01	0.18 ± 0.01 ^Δ	82±2.8	87±2.6	0.15±0.01	0.17±0.01	0.25 ± 0.03 ^Δ
Organic Matter 1 mM buffer + 5 ppm HA	136±3.4	137±3.6 ^v	0.09±0.01	0.10±0.01	-----	80±3.8 ^v	93±2.9	0.12±0.01	0.12±0.01	-----
Temperature 1 mM buffer 4 °C	-----	-----	0.02±4.0×10 ⁻³ ^v	0.02±3.0×10 ⁻³ ^v	-----	-----	0.08±0.01 ^v	0.07±0.01 ^v	-----	

^aImpacts of excessive buffer concentration (100 mM), ionic strength (500 mM), alkalinity/hardness (45 ppm), organic carbon (5 ppm), and low temperature (4 °C) were analyzed at pH 7 and 9.2 in comparison to 1 mM buffer controls. Experiments were conducted at two initial concentrations, C₀ = 50 mg L⁻¹ (assess relative sorption capacity) and C₀ = 10 µg L⁻¹ (environmentally relevant sorption kinetics). ^bTriangle superscripts indicate buffer systems where observed sorption capacities/rates were significantly higher than their respective controls (pH 7 or 9.2 1 mM buffer), while inverted triangles indicate buffer systems where sorption capacities/rates were significantly lower than the control. SE = standard error.

0.1876; 9%, *p* = 0.2199; respectively, Table S.16). However, when sorption capacity is normalized to the BET surface area, the sorption capacities of NH₂-CNTs were significantly lower than nF-CNTs for imidacloprid (*p* = 0.0398) and imidacloprid

urea (*p* < 0.0001, Figure S.8 and Table S.17). Desnitro-imidacloprid sorption to NH₂-CNTs was nearly linear and did not reach saturation, making direct comparison between COOH-CNTs and NH₂-CNTs somewhat tenuous (Figure

3C). Because $-\text{NH}_2$ is a hydrogen bond donor like desnitro-imidacloprid, this functional group may repel desnitro-imidacloprid, inhibiting sorption. Thus, desnitro-imidacloprid sorption is likely driven by hydrogen bonding and/or electrostatic interactions between the desnitro-imidacloprid pharmacophore and the functionalized CNT surface. In contrast, there was no significant difference between the capacities for COOH-CNTs and NH_2 -CNTs to adsorb imidacloprid or imidacloprid urea ($p > 0.05$). The $-\text{NH}_2$ group, as well as the other functionalities present (e.g., $\text{O}=\text{C}-\text{NH}_2$ and $\text{C}=\text{N}$), could facilitate sorption via hydrogen bonds with the hydrogen-accepting pharmacophores of imidacloprid or imidacloprid urea. The minimal impact of surface functionalization on the sorption capacity of imidacloprid or imidacloprid urea suggests that their sorption may be predominantly driven by $\pi-\pi$ or $\pi^+-\pi$ interaction.^{28,29,32} The extent to which black carbon adsorbs electron-rich (e.g., $\text{R}-\text{NH}_2$) or electron-deficient compounds (e.g., $\text{R}-\text{NO}_2$, $\text{R}=\text{O}$) is known to be influenced by surface functionalization; for example, adding heteroatomic nitrogen to multiwalled carbon nanotubes has been shown to increase naphthalamine sorption while decreasing 1,3-dinitrobenzene sorption.^{29,32,61} Although we suggest $\pi-\pi$ / $\pi^+-\pi$ interactions to be important in driving the differences in sorption we observed between imidacloprid, imidacloprid urea, and desnitro-imidacloprid, other factors including molecular volume and spatial arrangement may also be involved.

Impacts of Water Chemistry on Sorption Capacity and Kinetics. Changing water chemistry altered imidacloprid and desnitro-imidacloprid sorption behavior to GAC. Water chemistry parameters (pH, humic acid, and alkalinity/hardness) were chosen to represent those in environmentally relevant conditions at the DWTP where we previously detected neonicotinoids^{13,20} as well as in a broader range of conditions to probe possible sorption mechanisms (i.e., temperature, ionic strength, and buffer species concentration). We conducted experiments at 50 mg L^{-1} to assess the impact of water chemistry on the extent of sorption and at $10 \mu\text{g L}^{-1}$ to determine the impact of water chemistry in more DWTP-relevant conditions where kinetics may be the limiting factor (comparison of concentration effects for the Langmuir model are presented in the Supporting Information). Understanding how water chemistry parameters impacts sorption capacity and rate is crucial to understanding the removal of neonicotinoids and pharmacophore-altered metabolites under drinking water conditions.

Temperature. The rate imidacloprid ($C_0 = 10 \mu\text{g L}^{-1}$) sorbed to GAC was significantly less at 4°C compared to 25°C ($p < 0.0001$), with rate decreases of 78% at pH 7 and 82% at pH 9.2 (Table 1, Table S.27, and Figure S.13). Similarly, desnitro-imidacloprid ($C_0 = 10 \mu\text{g L}^{-1}$) sorption kinetics were also significantly inhibited ($p < 0.0001$) at 4°C compared to 25°C , with decreases in rate by 47% at pH 7 and 53% at pH 9.2 (Table 1, Table S.28, and Figure S.14). There are a limited number of studies concerning the effects of temperature on sorption kinetics to GAC; however, studies with *p*-chlorophenol also report decreased GAC sorption kinetics with lower temperatures,⁶⁴ which is likely due to diminished molecular diffusion.^{65–68} Analysis we conducted using the Weber–Morris kinetic sorption model (see the Supporting Information for details) suggests that intraparticle diffusion is likely involved in neonicotinoid sorption to GAC and may be the rate-determining step for desnitro-imidacloprid.^{66,67} Based on

estimated Arrhenius relationships for the diffusion coefficients and rate constants (Figure S.10 and Table S.18), the activation energies for imidacloprid and desnitro-imidacloprid are within the range of physical sorption and perhaps suggestive of stronger interactions for imidacloprid (see the Supporting Information for details).^{67,69}

pH. There were no significant ($p > 0.05$) impacts solely attributable to drinking water relevant pH (pH 7 and 9.2) on the GAC sorption capacity or kinetics for imidacloprid or desnitro-imidacloprid (Figures S.12 and S.16 and Tables S.21, S.22, S.25, and S.26). Although pH alone did not appear to specifically impact neonicotinoid sorption, pH in association with other water chemistry parameters (i.e., humic acid, CaCO_3 [also studied at pH 11], and ionic strength) had a significant impact on the sorption of imidacloprid and desnitro-imidacloprid to GAC (Table 1).

Humic Acid. The GAC sorption capacity for desnitro-imidacloprid at pH 7 was 11% lower when in the presence of 5 ppm Aldrich humic acid (HA) compared to buffers without HA ($p = 0.0496$, Table 1, Table S.24, and Figure S.12). Similarly, GAC sorption capacity for desnitro-imidacloprid was 14% lower in filtered Iowa River water (pH 8.1 with natural organic matter) than in filtered tap water ($p = 0.0202$; pH 8.9; Figure S.11 and Table S.20). The desnitro-imidacloprid ($C_0 = 10 \mu\text{g L}^{-1}$) sorption rate to GAC in buffer with HA (0.12 h^{-1}) was also 20% slower than without HA at pH 7 (0.15 h^{-1} ; $p = 0.0077$, Figure S.14 and Table S.28). There were no significant differences in desnitro-imidacloprid sorption rates or capacity between solutions with and without HA at pH 9.2 ($p > 0.05$). At circumneutral pH, protonated moieties on HA likely block or compete with desnitro-imidacloprid for GAC hydrogen bond acceptor sites.^{33,34,70} For imidacloprid, there were no significant differences ($p > 0.05$) in sorption rate in the presence of HA (compared to HA-free buffer) or in sorption capacity in river water (compared to tap water) (Figures S.11–S.13 and Tables S.20, S.21, S.23, and S.27). However, the sorption capacity for imidacloprid at pH 9.2 was significantly lower in the presence of HA (9% decrease, $p = 0.0080$), suggesting possible sorption site competition or blocking at an elevated pH.^{33,34,70}

Hardness/Alkalinity. We emulated conditions in a DWTP softening basin (pH 11) to evaluate the impacts of the carbonate anion specifically on neonicotinoid sorption kinetics.¹³ In solutions containing 45 ppm CaCO_3 , imidacloprid sorbed 64% and 100% faster at pH 11 (0.18 h^{-1}) than at pH 7 (0.11 h^{-1}) and 9.2 (0.09 h^{-1}), respectively ($p < 0.0001$; Table 1, Tables S.25 and S.27, and Figures S.13–S.16). Similarly, the desnitro-imidacloprid sorption rate in solutions with 45 ppm CaCO_3 at pH 11 (0.25 h^{-1}) was 67% and 47% faster than at pH 7 (0.15 h^{-1}) and pH 9.2 (0.17 h^{-1}), respectively ($p < 0.005$, Table 1 and Tables S.26 and S.28). The carbonate species at pH 7 and 9.2, however, did not significantly impact sorption kinetics for either imidacloprid or desnitro-imidacloprid ($p > 0.05$, Tables S.25–S.28).

Several factors could potentially explain the influence of CaCO_3 on neonicotinoid sorption to GAC, including cation bridging/cation coordination and charge shielding.^{28,29,34,71} We observed a small but significantly greater sorption capacity for imidacloprid to GAC at pH 7 compared to pH 9.2 in solutions containing 45 ppm CaCO_3 (12%, $p = 0.0036$; Figure S.12 and Table S.21) and a significantly greater capacity at pH 9.2 without CaCO_3 present compared to pH 9.2 solutions with CaCO_3 (14%, $p = 0.0080$, Table S.23); however, no such

impact of CaCO_3 occurred for desnitro-imidacloprid (Table S.24). This increase in sorption capacity for imidacloprid at pH 7 may be evidence of cation bridging via calcium between the electronegative (nitro-) group and electronegative GAC surface groups, while the decrease at pH 9 may be due to competition with bicarbonate anions.^{28,34,71} Desnitro-imidacloprid is unlikely to partake in cation bridging due to its more positive charge distribution, and thus enhanced kinetics of desnitro-imidacloprid at pH 11 with CaCO_3 may be more complicated, such as complexes between desnitro-imidacloprid and carbonate anions.^{31,34,71,72}

Ionic Strength and Buffer Species. We probed impacts of solution ionic strength and buffer species specifically to gain insights on potential sorption mechanisms, recognizing that these conditions will not likely occur at real treatment plants. A higher ionic strength solution at pH 9.2 increased the capacity for GAC to sorb desnitro-imidacloprid. The GAC sorption capacity for desnitro-imidacloprid in borate buffer (5 mM, pH 9.2) with NaCl ($\mu = 500$ mM) was 22% greater than the capacity in borate buffer without NaCl ($\mu = 5$ mM, $p < 0.0001$; Table 1, Table S.24, and Figure S.12). We do not attribute these effects to the borate buffer based on separate experiments isolating borate impacts on sorption (described in the Supporting Information). The GAC sorption capacity for desnitro-imidacloprid in solutions where ionic strength was held constant (NaCl , $\mu = 500$ mM) was greater at pH 9.2 compared to pH 7 (20%, $p = 0.0008$); however, there were no significant impacts on sorption kinetics (Tables S.22 and S.28). Although an increased ionic strength should theoretically decrease sorption capacity due to charge shielding dampening,^{73,74} the enhanced sorption capacity we observed at pH 9.2 with a high ionic strength may be due to desnitro-imidacloprid salting out onto the GAC surface (effectively increasing sorption capacity).^{39,55,75} Additionally, as more sorption sites become available due to proton dissociation at pH 9.2 (e.g., hydroquinone, phenol, nitrile, protonated amine, and aliphatic amine), increased charge shielding at high ionic strength may enable additional desnitro-imidacloprid sorption, increasing the sorption capacity.⁷⁴ We observed no significant impacts of ionic strength on imidacloprid sorption kinetics at either pH, but there was a slight, but significant, decline in sorption capacity for imidacloprid at pH 9.2 (Table 1, 6%, $p = 0.0475$, Tables S.23 and S.27), perhaps due to a reliance on $\pi-\pi$ or $\pi^+-\pi$ interactions rather than specific interactions with surface moieties that drive sorption.^{28,29,32} Sorption under elevated ionic strength conditions may be important when neonicotinoids are used in shrimp farming,^{76,77} where black carbon sorbents have been proposed to improve water quality in aquaculture.⁷⁸

Neonicotinoid Removal in a Full-Scale DWTP GAC Filter. At the Iowa City DWTP, clothianidin, thiamethoxam, imidacloprid, imidacloprid urea, and desnitro-imidacloprid were all detected in the GAC filter influent (Figure 4A and Table S.29). Thiacloprid was not detected above its LLD in either the GAC filter influent or effluent. Of the neonicotinoids detected in the GAC filter influent, only two (thiamethoxam and desnitro-imidacloprid) were detected in the GAC filter effluent above their LLDs, while clothianidin was detected below its LLD. Imidacloprid and imidacloprid urea were not detected in the GAC effluent. The concentrations of neonicotinoids and metabolites in GAC filter effluent were significantly lower than the influent ($p = 0.0006$). Although the scope of these data are limited (in sampling size and during a

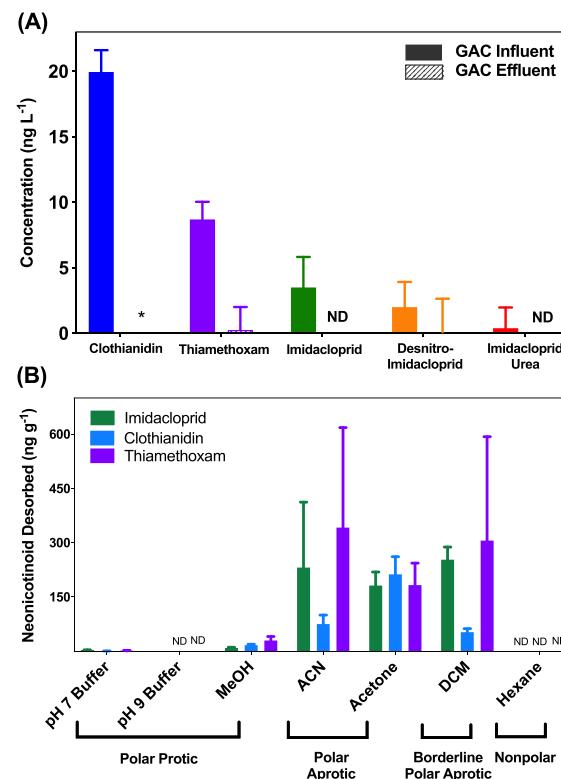


Figure 4. (A) Neonicotinoids imidacloprid, clothianidin, and thiamethoxam, and two metabolites of imidacloprid (imidacloprid-urea and desnitro-imidacloprid) measured in GAC “filter 5” influent (inlet) and effluent (outlet) at the City of Iowa City DWTP (September 4, 2018). Error bars represent the standard error of regression and include the variation between duplicate samples and sample processing/analysis (associated with the SPE process and analysis). Asterisks denote detections below the LLD and (ND) denotes non-detects. LLD values (ng/L): clothianidin, 0.488; imidacloprid, 0.428; thiamethoxam, 0.081; desnitro-imidacloprid, 0.026; imidacloprid-urea, 0.057. Neonicotinoid concentrations in the GAC influent and effluent were compared by two-tailed ratio paired *t*-test, where influent concentrations were significantly higher than the effluent ($p = 0.0006$). (B) Neonicotinoids imidacloprid, clothianidin, and thiamethoxam desorbed from 0.2 g of spent GAC following 6 days exposed to 4 mL of solvent (pH 7 buffer $n = 6$, pH 9 buffer $n = 6$, methanol $n = 5$, acetone $n = 5$, acetonitrile $n = 5$, dichloromethane $n = 6$, and hexane $n = 3$). Spent City of Iowa City GAC was in service for 5 years before being removed from the filter and obtained from the DWTP on April 2017.

time of year that is likely less concentrated than during spring flush), the concentrations detected in the GAC filter influent and effluent were consistent with our previous studies where we measured neonicotinoids in source and finished water from this DWTP.^{13,20} These are the first results confirming neonicotinoid removal attributable to a GAC filter with pre- and post-GAC treatment samples in a full-scale DWTP (rather than comparing source and finished drinking water samples at this DWTP as we did in our prior work²⁰ to initially assess neonicotinoid removal in a DWTP).

Neonicotinoids were present on, and subsequently desorbed from, GAC that had been in service for 5 years in the Iowa City DWTP GAC filter. Under environmentally relevant conditions (i.e., pH 7 phosphate and pH 9 borate buffers), <5 ng g^{-1} neonicotinoids were desorbed, which is consistent with our isotherm reversibility experiments and indicates that neon-

neonicotinoid desorption from GAC is minimal in aqueous environments (Figure 4B). Using polar aprotic solvents (acetonitrile, acetone, and dichloromethane), up to 600 ng g⁻¹ imidacloprid, clothianidin, and thiamethoxam was desorbed (Table S.31). No neonicotinoids desorbed in hexane. As a cross-check, analysis at the USGS laboratory in Sacramento validated these neonicotinoid measurements and additionally detected 31 other pesticides with a range of solubilities/hydrophilicities ($\log K_{ow} = 1.17\text{--}5.88$; Table S.32). Although the other pesticides detected are less soluble than neonicotinoids, some contain functional groups similar to neonicotinoids, including highly electronegative functional groups (e.g., the cyano-containing azoxystrobin, fipronil, and myclobutanil) and/or nitrogen-containing rings (e.g., atrazine, chlorantraniliprole, and prometon). These results also provide further evidence that the GAC filter, initially installed to improve water taste/odor and remove DBP-precursors, is removing non-regulated neonicotinoids and a suite of other pesticides via sorption at a full-scale DWTP.

We also contextualized these experimental results using poly parameter linear free energy relationships (pp-LFERs) available on the UFZ-LSER database⁷⁹ to predict desorption using different solvents (analysis details in the *Supporting Information*). Clothianidin was used for this analysis because it was the only neonicotinoid in the database with experimentally determined solute parameters;⁸⁰ coal tar⁸¹ was chosen as the most similar carbon sorbent to GAC available in the database. Based on the predicted solvent–coal tar partitioning for the solvents used in the desorption experiment (Figure 4B), clothianidin was predicted to desorb most with methanol > acetone > acetonitrile > dichloromethane. These predicted results generally align with the experimental data, with the exception of methanol (perhaps because compounds used to generate the pp-LFERs do not represent highly polar, slightly ionized compounds like neonicotinoids). The greatest clothianidin desorption was predicted with polar aprotic solvents ($DMSO \gg N\text{-methyl-2-piperidone} > N\text{-methylpyrrolidinone} > \text{dimethylacetamide} > \text{diethylacetamide}$), which is consistent with our experimental results (Table S.36). The greatest energetic contributions⁸² (Abraham parameters) to the predicted solvent desorption correlated most strongly with the solvent's ability to induce a dipole in clothianidin (system parameter for polarizability, $r = 0.82$) and the formation of hydrogen bonds with clothianidin (system parameter for hydrogen donor/electron acceptor, $r = 0.61$; Figures S.17 and S.18). This theoretical analysis further implicates electron donor/acceptor and hydrogen bond donor/acceptor interactions as key for neonicotinoid sorption to black carbon.

Limited neonicotinoid metabolites were desorbed from spent GAC analyzed by the USGS lab in Sacramento (20.7 ng g⁻¹ imidacloprid urea desorbed in DCM and 12 ng g⁻¹ desnitro-imidacloprid in acetone, Table S.31). The minimal desorption of imidacloprid metabolites from spent GAC is likely due to the low metabolite concentrations in source water or could imply that metabolites are more tightly bound to GAC than the parent neonicotinoids and therefore desorb less efficiently. Another possible explanation for limited desorption of imidacloprid metabolites from spent GAC could be *in situ* transformation on the GAC surface in the DWTP, which is known to occur for some other trace organic contaminants.^{83–87}

Environmental Implications. Granular activated carbon (GAC) represents a relatively inexpensive approach to improve

drinking water taste and odor but also markedly improves water quality for both regulated (e.g., DBPs/precursors)^{88–90} and unregulated emerging contaminants such as neonicotinoids. The results in this work demonstrate the capability for GAC to sorb the neonicotinoids imidacloprid, clothianidin, thiamethoxam, and thiacloprid and metabolites imidacloprid urea and desnitro-imidacloprid despite low neonicotinoid hydrophobicity. We would expect the GAC to lose some capability to sorb neonicotinoids over time (due to site exhaustion and sorption of competing compounds and dissolved organic matter),^{8,9,28–30,32,39,65,91} which could lead to more neonicotinoids/metabolites in finished water over extended periods. Although the sorption capacity for desnitro-imidacloprid to GAC is limited, engineered black carbon surfaces such as functionalized carbon nanotubes (CNTs) could be tuned to improve the removal of specific compounds. Neonicotinoids are used extensively globally and are being discovered in drinking water supplies and sources;^{5,12,21,92,93} thus, these novel findings could aid in engineering new sorbents to promote removal of neonicotinoid metabolites.

Neonicotinoids are among a growing class of pesticides that confer enhanced target specificity through use of a specialized molecular functional group. Although designed with intentions to minimize impacts to non-target organisms, target-specific pesticides can be transformed in natural and engineered systems via biotic and abiotic pathways, altering the molecular structure.^{19,94} Small structural changes at the insecticidal pharmacophore not only changes neonicotinoid toxicity^{15,18,43,95} but also reactivity during water treatment (e.g., chlorination, as we showed in past work).²⁰ We demonstrate here that transformation of the insecticidal pharmacophore (i.e., imidacloprid vs metabolites) causes differences in sorption to GAC, powdered activated carbon, and CNTs, which is consistent with previous studies in soils.^{96–98} It appears that this phenomenon is partially driven by the ability for the pharmacophore to form electron or hydrogen donor/acceptor interactions with the black carbon surface. Due to the growing use and interest in target-specific pesticides like neonicotinoids, it is critical to understand how environmentally relevant transformation processes can impact their toxicity, reactivity, sorption, and overall fate to protect the human health.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.est.0c04187>.

Additional method details, statistical analysis, quality assurance/control, additional detailed data/results/analysis in figures and tables (PDF)

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Notes

The authors declare no competing financial interest.

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