A Review of Neonicotinoid Insecticides and Occurrence in New Jersey Surface Water and Groundwater

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Abstract
Surface water and groundwater samples were collected between May and September 2019 and were analyzed to determine the concentrations of common neonicotinoids including acetamiprid, clothianidin, dinotefuran, imidacloprid, imidacloprid urea (an imidacloprid metabolite), nitenpyram, thiacloprid, and thiamethoxam. In total, 250 surface water samples (123 sites were sampled twice, 4 were sampled once) and 25 groundwater samples from unique locations were evaluated. Neonicotinoids were detected in just over half (51%, n=140) of the 275 samples analyzed. Imidacloprid was the compound that was detected most frequently (45%, 112 of 250 samples) and at the highest concentrations in surface water (median detected concentration: 22 ng/L), followed by dinotefuran, clothianidin, thiamethoxam, and acetamiprid. Nitenpyram and thiacloprid were not detected in any of the samples, while imidacloprid urea was detected in only four surface water samples (2%). Median concentrations of individual detected neonicotinoids ranged from 4 - 22 ng/L for surface water. Neonicotinoid detections were less frequent overall in groundwater wells. Clothianidin was most frequently detected in groundwater samples (20%, 5 of 25 samples, median concentration: 34 ng/L), followed by imidacloprid (16%, 4 of 25 samples, median concentration: 30 ng/L), and thiamethoxam (4%, 1 of 25, concentration: 25 ng/L). Imidacloprid concentrations exceeded EPA’s chronic aquatic life benchmark of 10 ng/L in 86 (34%) surface water samples. Additional work is needed to compare the potential risk of these neonicotinoids to resident New Jersey species and how neonicotinoid exposure relates to other risk factors in the environment including other chemical stressors and habitat suitability.

Introduction
Neonicotinoid pesticides are a class of systemic insecticides that are widely used throughout the world in agricultural, greenhouse/nursery, structural, landscape, and forestry applications to control aphids, beetles, and several other classes of insects. These insecticides are also used in pet products to prevent and control fleas and ticks. Neonicotinoids entered the pesticide market in the 1990s and were originally promising due to their systemic properties in plants, providing an extended period of protection against pests. Globally, neonicotinoids account for about one quarter of all insecticides being used (Craddock et al., 2019). Neonicotinoids are used in agriculture as a foliar spray, soil application, or as a seed coating to protect against soil pests. About 90% of corn acres in the U.S. are from seeds treated with clothianidin or thiamethoxam (Douglas et al., 2015; Stokstad, 2019), while nearly half of all soybeans planted in the U.S. were treated with imidacloprid or thiamethoxam (Cimino et al., 2017).

Neonicotinoids were expected to be less toxic to birds and mammals than some of their predecessor pesticides, such as organophosphates; however, recent studies have found that the systemic properties that make neonicotinoids appealing for pest control can also cause detrimental effects in nontarget organisms. Neonicotinoid usage threatens pollinators including honeybees and wild bees, which are critical in the production of seven of New Jersey’s top ten most valuable food crops (NJDA, 2018; Pollinator Partnership, n.d.). Bees and other pollinators are of primary concern because they can be exposed to toxic levels of neonicotinoids in plant pollen and nectar, as well as by encountering dust that is generated when planting neonicotinoid-treated seeds (Greatti et al., 2003; Tapparo et al., 2012). These exposures have been shown to alter pollinator behavior resulting in reduced foraging (Dively et al., 2015) and reproduction (Whitehorn et al. 2012), ultimately contributing to colony collapse disorder (Chensheng et al., 2014). Other non-target insects, such as the natural predators of target pests and aquatic invertebrates, can also be impacted by toxic concentrations of neonicotinoids in the environment (Pisa et al., 2017; Nowell et al., 2018).

Neonicotinoid impacts have also been observed in birds and mammals, including humans. Seeds that are treated with a neonicotinoid coating such as acetamiprid are highly toxic when consumed by small birds (Hallmann et al., 2014), impairing migration at low doses (white-crowned sparrows receiving 4.1 µg/g imidacloprid dosed by gavage daily for three days) (Eng et al., 2017) and causing lethal effects at higher doses (single acute dose LD50 of 13.9 mg/kg for gray partridges) (Gibbons et al., 2015). In white-tailed deer, imidacloprid exposure is associated with decreased fawn survival (Berheim et al., 2019). In humans, prenatal exposure to neonicotinoids has been linked to developmental and behavioral disorders (Cimino et al., 2017).

Imposing regulatory restrictions on neonicotinoid usage could
contribute to reduced impacts on pollinators, aquatic life, and the terrestrial environment. In 2013, the European Union restricted the use of three neonicotinoids (clothianidin, imidacloprid, and thiamethoxam) in Regulation (EU) No 485/2013 (EU 2018), forbidding their use in flowering crops that appeal to honeybees and other pollinating insects. The European Union subsequently expanded the neonicotinoid ban to all field crops in 2018 (European Commission, 2020). In the United States, specific states including Maryland, Connecticut, and Vermont have restricted application of neonicotinoids to only licensed applicators (MD House Bill 605, 2015; State of Connecticut, 2016; Vermont General Assembly, 2019). These restrictions are intended to protect pollinators as residential insecticide products can be much more concentrated than their agricultural counterparts.

The New Jersey Department of Environmental Protection (NJDEP) tracks and publishes in-state commercial pesticide usage in its pesticide use survey reports, which are generally updated every three years (NJDEP, n.d.). The neonicotinoid results from the most recent reports available (2016-2018) are reflected in Figure 1. In New Jersey, around 52,000 pounds of neonicotinoid insecticides are applied each year by licensed applicators. Lawn care application by licensed applicators is the largest reported usage category; however, these pesticide reports do not capture residential usage of over-the-counter neonicotinoid products. When broken down into individual neonicotinoid compounds, between 2016 and 2018 imidacloprid accounted for 90% of all neonicotinoid insecticides applied by licensed applicators, while dinotefuran and acetamiprid each accounted for 3%, and clothianidin and thiamethoxam each accounted for 2%.

![Figure 1. Total neonicotinoid insecticides applied annually in New Jersey by licensed applicators (pounds of active ingredient). Data shown in blue are based on the most recently published data from licensed pesticide applicators for each category of DEP’s Pesticide Use Reports (NJDEP, n.d.). Data shown in green are based on Mineau, 2019. This figure does not include neonicotinoid usage by homeowners.](image)

Based on the widespread usage of neonicotinoid insecticides and potential ecotoxicological impacts, NJDEP initiated a study in 2019 to investigate the occurrence of neonicotinoids in surface water and groundwater. Assessment of these data can assist decision-making concerning neonicotinoid use management and risk in the State of New Jersey. Surface water and groundwater sampling were conducted in the spring and summer of 2019 throughout the state of New Jersey and samples were analyzed for the presence of neonicotinoids. The goal of this study was to determine the levels of neonicotinoid compounds including acetamiprid, clothianidin, dinotefuran, imidacloprid, imidacloprid urea, nitenpyram, thiacloprid, and thiamethoxam in surface and groundwater across the state of New Jersey and to evaluate the potential for risk from the occurrence of these compounds.
Methods

Neonicotinoid occurrence data were collected as part of a larger routine monitoring program conducted by the NJDEP Office of Pesticide Evaluation and Monitoring with cooperation and assistance from the NJDEP Bureau of Freshwater and Biological Monitoring and USGS Water Science Center. Most of the selected surface water sites were sampled on two separate occasions. An initial sampling effort was conducted in May or June 2019 and then a subsequent sampling effort occurred in August or September 2019. In total there were 250 surface water samples (123 sites were sampled twice, 4 were sampled once) and each of 25 wells were sampled once (including 8 additional trip blanks) for groundwater. Detailed collection and chemistry methodologies are outlined in the respective surface water and groundwater Quality Assurance Project Plans retained by the Office of Pesticide Evaluation and Monitoring.

The NJDEP Office of Pesticide Evaluation and Monitoring prepared samples by filtering one liter of each surface and ground water sample, which were then spiked with an internal surrogate standard (D4-imidacloprid) and loaded onto a precleaned Oasis® hydrophilic lipophilic balanced (HLB) solid phase extraction (SPE) cartridge (6 ml, 500 mg). The water samples were pumped through the SPE cartridge at a flow rate of 10 ml/min and then dried for approximately one hour with air. Analytes were eluted into a clean glass concentrator tube using 10 ml of a 50:50 mixture of dichloromethane and acetone. The eluent was evaporated to dryness using a gentle stream of nitrogen and reconstituted into 0.5 ml of acetonitrile. Samples were analyzed using an Agilent 6410B liquid chromatograph/mass spectrometer triple quadrupole instrument (LC/MS/MS) to qualitatively identify and quantify the eight analytes of interest: acetamiprid, clothianidin, dinotefuran, imidacloprid, imidacloprid urea, nitenpyram, thiacloprid, and thiamethoxam. Sample analysis was performed in the dynamic multi-reaction method (DMRM) mode of operation, which produced characteristic mass transitions for each analyte. A liquid chromatographic gradient was utilized to separate the targeted analytes using methanol and 5 millimolar (mM) ammonium acetate as the mobile phases. A Poroshell EC-C18 (3.0 x 55 mm with 2.7 µm particle size) chromatographic column was used with a flow rate of 0.6 ml/min. An internal deuterated surrogate standard (D4-imidacloprid) was used to assess for discrepancies in recovery resulting from matrix suppression for each of the analytes. Of the 238 analyte detections, 106 had surrogate recoveries of less than 30%. All data, including those with acceptable surrogate recoveries, were corrected (adjusted) based on the ratio of recovered D4-imidacloprid to minimize underreporting detected concentrations.

Quantitative method detection limit (MDL) values were determined following the procedures described in EPA, 2016. Calculated MDLs for this study ranged from 4.5 ng/L to 7.4 ng/L (Table 1). The EPA defines an MDL as "...the minimum measured concentration of a substance that can be reported with 99% confidence that the measured concentration is distinguishable from method blank results" (EPA, 2016). However, the LC/MS triple quadrupole instrument used in this study is extremely sensitive and is capable of detecting the unique mass transitions of these compounds and thus the presence of targeted analytes at levels lower than the calculated MDL. This technology is capable of qualitatively detecting the presence of the neonicotinoid analytes at least an order of magnitude below the MDL in difficult matrices, albeit at a lower level of confidence than the defined MDLs. It is understood that at extremely low levels, the precision associated with quantification decreases (or broadens) significantly, which produces higher MDL values.

In this study, calibration curves were generated for each analyte on each day samples were analyzed and were consistently linear down to 4 ng/ml. Since the initial volume of the surface and ground water samples was approximately one liter and the final volume was 0.5 ml, results were quantified and reported down to 2 ng/L (ppt) based on the reproducibility of the calibration curves as well as their applicability to a research monitoring effort and that they are not used for regulatory or compliance purposes.

Analytes that were detected below 2 ng/L were not quantified but were reported as <2 ng/L to indicate the presence of the analyte in the sample. These lower end detections were set to a value of 1 ng/L (one-half of the reporting value) to be corrected based on laboratory recoveries and included in statistical summaries. If the ratio of an analyte’s mass transitions was not observed within the acceptance range, the result was reported as non-detectable (ND). Similar methods to these analytical and reporting approaches are described in Hladik et al. 2018, Hladik et al. 2014, Hladik and Callhoun 2012, Klarich et al. 2017, and Kuechle et al. 2019. Since detections of individual analytes are based on the precision of the sample extraction procedure along with the analysis, values below 2 ng/L were produced with less confidence than values above. It is often helpful for environmental monitoring purposes to evaluate qualified results, even if quantitatively some uncertainty remains.

Results

Neonicotinoids were detected in just over half (51%) of the water samples collected in this study. A summary of the detections for both surface water and groundwater samples is presented in Table 1. At least one detection occurred in 53% of the surface water samples and 28% of the groundwater samples. Imidacloprid was detected most frequently in surface water samples (45%, n=112), followed by dinotefuran (18%, n=44), clothianidin (12%, n=30), thiamethoxam (11%, n=28), and acetamiprid (4%, n=10). Nitenpyram and thiacloprid were not detected in this study, while imidacloprid urea was detected in only four surface water samples (2%). Median concentrations of individual detected neonicotinoids ranged from 4 - 22 ng/L for surface water. The median surface water concentration for total (additive) neonicotinoids on a per site basis was 20 ng/L (Figure 2). Imidacloprid was consistently the dominant neonicotinoid detected and had the highest median concentration across this study, although acetamiprid and thiamethoxam had the highest observed concentration at a small...
number of sites (3 and 7 sites, respectively). Detections were less frequent among the groundwater samples. Clothianidin was most frequently detected in groundwater samples (20%, n=5), followed by imidacloprid (16%, n=4), and thiamethoxam (4%, n=1). The maximum groundwater concentration of clothianidin and imidacloprid were 110 and 350 ng/L, respectively.

Table 1. Summary of occurrence data. Detection frequencies were calculated out of the total 250 surface water samples and 25 groundwater samples. Combined neonicotinoids are the additive values of detected concentrations at each site, which is not expected to equal summation of columns as multiple neonicotinoids may be detected in each surface or groundwater sample. Median, Maximum, and MDL concentrations are represented in ng/L.

<table>
<thead>
<tr>
<th>Neonicotinoid</th>
<th>MDL</th>
<th>Detects</th>
<th>Detection Frequency</th>
<th>Median</th>
<th>Max</th>
<th>Detects</th>
<th>Detection Frequency</th>
<th>Median</th>
<th>Max</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetamiprid</td>
<td>6.0</td>
<td>10</td>
<td>4%</td>
<td>6.0</td>
<td>&gt;12,000</td>
<td>0</td>
<td>0%</td>
<td>NA</td>
<td>ND</td>
</tr>
<tr>
<td>Clothianidin</td>
<td>6.5</td>
<td>30</td>
<td>12%</td>
<td>4.0</td>
<td>39</td>
<td>5</td>
<td>20%</td>
<td>34</td>
<td>110</td>
</tr>
<tr>
<td>Dinotefuran</td>
<td>6.8</td>
<td>44</td>
<td>18%</td>
<td>5.0</td>
<td>193</td>
<td>0</td>
<td>0%</td>
<td>NA</td>
<td>ND</td>
</tr>
<tr>
<td>Imidacloprid</td>
<td>7.4</td>
<td>112</td>
<td>45%</td>
<td>22.0</td>
<td>640</td>
<td>4</td>
<td>16%</td>
<td>30</td>
<td>350</td>
</tr>
<tr>
<td>Imidacloprid Urea</td>
<td>5.9</td>
<td>4</td>
<td>2%</td>
<td>18.5</td>
<td>29</td>
<td>0</td>
<td>0%</td>
<td>NA</td>
<td>ND</td>
</tr>
<tr>
<td>Nitenpyram</td>
<td>4.5</td>
<td>0</td>
<td>0%</td>
<td>NA</td>
<td>ND</td>
<td>0</td>
<td>0%</td>
<td>NA</td>
<td>ND</td>
</tr>
<tr>
<td>Thiacloprid</td>
<td>5.0</td>
<td>0</td>
<td>0%</td>
<td>NA</td>
<td>ND</td>
<td>0</td>
<td>0%</td>
<td>NA</td>
<td>ND</td>
</tr>
<tr>
<td>Thiamethoxam</td>
<td>6.2</td>
<td>28</td>
<td>11%</td>
<td>5.0</td>
<td>275</td>
<td>1</td>
<td>4%</td>
<td>NA</td>
<td>25</td>
</tr>
<tr>
<td>Combined Neonicotinoids</td>
<td>NA</td>
<td>133</td>
<td>53%</td>
<td>20</td>
<td>&gt;12,000</td>
<td>7</td>
<td>28%</td>
<td>34</td>
<td>462</td>
</tr>
</tbody>
</table>

*MDL= Quantitative method detection limit; ND=Non-Detect. NA= Not applicable*

Figure 2. Box plot of detected concentrations of the total neonicotinoids in surface water (the sum of all neonicotinoid concentrations in each sample) and the four most often detected neonicotinoids in surface water. Median concentrations of detected neonicotinoids (not including ND data) and overall detection frequency (as a percentage of total samples, n=250) is included with the parameter name. Boxes represent median and the first and third quartile concentrations of detected neonicotinoids in surface water. Whisker represents ± 1.5 times the interquartile range. Each dot above the upper whisker represents a statistical outlier.
Potential for Toxic Impacts and Associated Risk

The USEPA has recently updated individual neonicotinoid aquatic life benchmarks for both fish and aquatic invertebrates (Table 2) (USEPA, 2017). These benchmark values represent the acute and chronic concentrations below which pesticides are not expected to represent a risk of concern for aquatic life. Typically, the No Observed Adverse Effect Concentration (NOAEC) for a sensitive species is used to determine the benchmark. For example, the value of 10 ng/L is the EPA chronic aquatic life benchmark for imidacloprid. This value is the 28-day NOAEC for the mayfly species, *Caenis horaria*, exposed to imidacloprid (Roessink et al., 2013). EPA also recommends an imidacloprid acute toxicity benchmark for invertebrates of 385 ng/L (USEPA, 2017). Aquatic life benchmarks are a useful screening tool to determine if a waterbody should be investigated further for chemicals of concern, but do not necessarily indicate that adverse effects are occurring (USGS, 2019). Several of these benchmarks were exceeded based on the detected concentrations in the current study (Table 2) and may warrant site specific reviews to determine impacts. Imidacloprid exceeded the EPA chronic benchmark concentration for invertebrates in 86 surface water samples (from 60 of the 127 sites; 34 were over once and 26 were over both times sampled) (Figure 3), suggesting that there may be impacts to sensitive species if they are exposed to these concentrations for an extended period of time. Other benchmarks have been proposed by several sources, including Morrissey et al. (2015). Morrissey et al. conducted a robust literature review on neonicotinoid occurrence and toxicity spanning 12 invertebrate orders. Using probabilistic approaches (species sensitivity distributions), the authors recommended an acute ecological threshold of 200 ng/L and a chronic aquatic threshold of 35 ng/L for total neonicotinoid concentrations. These presented values are different than EPA’s due to differences in methodology.

<table>
<thead>
<tr>
<th>Source</th>
<th>Value (ng/L)</th>
<th>Number of Exceedances</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ace</td>
<td>Clo</td>
</tr>
<tr>
<td>USEPA Aquatic Life Benchmarks</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(USEPA, 2017)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acute</td>
<td>10,500</td>
<td>11,000</td>
</tr>
<tr>
<td>Chronic</td>
<td>2,100</td>
<td>50</td>
</tr>
<tr>
<td>Morrissey et al. (2015)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acute</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Chronic</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Ace = Acetamiprid; Clo = Clothianidin; Din = Dinofuran; Imd = Imidacloprid; Thx = Thiamethoxam; Tot = Total Neonicotinoids; "-" = Not applicable. *USEPA provides acute and chronic values of > 484,150,000 ng/L and > 95,300,000, respectively. Due to the uncertainty associated with these values they are omitted from the table.
Figure 3. Box plots of detected concentrations of Imidacloprid in surface water by month, with overall detection frequency and USEPA acute and chronic toxicity benchmarks for invertebrates also graphed. Boxes represent median and the first and third quartile concentrations of detected neonicotinoids in surface water. Whisker represents ± 1.5 times the interquartile range. Each dot represents a single measurement, and horizontal dots represent multiple measurements at that concentration. The orange line at 10 ng/L is the EPA chronic toxicity benchmark and the red line at 385 ng/L is the imidacloprid acute toxicity benchmark for aquatic invertebrates (USEPA, 2017).

Discussion

Neonicotinoid occurrence in this study is consistent with reported occurrence data from elsewhere in North America. Hladik et al. (2018) found at least one neonicotinoid in 74% of surface water samples from Great Lakes tributaries. Imidacloprid was their most commonly detected neonicotinoid (53% of samples) and was also the most prevalent neonicotinoid detected in the surface water samples of this study (45% of samples). This is not surprising considering imidacloprid is the most frequently detected and used neonicotinoid in New Jersey (NJDEP, n.d.) and North America, based on usage patterns compiled by USGS (n.d.a).

Median concentrations of neonicotinoids were also comparable to other studies. Median concentrations of the detected neonicotinoids in surface water ranged from 4 ng/L for clothianidin to 22 ng/L for imidacloprid in this study. Hladik et al. (2018) reported median concentrations of 2 - 27 ng/L for clothianidin and 2.2 - 10.3 ng/L for imidacloprid. The study by Hladik et al. evaluated medians based on watershed-wide sampling, providing a range of values. In another study by Hladik et al. (2014), clothianidin was detected in 75% (max: 257 ng/L; median: 8.2 ng/L) of stream samples from the Midwest associated with corn and soybean production. Other detection data from Hladik et al. (2014) included thiamethoxam (47% detection, max: 185 ng/L; median: <2 ng/L) and imidacloprid (23% detection, max: 42.7 ng/L; median: <2 ng/L).

Previously in New Jersey, USGS sampled for imidacloprid at two new sites in Bergen County as part of its Northeast Stream Quality Assessment. Imidacloprid was detected in nearly 90% of samples at both Saddle River at Ridgewood and a tributary of Ho-Ho-Kus Brook in 2016, with 30% of recorded values exceeding EPA’s chronic aquatic life benchmark value of 10 ng/L (USGS, n.d.b). These sites sampled suburban areas where lawn care is theorized to be the primary source of imidacloprid. Data from this 2016 study and the current study suggest that neonicotinoid use in New Jersey is resulting in stream levels high enough to negatively impact aquatic ecosystems.

Bradford et al. (2018) studied the presence of neonicotinoids in Central Wisconsin ground water and detected clothianidin most frequently in their study (13%), followed by imidacloprid (11%), and thiamethoxam (9%). In their study, Bradford et al. conducted more extensive sampling over a longer period of time (2011-2017) but results are similar to this study’s groundwater results in regard to detection frequency (clothianidin 20%, imidacloprid 16%, thiamethoxam 4%). Additional investigation into use patterns and environmental degradation is needed to understand the seemingly elevated prevalence of clothianidin in groundwater relative to other neonicotinoids.

Conclusions

Overall detection frequencies and concentrations of neonicotinoids from this New Jersey based sampling event appears consistent with other studies from North America. Imidacloprid concentrations exceeded EPA’s chronic aquatic life benchmark of 10 ng/L in 86 surface water samples (34% of the total) at 60 unique sites. These concentrations are high enough to warrant further investigation into how neonicotinoid exposure relates to other risk factors in the environment including other chemical stressors and habitat suitability. Repeated water sampling and assessments of the macroinvertebrate communities are critical to evaluate chronic risk
to sensitive organisms like the mayfly. Neonicotinoids are water soluble, and some degrade relatively rapidly compared to other pollutants of concern including other pesticides and traditional persistent, bioaccumulative, and toxic (PBT) compounds. Site-specific factors including the fate and transport of the active ingredient(s), what aquatic species are present (based on gradient and habitat type), and the potential mode of action (for toxicity) are all important to understand when evaluating the overall risk of these pesticides in New Jersey. The fate and transport of pesticides will vary due to changes in meteorological conditions, run-off characteristics, methods of application, and degradation rates of active ingredient in the environment (USEPA, 2004).

Future studies should include more frequent samples and focus on sites with a greater perceived risk, such as those with repeated exceedances of chronic benchmarks and high-quality habitats to determine if neonicotinoids are a driving risk factor to aquatic invertebrates in New Jersey.

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References


