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Occurrence of Neonicotinoid Insecticides in Finished Drinking Water and Fate during Drinking Water Treatment

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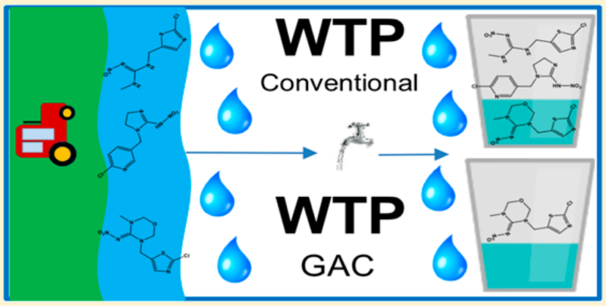
S *Supporting Information*



ABSTRACT: Neonicotinoid insecticides are widespread in surface waters across the agriculturally intensive Midwestern United States. We report for the first time the presence of three neonicotinoids in finished drinking water and demonstrate their general persistence during conventional water treatment. Periodic tap water grab samples were collected at the University of Iowa over 7 weeks in 2016 (May–July) after maize/soy planting. Clothianidin, imidacloprid, and thiamethoxam were ubiquitously detected in finished water samples at concentrations ranging from 0.24 to 57.3 ng/L. Samples collected along the University of Iowa treatment train indicate no apparent removal of clothianidin or imidacloprid, with modest thiamethoxam removal (∼50%). In contrast, the concentrations of all neonicotinoids were substantially lower in the Iowa City treatment facility finished water using granular activated carbon (GAC) filtration. Batch experiments investigated potential losses. Thiamethoxam losses are due to base-catalyzed hydrolysis under high-pH conditions during lime softening. GAC rapidly and nearly completely removed all three neonicotinoids. Clothianidin is susceptible to reaction with free chlorine and may undergo at least partial transformation during chlorination. Our work provides new insights into the persistence of neonicotinoids and their potential for transformation during water treatment and distribution, while also identifying GAC as a potentially effective management tool for decreasing neonicotinoid concentrations in finished drinking water.

INTRODUCTION

Neonicotinoid pesticides have become the most widely used insecticides in the world.[1,2] Neonicotinoids are systemic, insect-targeting,[3−5] potent neurotoxins that are often applied as seed treatments to crops in the United States and in urban pest control applications.[1,6] Neonicotinoids have also been implicated in a variety of ecosystem effects,[7] including declines in populations of pollinators[8,9] (e.g., honeybees) and effects on nontarget organisms.[10−15] They are substantially more toxic to insects than vertebrates;[6] however, most vertebrate toxicity research has focused on acute exposure, and chronic exposure remains a concern.[13] Several studies report associations between chronic exposure to neonicotinoids and adverse developmental or neurological outcomes.[16] Other studies highlight potential concerns, including inflammation of the liver and central nervous system due to chronic exposure to neonicotinoids,[17] loss of insect selectivity in transformation products,[4,18,19] and negative effects on nontarget species in aquatic ecosystems.[10]

High use and chemical properties have resulted in proliferation of neonicotinoids in surface waters.[20−23] In a nationwide study of streams in the United States, at least one neonicotinoid compound was detected in 63% of the 48 streams measured.[21] Neonicotinoids were ubiquitously detected at all streams sampled that drain intensively row-cropped areas of the Midwestern United States,[20] with maximal concentrations of 260, 43, and 190 ng/L for clothianidin, imidacloprid, and thiamethoxam, respectively, which represent the most widely used and commonly observed compounds in this class of insecticides. Neonicotinoids are water-soluble[6] (340, 610, and 4100 mg/L for clothianidin, imidacloprid, and thiamethoxam, respectively) and polar[20] (log K_{ow} = 0.91, 0.57, and −0.13 for clothianidin, imidacloprid, and thiamethoxam, respectively). Research to date suggests general neonicotinoid

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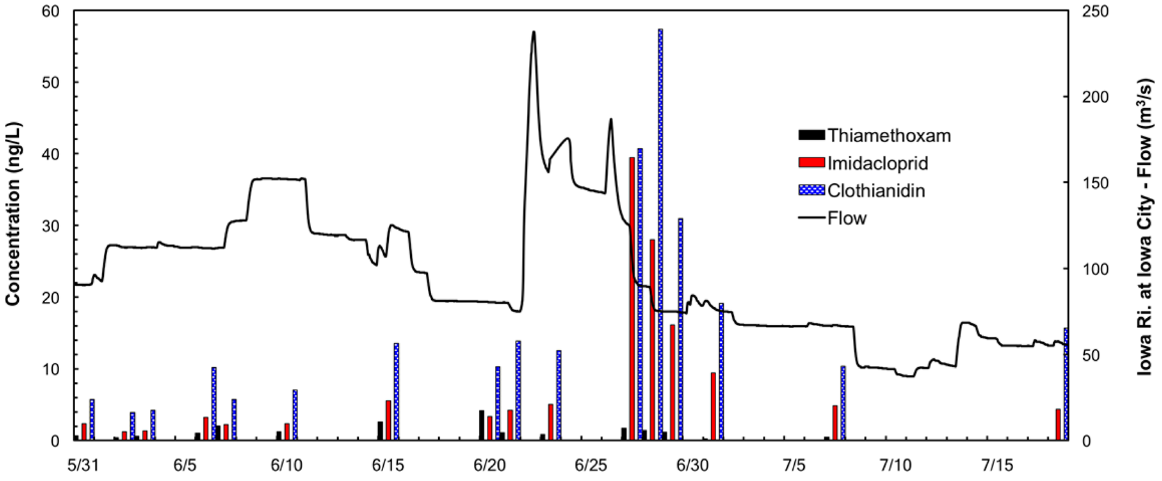

Figure 1. Concentrations of clothianidin, imidacloprid, and thiamethoxam in samples collected from University of Iowa tap water in 2016. Concurrent streamflow in the Iowa River in Iowa City, IA, is shown. Iowa River flow is regulated by a reservoir, generating the hydrograph pictured.

persistence in the environment[24] (e.g., imidacloprid and clothianidin were documented to have conservative transport through a study stream reach[21]), although photolysis can occur to various extents among the different neonicotinoids.[19,25]

On the basis of limited data, neonicotinoids appear to be poorly removed via treatment systems, with insignificant or very marginal removal observed during conventional wastewater treatment and no removal in a constructed treatment wetland.[26,27] To date, no known research has examined the presence of neonicotinoids in finished drinking water, particularly for communities relying on agriculturally impacted surface water sources. Here, we present results of field analyses and laboratory experiments measuring the fate of neonicotinoids during drinking water treatment. Our objectives were (1) to quantify neonicotinoid residues in two public drinking water facilities that derive their water from agriculturally impacted sources and (2) to determine the efficacy of drinking water treatment operations to remove neonicotinoids.

■ MATERIALS AND METHODS

Between May and July 2016 following maize/soy planting, finished drinking water samples were collected from taps at the University of Iowa and at three locations in Iowa City, IA. The University of Iowa drinking water treatment plant (UI DWTP) serves the University of Iowa (UI), while the Iowa City water treatment plant (City DWTP) serves Iowa City (City). The UI DWTP (Figure S1) uses the Iowa River for source water and uses screening, chemical pretreatment, sedimentation, lime softening, recarbonation, chlorination, and sand filtration for treatment. The City DWTP (Figure S1) uses water from alluvial wells fed by the Iowa River (i.e., groundwater influenced by surface water) and provides treatment via aeration, lime softening, recarbonation, granular activated carbon (GAC) filtration, and chlorination. The Iowa River drains a watershed that is 8150 km^2 in a heavily row-cropped agroecosystem,[28,29] where prior work has demonstrated frequent detection of neonicotinoid pesticides.[20] The river flow is composed of overland flow and tile drainage (from rainfall, no snowmelt during the study period) and groundwater. The City alluvial wells and UI DWTP intakes are located approximately 10 and 15 km downstream of the Coralville reservoir, respectively. University drinking water samples were collected periodically from a tap in the laboratory located in the Seamans Center at the University of Iowa. Samples of the City drinking water were collected from three residential taps at separate locations in Iowa City. To assess neonicotinoid fate during treatment, the raw source water, sedimentation basin effluent, recarbonation effluent (prechlorination), recarbonation effluent (postchlorination), filtration effluent, and finished water were sampled at the UI DWTP, and the source and finished water were sampled at the City DWTP (Figure S1). Water samples were enriched via solid phase extraction (SPE), analyzed using liquid chromatography with tandem mass spectrometry (LC−MS/MS), and quantified according to established U.S. Geological Survey methods.[30] Fate during unit processes was tested in laboratory batch systems using free chlorine, GAC, and pH adjustment, with neonicotinoid concentrations measured by LC with a diode array detector and mass spectrometry (LC−DAD/MS). Field and laboratory QA/QC samples were analyzed throughout the study (described in the Supporting Information). Experimental details and analytical methods are provided in the Supporting Information.

■ RESULTS AND DISCUSSION

Occurrence of Neonicotinoids in Drinking Water. Clothianidin, imidacloprid, and thiamethoxam were ubiquitously present (i.e., 100%) in all samples (n = 16) collected from UI tap water, with concentrations ranging between 3.89 and 57.3 ng/L, between 1.22 and 39.5 ng/L, and between 0.24 and 4.15 ng/L, respectively (Table S4). Maximal concentrations of clothianidin and imidacloprid occurred a few days after peak flow in the Iowa River (Figure 1), indicating a possible relationship between neonicotinoid concentration and river flow. The delay between maximal river flow and maximal tap water concentration may be due to the residence time in the distribution system, which is typically <1−3 days but can be in some locations up to 6 days.[31] Samples of City finished tap water collected at private residences (Table S5) contained up to 0.52 ng/L thiamethoxam; however, clothianidin and imidacloprid were not present above detection limits.

The concentrations of clothianidin, imidacloprid, and thiamethoxam measured in UI tap water are consistent with documented environmental concentrations.[20,30−32] In a nationwide study, at least one neonicotinoid was detected in 63% of the 48 streams monitored.[21] Similarly, in a study of streams in Iowa, at least one neonicotinoid compound was detected in all samples.[20] These detections include clothianidin (3.5−79 ng/L), imidacloprid (not detected to 15 ng/L), and thiamethoxam (not detected to 43 ng/L) as measured in the Iowa River in Wapello, IA (approximately 45 miles downstream of Iowa City),[20] and imidacloprid measured in Old Man's Creek near Iowa City (4.5−35 ng/L).[20] In other studies, imidacloprid was measured in a stream (3.4−10 ng/L) in Georgia,[30] as well as in other small streams[32] throughout the Midwest (not detected to 2900 ng/L; measured via grab and passive sampling).

Fate of Neonicotinoids during Drinking Water Treatment. Samples collected from the UI DWTP (Figure 2) suggest that clothianidin and imidacloprid persist throughout conventional water treatment processes, while thiamethoxam is partially removed. Neonicotinoid concentrations on the two different sampling dates (Figure 2) varied, but trends across the treatment train were consistent. Raw source water (i.e., Iowa River) concentrations ranged from 10.7 to 25.9 ng/L for clothianidin, from 2.15 to 13.3 ng/L for imidacloprid, and from 1.93 to 8.23 ng/L for thiamethoxam, whereas finished water concentrations ranged from 10.6 to 31.2 ng/L for clothianidin, from 1.97 to 13.6 ng/L for imidacloprid, and from 1.07 to 3.11 ng/L for thiamethoxam. Although we did not attempt to follow a single parcel of water through the treatment process (i.e., all samples were collected at approximately the same time in a given sampling round), little to no concentration change for clothianidin and imidacloprid was measured. In contrast, thiamethoxam concentrations exhibited a clear drop of ∼40−60% after lime softening and recarbonation but were essentially stable thereafter.

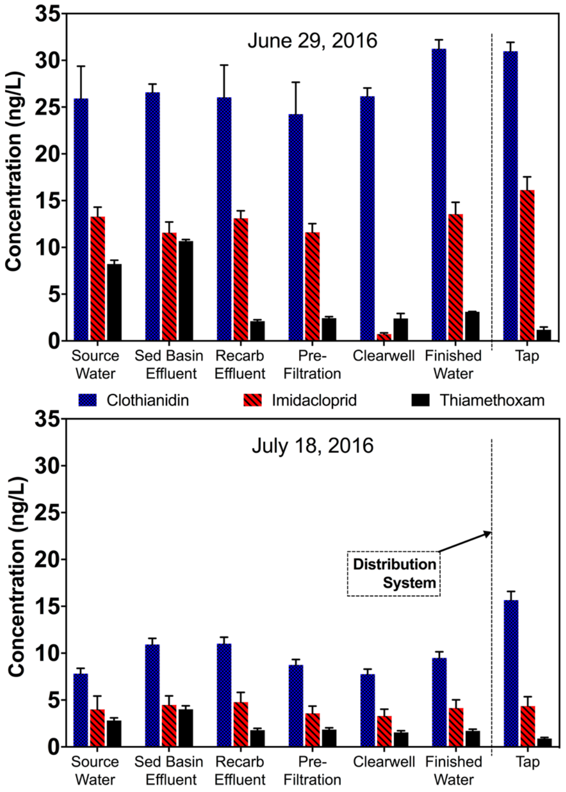

Figure 2. Concentrations of clothianidin, imidacloprid, and thiamethoxam measured at different unit operations at the UI DWTP on the two indicated sampling dates (additional data in Tables S6−S8). Neonicotinoid concentrations differed on the two sampling dates, but overall trends across the treatment train were consistent. Error bars represent the standard error of regression associated with the composite enrichment sample extraction and analysis (1 L enriched to 1 mL).

We also collected samples from the City and UI DWTP to compare source water and finished water concentrations of clothianidin, imidacloprid, and thiamethoxam (Figure 3 and Tables S9−S11) between the two treatment plants. Samples from the UI DWTP were collected within 3 h of City DWTP samples. Source water concentrations of the three compounds were within 30% between sites for a given compound, despite the fact that UI DWTP water originates from the Iowa River and the City DWTP water originates from the shallow alluvial aquifer under the influence of the Iowa River.

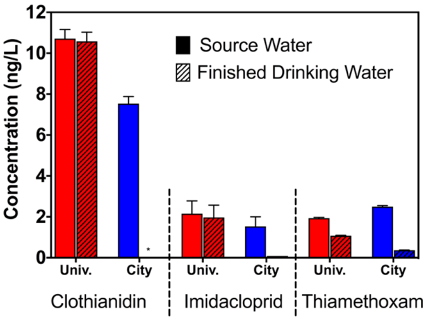

Figure 3. Concentrations of the three neonicotinoids measured in City and UI DWTP source and finished drinking waters (August 9, 2016). The City DWTP uses granular activated carbon (GAC) filtration compared to rapid sand filtration at the UI DWTP. The asterisk indicates no detection. Error bars represent the standard error of regression associated with the composite enrichment sample extraction and analysis (1 L enriched to 1 mL).

Decreases in neonicotinoid concentrations appeared to be greater at the City DWTP (∼100, 94, and 85% for clothianidin, imidacloprid, and thiamethoxam, respectively) than at the UI DWTP (∼1, 8, and 44%, respectively). A notable distinction is that the City DWTP uses GAC filtration compared to rapid sand filtration at the UI DWTP; the latter process removes only particles. These analyses were consistent with earlier UI DWTP process train results that indicated no discernible changes in concentration for clothianidin or imidacloprid and a modest loss of thiamethoxam. Additionally, finished water concentrations of clothianidin, imidacloprid, and thiamethoxam from each treatment plant were similar to the corresponding measurements from tap water samples.

Hydrolysis of Thiamethoxam. We attribute thiamethoxam removal to base-catalyzed hydrolysis. Base-catalyzed hydrolysis of thiamethoxam has been reported with half-lives ($t_{1/2}$ values) ranging from 2.1 days[33] at pH 9.2 and 28 °C (corresponding to a pseudo-first-order rate constant, k_{obs}, value of 0.33 day^{-1}) to 6.1 days[34] at pH 9.0 and 25 °C (k_{obs} = 0.11 day^{-1}). Furthermore, the stability of thiamethoxam is known to decrease with increasingly alkaline conditions.[19,33,35]

Batch tests confirmed that thiamethoxam hydrolysis is likely to occur over time scales relevant to treatment and distribution (Figures S2−S4 and Table S1). Using a UI DWTP softening basin water sample spiked with 100 μM thiamethoxam, we measured a $t_{1/2}$ of 0.75 day (k_{obs} = 0.9 day^{-1}) at pH 10.4 (the softening basin pH) and 20 °C. During the lime softening process at the UI DWTP, the pH is increased to ≥10.3 with a residence time of 1.5−3.2 h. Accordingly, thiamethoxam removal observed in Figures 2 and 3 reflects degradation

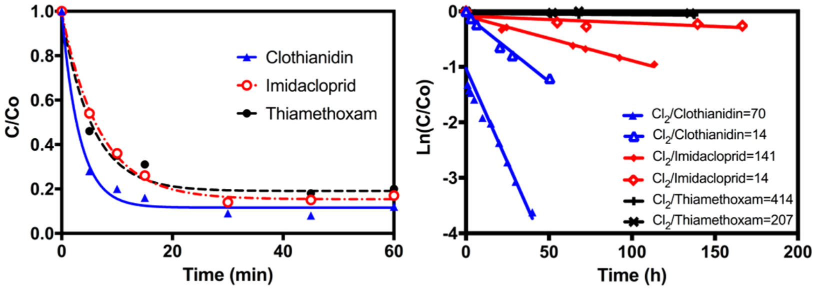

Figure 4. Neonicotinoid batch kinetic tests. The left panel shows the change in aqueous neonicotinoid concentration (C_0 = 100 μg/L) in suspensions of granular activated carbon (5 g/L GAC in pH 7 phosphate buffer). Data fitted to an exponential decay model (Table S12 and Figure S5). The right panel shows chlorination loss kinetics. Cl_2/neonicotinoid values reported as molar ratio (M/M). Titrations with FAS revealed chlorine concentrations (10, 50, and 100 mg/L as Cl_2) that were constant during the experiment, allowing calculation of k_{obs} from the slopes of linear regressions.

from hydrolysis during treatment and distribution (finished water pH of ~9.9), as well as during the handling time between sample collection and processing (typically 24 h). Thiamethoxam hydrolysis is also expected to occur in the City DWTP, which also employs lime softening (finished water pH of ~9.2).

Removal of Neonicotinoids via Sorption onto Granular Activated Carbon. All three neonicotinoids studied exhibited relatively rapid removal via sorption onto GAC, with >80% removal in suspensions after 1 h of contact time (Figure 4). Initial sorption was rapid, followed by stabilized aqueous concentrations consistent with equilibrium by 30 min. Some heterocyclic aromatic nitrogen compounds and protonated bases, such as the neonicotinoids studied herein, have been reported[36] to exhibit greater removal by GAC than would be predicted by K_{ow} values alone. Neonicotinoid removal by GAC is likely attributable to specific binding interactions between surface sites on GAC and specific structural moieties in the neonicotinoids, although additional experimental studies are recommended to evaluate adsorption mechanisms, long-term effectiveness, optimal dosing, and overflow rates.

Transformation of Neonicotinoids during Chemical Disinfection with Free Chlorine. Both treatment plants employ chlorination, with typical contact times of 3−4 h (City DWTP) and 20 min to 3 h (UI DWTP), and with residuals of 1.8 mg/L Cl_2 (City DWTP) and 2.5 mg/L Cl_2 (UI DWTP). Laboratory batch studies revealed a range of reactivities of neonicotinoids toward free chlorine [HOCl (Figure 4)]. Thiamethoxam was generally recalcitrant, exhibiting no significant loss ($p > 0.50$) at even the greatest free chlorine concentrations tested (Cl_2:thiamethoxam molar ratio of 12500) over a prolonged reaction time. In contrast, imidacloprid and clothianidin exhibited greater reactivity, with clothianidin being most reactive. Second-order rate coefficients for the reaction of HOCl with clothianidin (4.7×10^{-2} M^{-1} s^{-1}) and imidacloprid (1.6×10^{-3} M^{-1} s^{-1}) were calculated from measured pseudo-first-order rate constants (Figure 4) assuming a constant HOCl concentration ($k_2 = k_{obs}/[\text{HOCl}]$). At chlorine concentrations more typical for disinfection (i.e., 5 mg/L as Cl_2) and assuming a constant residual, half-lives for clothianidin and imidacloprid would be ~2.5 and ~70 days, respectively. Although imidacloprid is practically resistant to transformation, a modest degree of clothianidin decay may be expected during chemical disinfection, particularly in distribution systems with longer residence times.[37] We note that using conditions more representative of drinking water treatment (C_0 = 5 mg/L HOCl as Cl_2; 0.10−1.25 mg/L clothianidin), extensive transformation of clothianidin occurred [>80% in 1.5 h (Figure S7)] at rates greater than those expected from estimated k_2 values. We suspect that differences in the clothianidin transformation rate across a range of chlorine concentrations reflect the formation of highly reactive intermediates that contribute to chlorine demand, which in turn influences the extent of clothianidin degradation (Figure S9).

Environmental Implications. To the best of our knowledge, this is the first peer-reviewed study to document the presence of neonicotinoids in finished tap water samples. Conventional water treatment results in no measurable removal of clothianidin or imidacloprid, although the alkaline conditions of lime softening result in the partial transformation of thiamethoxam via base-catalyzed hydrolysis. Because of their pervasiveness in source waters[20,21,30,32] and persistence through treatment systems,[27] neonicotinoids are likely present in other drinking water systems across the United States. Transformation products formed by chlorination or hydrolysis warrant great consideration because of the potential to form toxic transformation products (Figures S3 and S10). For example, the metabolite desnitro-imidacloprid exhibits a mammalian receptor binding affinity 300 times greater than that of imidacloprid because of the loss of the nitro group that confers insect specificity.[4] For management, GAC filtration presents a treatment option for removal of neonicotinoids in resource-constrained communities that rely of agriculturally impacted surface waters or point-of-use systems that is substantially more economical than reverse osmosis or advanced oxidation processes.[38]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.estlett.7b00081.

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

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Notes

The authors declare no competing financial interest.

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Supporting Information

Occurrence of Neonicotinoid Insecticides in Finished Drinking Water and Fate during Drinking Water Treatment

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Supporting information includes: chemicals, water treatment plant schematics, QA/QC procedures, analytical methods, and an additional 12 tables and 10 figures.

CHEMICALS.

Important chemicals used in the experiments include: clothianidin (99.9%, CAS 210880-92-5), imidacloprid (99.9%, CAS 138261-41-3), imidacloprid-d_4 (99.9%, CAS 1015855-75-0), and thiamethoxam (99.6%, CAS 153719-23-4). All neonicotinoids were manufactured by Fluka and used as received. All solvents used for LC-MS analysis were of LC-MS grade.

Solvents: Acetonitrile (optima grade, HPLC grade)**.** Acetone (optima grade). Dichloromethane (>99%).

Other Chemicals: Sodium hypochlorite solution 5.65-6% (Fisher Scientific). Granular Activated Carbon (Calgon Centaur 12X40). 5 mM potassium phosphate buffer (made in lab). Sodium Sulfite (Fisher).

METHOD DETAILS.

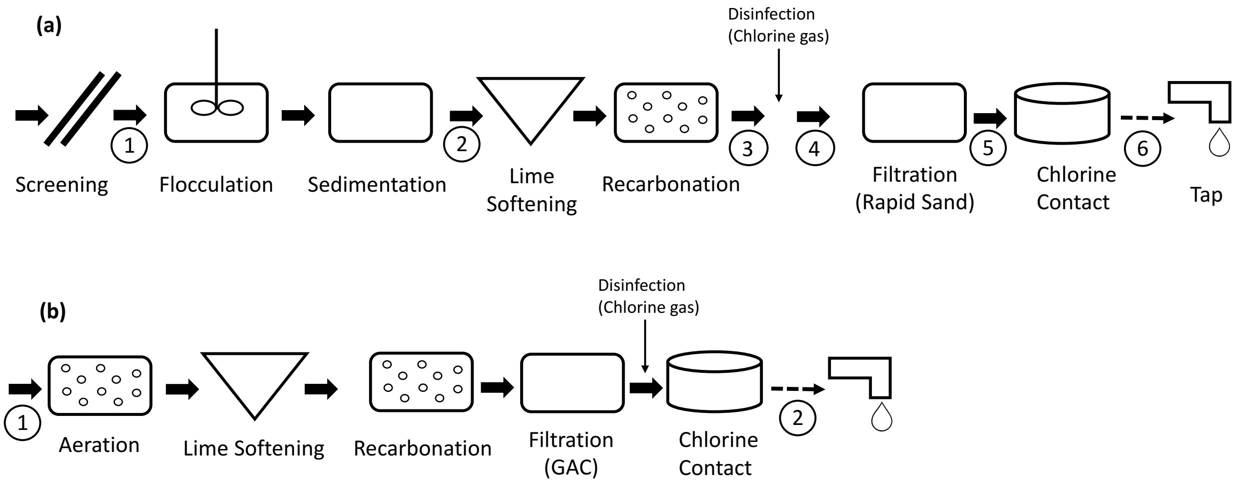

Figure S1: Schematic of sampling locations (circled) at the two drinking water treatment plant (DWTP) systems studied. **a**. University of Iowa DWTP schematic. Samples: (1) Raw source water, (2) Sedimentation basin effluent (3) Recarbonation effluent – pre-chlorination, (4) Recarbonation effluent – post chlorination (5) Filtration effluent (6) Finished water. **b**. Iowa City DWTP Schematic. Samples (1) Source water (2) finished water.

Table S1: Hydraulic residence times for the University of Iowa Water Treatment Plant unit operations. Ranges based on minimum expected flow (2.0 mgd) and maximum expected flow (4.25 mgd).

Operation	**Residence time (h)**
Flocculation and Sedimentation	2.7-5.7
Softening	1.5-3.2
Filtration	1.1-2.3
Total	5.3-11.2

QA/QC Procedure: Deionized water (5 mL) was spiked with clothianidin (1 µM). A sample of the 1 µM solution was run on the LC-MS/MS as a control. Three jars were filled with 1 L of deionized water, and each jar was spiked with 1 mL of the 1 µM clothianidin solution (the concentration in each 1 L jar is 1 nM). The 1 nM samples were each run through the entire SPE process, concentrating the 1 L samples down to 1 mL. The concentrated samples were analyzed by the LC/MS/MS, and peak areas were compared to the control to estimate recovery. Recovery of clothianidin was 95%, 95% and 96% percent (average = 95%, SD=0.4%) for the three samples.

All water samples (*i.e.*, tap water and those from the DWTP process trains) were collected directly into clean 1 L amber glass jars (pre-baked at 550 °C) with minimal headspace. DWTP samples were collected from each unit operation and analyzed within 48 h of collection. For tap water samples, the faucet was flushed for at least two minutes prior to sample collection, and samples were stored for a maximum of 30 d at 11 °C to analysis.

A five-point internal standard normalized external calibration curve was used to account for surrogate recovery and matrix effects during ionization. A calibration curve was run with each set of samples. The instrument response was linear throughout the calibration range. Multiple blanks were run with each set of samples, and no contamination was observed in the blanks. Lab blanks only were generated (i.e., no “field blanks”) because neonicotinoids are non-volatile making cross-contamination unlikely and residential samples were all collected by the authors in their private residences where neonicotinoids were not used.

Sorption of Neonicotinoids to Granular Activated Carbon: Batch experiments measured the extent and timescale of neonicotinoid sorption onto granular active carbon (GAC). Reactors were assembled in clear, crimp-top glass vials (10-40 mL) and contained 5 g/L of GAC (Calgon) and 100 µg/L of an individual neonicotinoid (clothianidin, imidacloprid, or thiamethoxam) in deionized water. A second set of experiments was conducted in pH 7-phosphate buffer (Figure S.2). Once assembled, reactors were mixed by an end-over-end rotator for up to 4 h. Periodically, samples (0.5 mL) of the suspension supernatant were collected at specified time intervals for LC-DAD/MS analysis.

Chlorination of Neonicotinoids: Bench scale chlorination experiments were conducted to assess the potential for neonicotinoid transformation during chemical disinfection and distribution in the presence of residual disinfectant. To initiate reaction, hypochlorous acid (HOCl) was added to a closed reactor (10 – 50 mL) containing either clothianidin, imidacloprid, or thiamethoxam in 5 mM phosphate buffer at pH 7. A range of neonicotinoid (from 0.34 – 10 μM or 0.10 – 2.9 μg/L) and HOCl (0.0014-1.41 mM or 0.1-100 mg/L as Cl_2) concentrations were tested. Samples (0.5 – 1.0 mL) were collected at defined intervals and transferred to amber glass vials for immediate analysis via high performance liquid chromatography coupled with a diode array detector and single quadrupole mass spectrometer (LC-DAD/MS). Measurements of solution pH and chlorine concentration (via titration of ferrous ammonium sulfate or FAS[1]) were conducted immediately after chlorine addition and at the conclusion of each experiment. We note that for experiments with clothianidin, which was most reactive toward free chlorine, residual chlorine in samples was quenched with 1.8 mg sodium sulfite (Na_2SO_3) per mg of chlorine[2] (as Cl_2) prior to LC-DAD/MS analysis. Sodium sulfite was not used for reaction samples with imidacloprid and thiamethoxam; both reacted sufficiently slowly such that samples could be immediately analyzed without altering the extent of decay.

Analytical Methods: Water samples collected from the taps and treatment plants were enriched by solid phase extraction (SPE) methods adapted from the USGS.[3] Briefly, DWTP samples were filtered using a 0.7 μm glass filter (GF/F, Whatman) prior to SPE. Tap water samples were not filtered. Samples were then spiked with imidacloprid-d_4 as an internal standard before being loaded onto an Oasis SPE cartridge (500 mg HLB; Waters). Prior to use, cartridges were conditioned with 5 mL of dichloromethane (DCM), 5 mL of acetone, and 10 mL of deionized water. One liter of sample (containing imidacloprid-d_4) was loaded onto the cartridge using negative pressure at a flow rate of ~10 mL/min or less. Sample bottles were washed with 100 mL of DI and the rinsate was also loaded onto the cartridge. Following extraction, the cartridge was dried under vacuum until visibly dry. The sample was then eluted into an acid-washed glass vial using 10 mL of 50/50 DCM:acetone. The solvent was evaporated until just dry using a gentle stream of nitrogen. The sample was then reconstituted into 1 mL of 50/50 acetonitrile: DI water and stored at -20 °C until analysis via LC-MS/MS (Tables S.1 and S.2). Clean water controls indicated a method recovery of 95 ± 0.4% (average ± SD, n = 3). Additional details are included in the quality assurance and control (QA/QC).

Neonicotinoid samples were analyzed via high performance liquid chromatography (Agilent 1260) coupled to a MS/MS spectrometer (LC-MS/MS; Agilent 6460 Triple Quadrupole MS with MassHunter, version B.07.00) for tap water samples or DAD/MS (Agilent 6140 Quadrupole LC/MS and diode array detector with OpenLab ChemStation C.07.00) for chlorination or GAC experiments. The chromatography column was a C18 Zorbax Eclipse Plus (4.6 mm x 150 mm, 5 μm) held at 50 °C for LC-MS/MS and ambient temperature for LC-DAD/MS. An injection volume of 20 μL was used, and the mobile phases were acetonitrile and water with 0.1% formic acid at 0.8 mL/min. The mobile phase gradient is described in Table S.1.

Samples were quantified using the DAD at a wavelength of 260 nm (clothianidin and thiamethoxam) and 280 nm (imidacloprid) and by mass spectrometry where possible. For detection with mass spectrometer, samples were analyzed on electrospray ionization positive mode, gas temperature 300 °C, gas flow 5 L/min, nebulizer 45 psi, sheath gas temp 250 °C, sheath gas flow 11 L/min, capillary voltage 3500 V. Data were collected in multiple-reaction-monitoring (MRM) mode using two transition ions (quantitation and verification). Optimum MRM parameters were determined using Agilent Optimizer software (version B.07.00) by injecting a 1 mg/L solution of each compound (clothianidin, imidacloprid, thiamethoxam) onto the LC-MS/MS. MRM parameters are provided in Table S.2.

A five-point internal standard normalized external calibration curve was used to account for surrogate recovery and matrix effects during ionization, and was run with each set of samples. Multiple blanks were run with each set of samples, and no contamination was observed in the blanks. The lower level of detection (LLD) on the LC-MS/MS without sample enrichment for clothianidin, imidacloprid and thiamethoxam were 167, 99.7 and 204 ng/L, respectively. The LLD following sample enrichment for clothianidin, imidacloprid and thiamethoxam were 0.167, 0.010 and 0.204 ng/L respectively.

Table S2: HPLC mobile phase gradient.

Time (min)	% Acetonitrile	% Deionized Water
0	15	85
11	25	75
13	25	75
15	95	5
15.5	15	85
21	15	85

Table S3: Multiple Reaction Monitoring (MRM) Parameters

Compound	Precursor Ion (m/z)	Quantitation Ion (m/z)	Qualitative Ion (m/z)	Fragmentor (V)	Quantitation ion collision energy (V)	Qualitative ion collision energy (V)	Retention time (min)
Imidacloprid	256.06	209	175.1	59	12	12	11.2
Clothianidin	250.02	169.1	131.9	67	8	12	10.0
Thiamethoxam	292.03	211	181	63	8	20	7.8
Imidacloprid-d4	260.09	213	179.1	59	12	16	11.1

FAS titration method:

Reagents **(**see full description in standard methods):
Phosphate buffer solution (169 mM as PO_4)
N,N-Diethyl-p-phenylenediamine (DPD) indicator solution (5.72 mM)
Ferrous ammonium sulfate (FAS) titrant (2.8 mM as FeII)

1. Measure 100 mL of DI water using a volumetric flask
2. Pour DI water into a beaker
3. Add 1 mL of sample to the 100 mL of DI water
4. Add 5 mL of phosphate buffer solution and 5 mL of N,N-Diethyl-p-phenylenediamine (DPD) indicator solution
5. Titrate with Standard ferrous ammonium sulfate (FAS) until the red color is gone
6. Calculate free chlorine concentration: (volume of FAS added)*100=Free chlorine (mg/L as Cl_2)

Lower Level of Detection Calculation:

Based on Standard Methods 1030 E Method Detection Level[1]. Method overview:

1. A standard containing 0.1 uM of clothianidin, imidacloprid and thiamethoxam was injected seven times in a row on the LC-MS/MS.
2. The standard deviation (s) of the concentration measured was calculated for each compound
3. To reduce the probability of a type I error, the standard devation was multiplied by two times 1.645 from a cumulative normal probability table: LLD = 2*1.645*s.

Table S4: University of Iowa tap water sample results. Samples collected from the same tap in the laboratory at Seaman's Center for Engineering.

Date	**Location**	**Thiamethoxam (ng/L)**	**Imidacloprid (ng/L)**	**Clothianidin (ng/L)**
5/31	**SC 4249**	**0.65**	**2.32**	**5.73**
6/2	**SC 4249**	**0.42**	**1.22**	**3.89**
6/3	**SC 4249**	**0.61**	**1.38**	**4.24**
6/6	**SC 4249**	**1.04**	**3.26**	**10.19**
6/7	**SC 4249**	**2.04**	**2.26**	**5.73**
6/10	**SC 4249**	**1.22**	**2.33**	**7.02**
6/15	**SC 4249**	**2.61**	**5.53**	**13.57**
6/20	**SC 4249**	**4.15**	**3.38**	**10.29**
6/21	**SC 4249**	**1.13**	**4.24**	**13.88**
6/23	**SC 4249**	**0.84**	**5.05**	**12.58**
6/27	**SC 4249**	**1.19**	**26.36**	**27.27**
6/28	**SC 4249**	**0.85**	**16.30**	**33.46**
6/29	**SC 4249**	**1.19**	**16.13**	**30.97**
7/1	**SC 4249**	**0.26**	**10.20**	**20.51**
7/7	**SC 4249**	**0.49**	**5.27**	**11.19**
7/18	**SC 4249**	**0.77**	**3.69**	**13.30**

Table S5: Iowa City tap water results summary from samples collected from three residential locations in Iowa City.

Date	Location	Clothianidin (ng/L)	Imidacloprid (ng/L)	Thiamethoxam (ng/L)
7/18/16	1	ND	ND	0.34
7/18/16	2	ND	ND	<0.20
7/18/16	3	ND	ND	0.37
7/27/16	1	ND	<0.10	0.47

**ND indicates non-detect, <LLD indicates that compound was detected at concentrations below the LLD

Table S6: Clothianidin concentrations in samples from the University of Iowa water treatment plant (concentrations in nanograms per liter)

Date	**Source Water (1)**	**Sedimentation Basin (2)**	**Recarbonation (Pre-chlorination)(3)**	**Recarbonation (Post-chlorination) (4)**	**Filtration effluent (5)**	**Finished Water (6)**
6/29/16	26.0	26.6	26.0	24.3	26.2	31.2
7/18/16	7.82	10.9	11.0	8.75	7.76	9.50

Table S7: Imidacloprid concentrations in samples from the University of Iowa water treatment plant (concentrations in nanograms per liter)

Date	**Source Water (1)**	**Sedimentation Basin (2)**	**Recarbonation (Pre-chlorination) (3)**	**Recarbonation (Post-chlorination) (4)**	**Filtration effluent (5)**	**Finished Water (6)**
6/29/16	13.3	11.6	13.1	11.6	0.72	13.6
7/16/16	4.00	4.48	4.78	3.58	3.30	4.14

Table S8: Thiamethoxam concentrations in samples from the University of Iowa water treatment plant (concentrations in nanograms per liter)

Date	**Source Water (1)**	**Sedimentation Basin (2)**	**Recarbonation (Pre-chlorination) (3)**	**Recarbonation (Post-chlorination) (4)**	**Filtration effluent (5)**	**Finished Water (6)**
6/29/16	8.23	10.7	2.12	2.43	2.40	3.11
7/18/16	2.81	4.01	1.78	1.84	1.55	1.71

Table S9: Clothianidin concentrations in the University of Iowa and Iowa City Source and Finished waters (August 9, 2016)

WTP	**Source Water (ng/L)**	**Finished Water (ng/L)**
UI	10.7	10.6
City	7.53	ND

Table S10: Imidacloprid concentrations in the University of Iowa and Iowa City Source and Finished Waters (August 9, 2016).

WTP	**Source Water (ng/L)**	**Finished Water (ng/L)**
UI	2.15	1.97
City	1.53	0.09

Table S11: Thiamethoxam concentrations in the University of Iowa and Iowa City Source and Finished Waters (August 9, 2016).

WTP	Source Water (ng/L)	Finished Water (ng/L)
UI	1.93	1.07
City	2.50	0.37

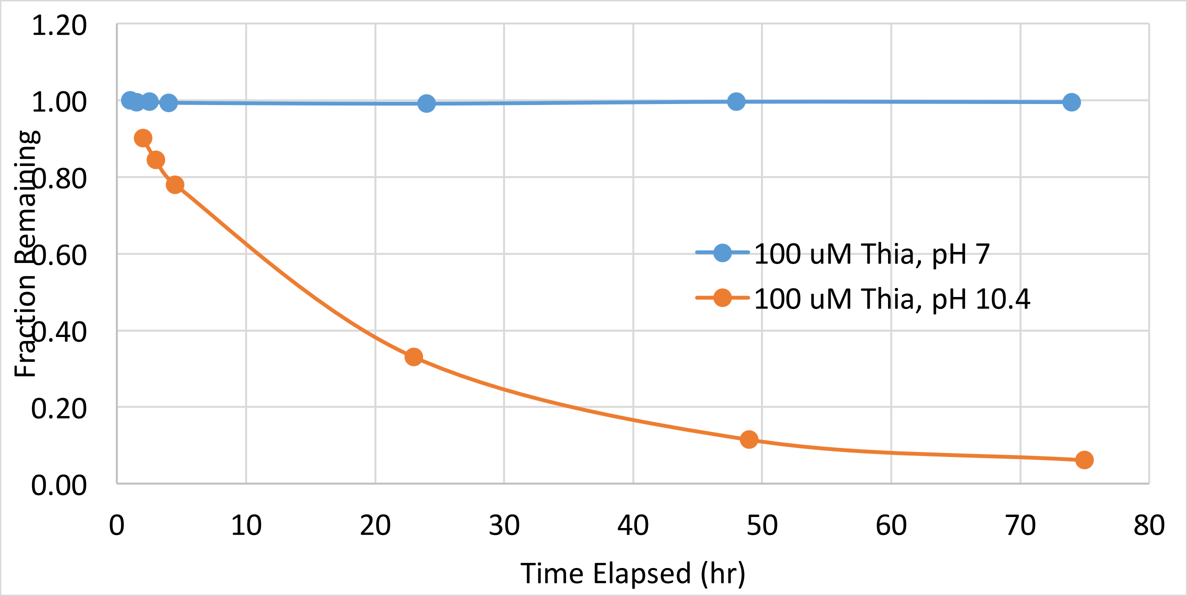

Figure S2: Thiamethoxam hydrolysis in ambient pH University DWTP softening basin water (pH 10.4) compared to University DWTP softening basin water adjusted to pH 7

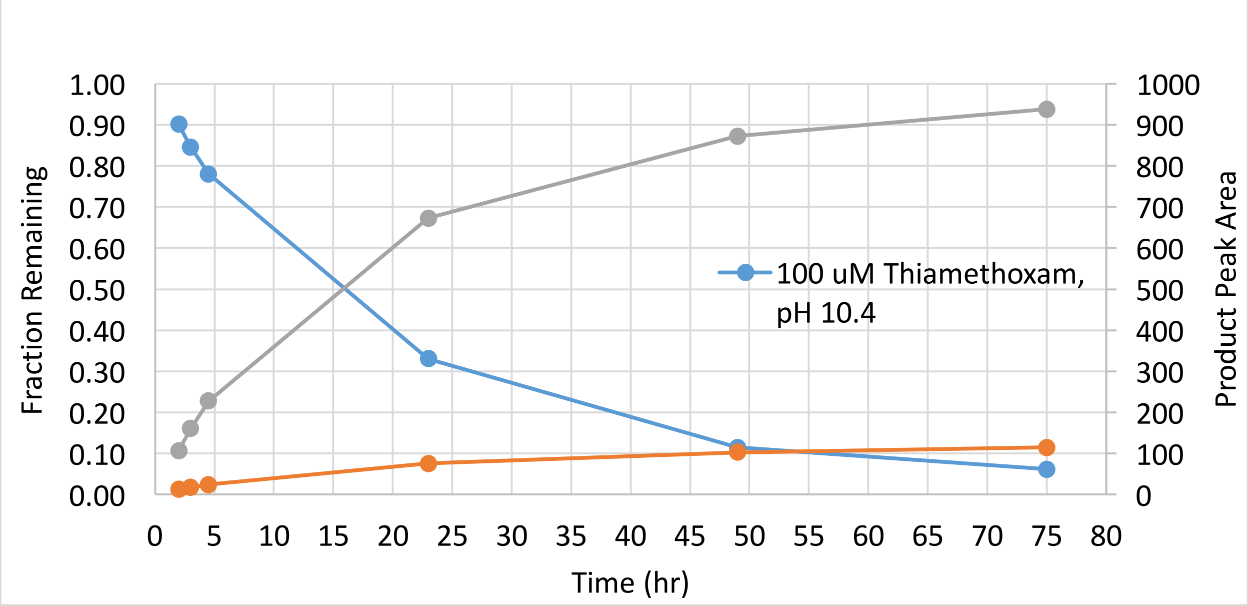

Figure S3: Product formation during thiamethoxam hydrolysis in University DWTP softening basin water

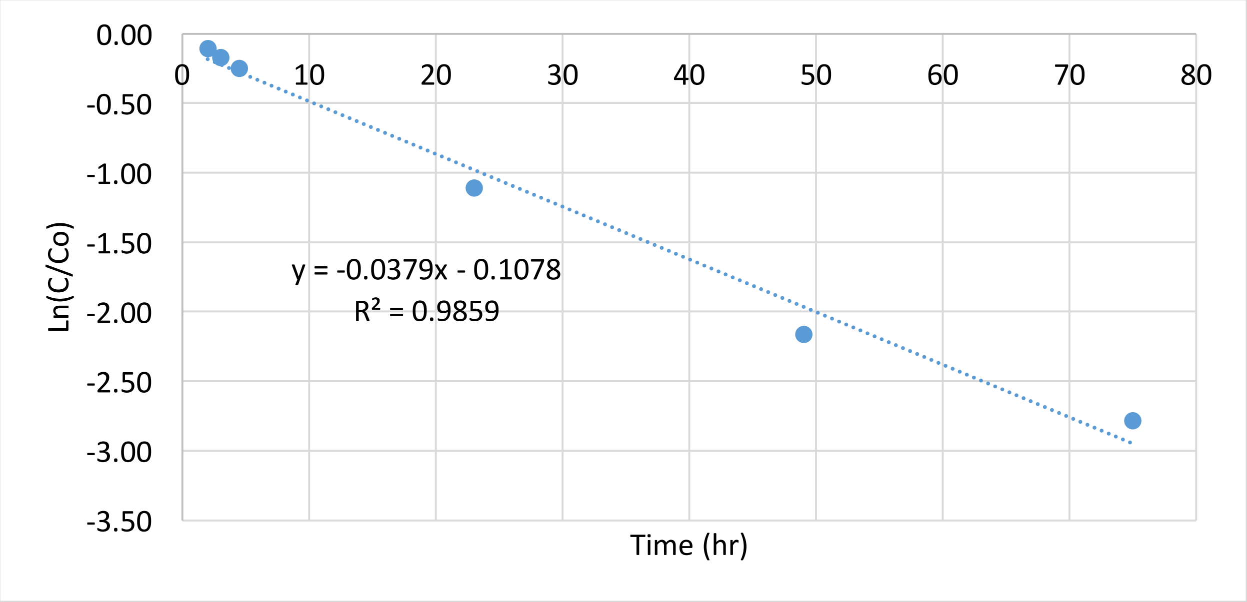

Figure S4: Ln(C/C_o) versus time for thiamethoxam hydrolysis in University DWTP softening basin water. $K_{obs} = 0.0379\ h^{-1}$, $t_{1/2} = \ln(0.5)/K_{obs} = 18.3$ h.

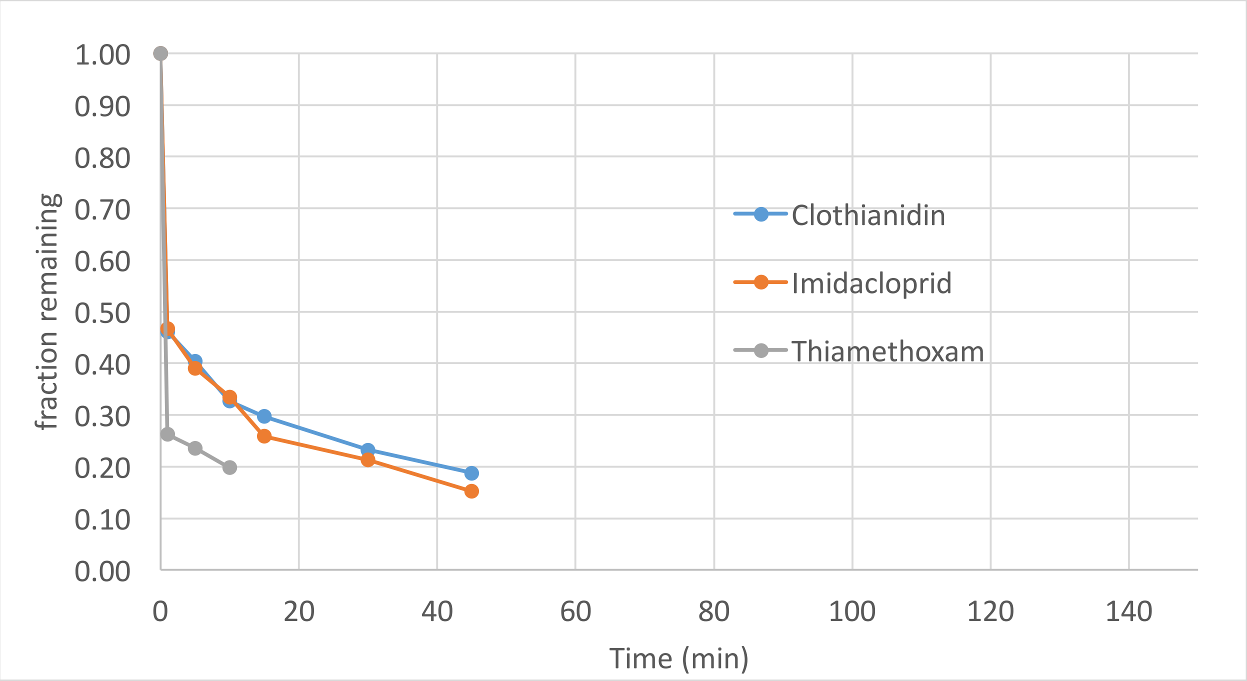

Figure S5: Adsorption of clothianidin, imidacloprid, thiamethoxam to GAC. Experimental conditions: GAC 5 g/L, chemical concentration 100 ug/L (clothianidin, imidacloprid and thiamethoxam), experiment conducted in pH 7 phosphate buffer.

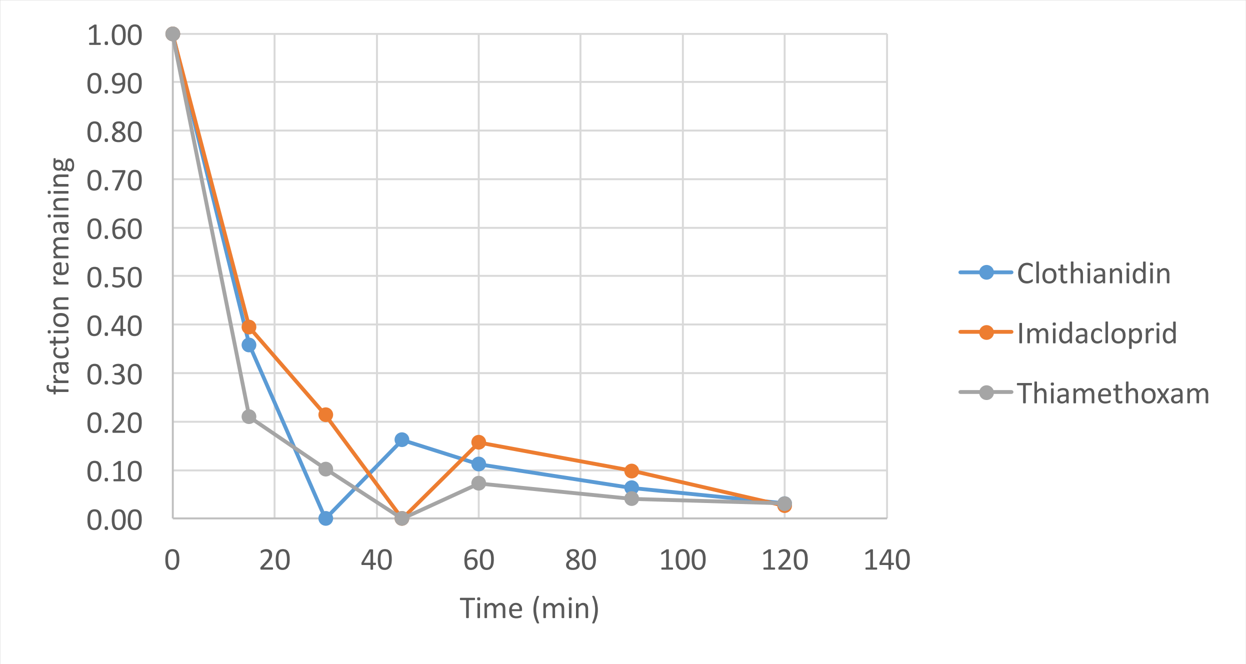

Figure S6: Replication experiment of adsorption of clothianidin, imidacloprid, thiamethoxam to GAC. Experimental conditions: GAC 5 g/L, chemical concentration 100 ug/L (clothianidin, imidacloprid and thiamethoxam), experiment conducted in DI water.

Table S12: Exponential decay parameters for GAC adsorption (Figure 4)

Compound	**Clothianidin**	**Imidacloprid**	**Thiamethoxam**
K (h^{-1})	0.3098	0.1469	0.1812
R^2	0.9910	0.9974	0.9784

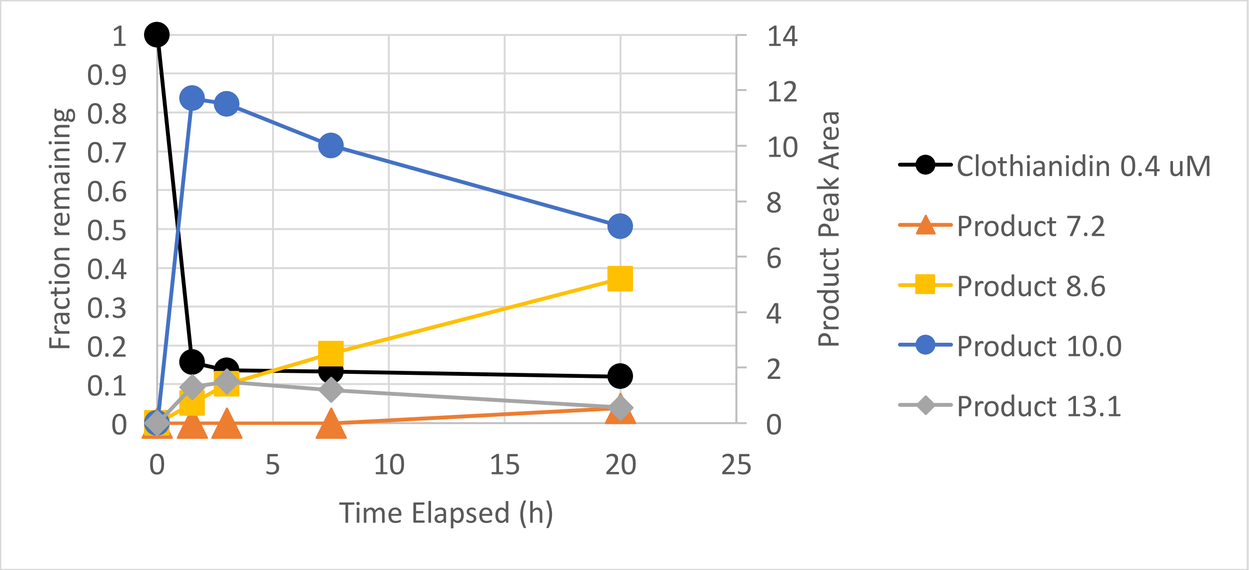

Figure S7: Product formation during chlorination of clothianidin. Experimental conditions: Chlorine 10 mg/L as Cl_2, clothianidin 0.4 μM, pH 7. The formation of intermediates (shown in this figure) may explain why we observe initial fast reaction rates followed by slow decay of clothianidin. We hypothesize that the intermediates are more reactive and may outcompete clothianidin for chlorine causing the decay of clothianidin to slow after a fast initial reaction.

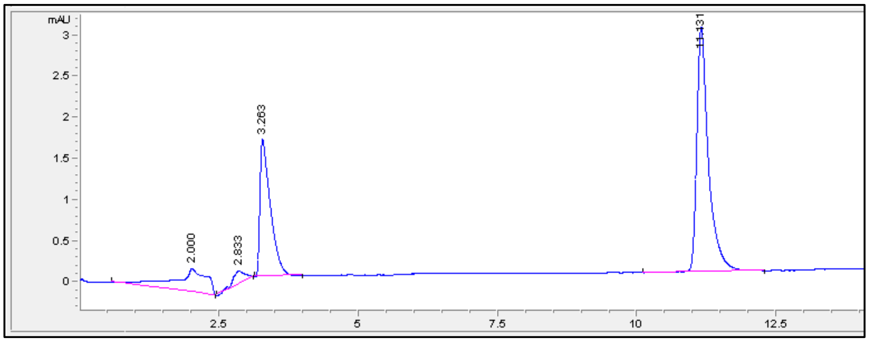

Figure S8: Chromatogram of chlorination reaction shown in Figure S7. Clothianidin concentration 100 μg/L, just prior to adding chlorine (0 mg/L Cl_2, t=0). Clothianidin residence time = 11.13 min, wavelength = 260 nm.

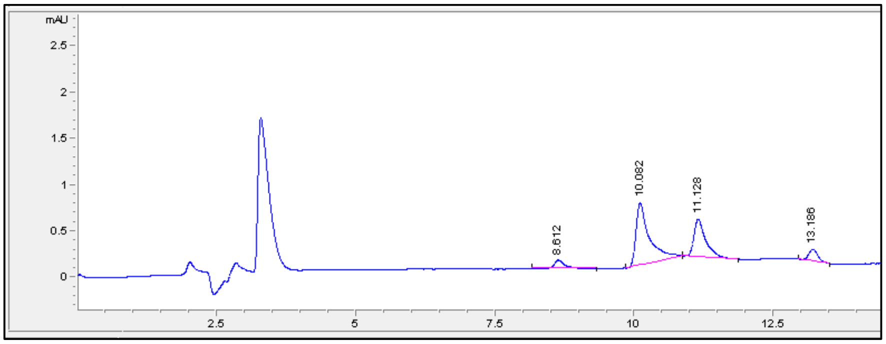

Figure S9: Chromatogram of chlorination reaction shown in Figure S7. Clothianidin concentration 100 µg/L, chlorine concentration 10 mg/L Cl_2, time = 3 h. Clothianidin residence time = 11.13 min, wavelength = 260 nm.

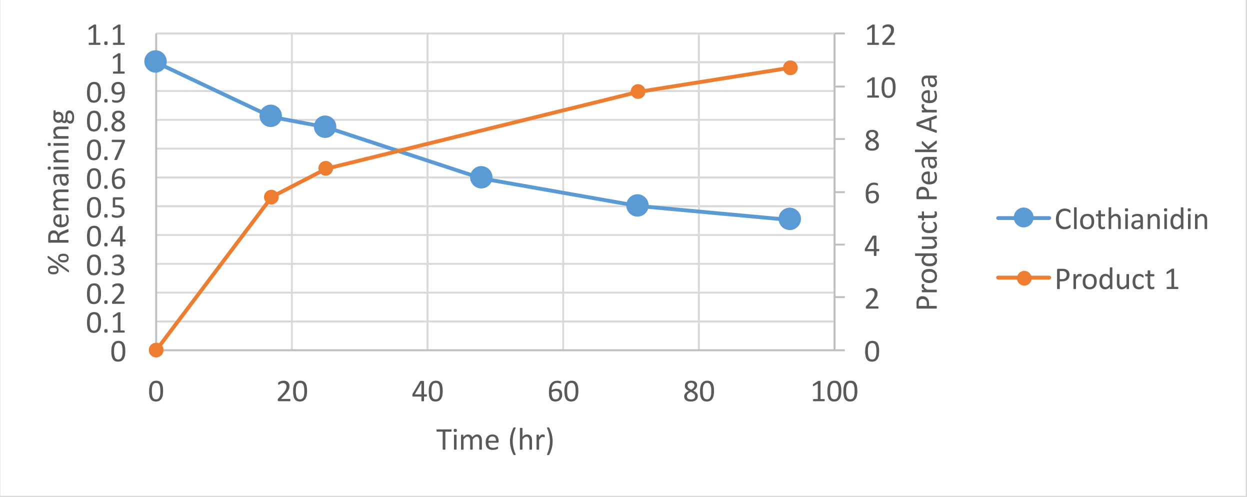

Figure S10: Product formation during chlorination of clothianidin. Experimental conditions: Chlorine 5 mg/L as Cl_2, clothianidin 5 µM, pH 7. The formation of intermediates (shown in this figure) may explain why we observe initial fast reaction rates followed by slow decay of clothianidin. We hypothesize that the intermediates are more reactive and may outcompete clothianidin for chlorine causing the decay of clothianidin to slow after a fast initial reaction.

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