APPENDIX 3-3. Clothianidin Open Literature Monitoring Data

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The following open literature information was available from the Preliminary Aquatic and Non-Pollinator Terrestrial Risk Assessment to Support Registration Review (USEPA, 2017) and addendum (USEPA, 2020), unless otherwise noted. Detected clothianidin concentrations in surface waters vary and are typically within an order of magnitude of the estimated environmental concentrations (EEC) modeled in this BE.

**Hladik *et al.* (2014)** investigated an area of intense corn and soybean production in the Midwestern United States to evaluate neonicotinoid presence in surface water. Study authors reported high agricultural use of neonicotinoids via both seed treatments and other forms of application occuring in this region. Water samples were collected from nine stream sites (eight in Iowa and one in Nebraska, basin areas spanning 521 to 836,000 km2) during the 2013 growing season (3/9/2013 to 11/1/2013). Reported clothianidin concentrations ranged from non-detect to 257 ng/L, with a median value of 8.2 ng/L (n=79, number of non-detects = 20). Clothianidin was detected at all nine sites sampled. Study authors reported temporal patterns in concentrations associated with rainfall events during crop planting, suggesting seed treatments as the likely source of the neonicotinoids.

According to **Raina-Fulton, R. (2016)**, neonicotinoids have been detected in 63% of the 48 streams sampled across the United States with clothianidin having a detection frequency of 24% (maximum 66 ng/L; Hladik *et al.* (2016). Clothianidin concentrations in surface water were positively correlated with land use in cultivated crops. Precipitation was identified as an important driver for neonicotinoid transport in the environment following periods of use (Hladik *et al.*, 2016). In maize producing counties of southwestern Ontario in Canada, 100% of 76 samples collected had clothianidin with mean concentrations of clothianidin at 2,280 (maximum 43,600; Schaafsma *et al.*, 2015). The highest concentrations in the field occurred in a puddle with a total concentration of neonicotinoid insecticides (clothianidin and thiamethoxam) of 44,380 ng/L as compared to outside the treated seed field in puddle, ditch and drain concentrations at 17,830, 12,250, and 6,210 ng/L; Schaafsma *et al.*, 2015). Total concentrations of neonicotinoids were 4.6 and 5.9 times higher in week 1-3 and 4-5 after planting with treated corn seed as compared to 1-2 weeks before planting and returned to similar concentrations of neonicotinoids to before planting by week 6-7; Schaafsma *et al.*, 2015). In water from Canadian prairie wetlands of central Saskatchewan (located within a region of high neonicotinoid seed treatment use for wheat and canola) the highest detection frequency (62%) and highest concentrations of neonicotinoids (maximum 3,110 ng/L, mean 76.8 ng/L) occurred in summer with clothianidin concentrations greater than those of thiamethoxam (Main *et al.*, 2015). Other areas with soil-applied neonicotinoids (thiamethoxam, clothianidin and imidacloprid) for potato production have detected thiamethoxam and clothianidin at 210 to 3,340 ng/L (average 620 ng/L) and 260-3,340 ng/L (average 790 ng/L) in ground water with the highest frequency of detection for thiamethoxam (during 2008-2012) suggesting high leaching potential(Huseth *et al.*, 2014). In addition, cycling of contaminated ground water due to use of high-capacity irrigation wells occurred.

**Struger *et al* (2017)** conducted a wide scale investigation of neonicotinoid insecticides used across the range of agricultural activities from fifteen surface water sites in southern Ontario. The fifteen sites consisted of nine streams near agricultural areas (drainage area <100 km2), and six larger streams/rivers (drainage area >100 km2). The stream sites reflected a range of agricultural activities including row crops, fruits and vegetables, orchards and grapes, greenhouses, ornamental nurseries, and turf. The sites also included an urban stream (Indian Creek) and a reference stream (Spring Creek) located adjacent to a national park removed from agricultural activities. All neonicotinoid insecticide concentrations in samples from Spring Creek were below the method detection limits (1.76 ng/L for clothianidin and 1.39 ng/L for thiamethoxam). Seventeen precipitation samples in total were collected between May and October 2013 at Bear Creek in southern Ontario. Bi-monthly integrated precipitation samples were collected using a MIC-B-wet-only automated precipitation sampler. Concentrations for clothianidin are presented in **Table 1**. Clothianidin concentrations ranged from non-detect to 399 ng/L in surface water. Neonicotinoids were rarely detected in precipitation at Bear Creek in 2013; most detections were during the period of 14-31 May 2013. The concentration in precipitation of clothianidin on May 14th, 2013 was 120 ng/L. The study authors speculated that the detections may have been the result of drift of dust generated during application on row crops or planting of treated seeds during the spring planting period, as the Bear Creek site is in proximity to the Lebo Drain and Sturgeon Creek stations, both of which are characterized by greater than 60% row crop agriculture. Using statistical analysis, study authors investigated the correlation of individual compounds with land use and assessed the relationship between neonicotinoid occurrence and hydrologic parameters in calibrated water courses. Of the five neonicotinoids studied, clothianidin and thiamethoxam exhibited detection rates above 90% at over half the sites sampled over a three-year period (2012-2014). For some watersheds, study authors found correlations between the occurrence of neonicotinoids and precipitation and/or stream discharge. Some watersheds exhibited seasonal maxima in concentrations of neonicotinoids in spring and fall, particularly for those areas where row crop agriculture is predominant; these seasonal patterns were absent in some areas characterized by a broad range of agricultural activities.

Table 1. Summary statistics for clothianidin measured in southwestern Ontario surface waters[[1]](#footnote-2)

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| **Site** | **N** | **N****(non-detect)** | **Median****(ng/L)** | **Mean****(ng/L)** | **Stdev** | **Detection Frequency (%)** | **Maximum****(ng/L)** |
| Twenty Mile Creek | 36 | 0 | 22.1 | 31.6 | 27.6 | 100.0% | 133 |
| Two Mile Creek | 42 | 28 | <1.76 | 13.8 | 63.3 | 33.3% | 399 |
| Four Mile Creek | 41 | 6 | 4.01 | 13.3 | 32.9 | 85.4% | 177 |
| Big Creek | 14 | 8 | <1.76 | 4.19 | 8.67 | 42.9% | 32.7 |
| West Holland River | 13 | 1 | 6.7 | 7.78 | 5.44 | 92.3% | 19.1 |
| Indian Creek | 35 | 27 | <1.76 | 2.65 | 1.75 | 22.9% | 9.07 |
| Innisfil Creek | 26 | 2 | 4.83 | 7.28 | 8.11 | 92.3% | 42.8 |
| Lebo Drain | 27 | 0 | 31.4 | 41.8 | 27.3 | 100.0% | 125 |
| Nissouri Creek | 12 | 0 | 11.6 | 22.8 | 27.6 | 100.0% | 104 |
| Nottawasaga River | 26 | 5 | 7.28 | 11.1 | 11.2 | 80.8% | 50.7 |
| Spring Creek | 18 | 18 | <1.76 | - | - | 0.0% | <1.76 |
| Sturgeon Creek | 39 | 8 | 3.81 | 5.17 | 5.05 | 79.5% | 27.7 |
| Sydenham River | 42 | 0 | 18 | 28.7 | 32 | 100.0% | 182 |
| Thames River | 30 | 0 | 11.7 | 17.5 | 16 | 100.0% | 61.1 |
| Prudhomme Creek | 39 | 2 | 7.66 | 22.3 | 32.6 | 94.9% | 132 |

In 2017, **Miles *et al****.* conducted field surveys to determine neonicotinoid concentrations in soil and water samples from multiple sites in Tippecanoe Co., Indiana. Study authors tested for acetamiprid, clothianidin, imidacloprid, and thiamethoxam in soil and water. The four sampled locations had an associated stream or ditch that served as a location for our water samples. One site was selected because it contained wetland areas that would allow assessment of neonicotinoid concentrations in lentic water bodies. Sampling was performed at each site two weeks prior to planting and weekly from two through eight weeks post-planting. Only water sampling was conducted at two of the sites. Clothianidin was detected in 81% of the soil samples (n = 32). The mean clothianidin concentration in soils across all sites and sampling periods was 24,200 ng/kg, with a maximum concentration across all sites and sample periods of 176,000 ng/kg. Peak concentrations tended to occur 4 weeks after planting. Clothianidin was detected in 96% of water samples (n = 48). The mean clothianidin concentration across all sites and sample periods was 100 ng/L, with a maximum concentration of 670 ng/L.

Since 2003, the **Washington State Departments of Agriculture and Ecology** (Tuttle G., 2014) have been conducting a multi-year monitoring program to characterize pesticide concentrations in selected salmon-bearing streams during the typical pesticide application season (March – September) in Washington. In 2014 monitoring was conducted in seven Water Resource Inventory Areas (WRIAs), five agricultural and two urban basins, for a total of 15 sample sites. Sampling was conducted weekly at most monitoring locations for 27 consecutive weeks, beginning the second week in March and continuing through to the second week in September. Surface water samples were collected by hand-compositing grab samples from quarter-point transects across each stream. In situations where streamflow was vertically integrated, a one-liter transfer container was used to dip and pour water from the stream into sample containers. Additionally, several conventional water quality parameters were measured: pH, conductivity, continuous temperature data (collected at 30-minute intervals), dissolved oxygen, and streamflow. Laboratory surrogate recovery, laboratory blanks, laboratory control samples (LCS), and laboratory control sample duplicates (LCSD) were analyzed as the laboratory component of QA/QC. Field blanks, field replicates, matrix spikes (MS), and matrix spike duplicates (MSD) integrated field and laboratory components. Sixteen percent of the field samples analyzed in 2014 were QA samples. In 2014, the program began to monitor for clothianidin (lower practical quantitation limit of 50 ng/L). None of the samples collected in 2014 contained detectable levels of clothianidin.

From 2012-2013**, Main *et al****.* evaluated the potential impact to ecologically significant wetlands in Canada’s major Prairie crop growing region from seed treatments of neonicotinoids. Study authors modelled the spatial distribution of neonicotinoid use across central Saskatchewan in combination with temporal assessments of water and sediment concentrations in wetlands to measure four active ingredients (clothianidin, thiamethoxam, imidacloprid and acetamiprid). From 2009 to 2012, neonicotinoid use increased from 7.7 million hectares to nearly 11 million hectares (44% of Prairie cropland) and from 150,000 kg to 216,000 kg of active ingredients. The dominant seed treatments by mass and area were thiamethoxam followed by clothianidin. Areas of high neonicotinoid use were identified as high-density canola or soybean production. Water sampled four times (spring, summer, fall 2012 and spring 2013) from 136 wetlands across four rural municipalities in Saskatchewan similarly revealed clothianidin and thiamethoxam in the majority of samples. A summary of the results is provided in **Table 2**. In spring 2012 prior to seeding, 36% of wetlands contained at least one neonicotinoid. Detections increased to 62% in summer 2012, declined to 16% in fall, and increased to 91% the following spring 2013 after ice-off. Peak concentrations were recorded during summer 2012 for both thiamethoxam (1490 ng/L, LOQ=1.8 ng/L) and clothianidin (3110 ng/L, LOQ=1.2 ng/L). Sediment samples collected during the same period rarely (6%) contained neonicotinoid concentrations (≤ 20 ng/L). Wetlands situated in barley, canola and oat fields consistently contained higher mean concentrations of neonicotinoids than in grasslands, but no individual crop singularly influenced overall detections or concentrations. Study authors concluded that frequently detected neonicotinoid concentrations in Prairie wetlands suggested high persistence and transport into wetlands.

In 2015 **Morrissey *et al****.* conducted a review to synthesize the current state of knowledge on the reported concentrations of neonicotinoids in surface waters from 29 studies in 9 countries world-wide. Neonicotinoids were detected in most surface waters sampled, including puddled water, irrigation channels, streams, rivers, and wetlands in proximity to, or receiving runoff from, agricultural cropland. Strong evidence exists that water-borne neonicotinoid exposures are frequent, long-term and at levels (geometric means = 130 ng/L (averages) and 630 ng/L (maxima)) which commonly exceed several existing water quality guidelines. Clothianidin was assessed in eight studies, six of which were conducted in the United States or Canada with dates ranging from 2008 to 2013. Reported detection limits ranged from 0.62 to 1,000 ng/L. Mean detected concentrations across the studies ranged from 4 to 4,600 ng/L, while maximum detected concentrations across the studies ranged from 225 to 55,700 ng/L. Reported detections ranged from 5-100% of the samples collected. In one study clothianidin was detected in ground water in Wisconsin at a maximum concentration of 3,430 ng/L and a mean concentration of 620 ng/L. A summary of the results is provided in **Table 3**. The highest concentrations in surface water resulted from the sampling of ponded water on fields in Quebec, Canada.

Table 2. Neonicotinoid concentrations in Canadian prairie wetlands

| **Season** | **Crop** | **Wetlands** | **Detection** | **Total Neonic. (ng/L)** | **Clothianidin (ng/L)** |
| --- | --- | --- | --- | --- | --- |
| **(n)** | **(%)** | **Mean** | **Max** | **Mean** | **Max** |
| Spring, 2012 (pre-seed) | Barley | 28 | 29 | 5.8 | 41.1 | 3.9 | 39.4 |
| Canola | 54 | 52 | 20.7 | 184 | 16.3 | 144 |
| Oats | 15 | 47 | 5.8 | 21.7 | 3.6 | 20 |
| Peas | 0 | NS | NS | NS | NS | NS |
| Wheat | 24 | 25 | 8.3 | 52.7 | 3.1 | 20.2 |
| Grassland | 15 | 7 | 1.1 | 7.9 | 1.1 | 7.9 |
| Overall | 136 | 36 | 8.3 | 184 |  | 144 (36%) |
| Summer, 2012 (growing) | Barley | 18 | 83 | 78.9 | 322 | 57.8 | 277 |
| Canola | 61 | 70 | 185 | 3110 | 142 | 3110 |
| Oats | 3 | 100 | 131 | 235 | 9.4 | 27 |
| Peas | 8 | 50 | 9.6 | 28.4 | 9.6 | 28.4 |
| Wheat | 29 | 62 | 53.5 | 524 | 35 | 518 |
| Grassland | 15 | 13 | 2.7 | 5.8 | 0.8 | 4.1 |
| Overall | 134 | 62 | 76.8 | 3110 |  | 3110 (51%) |
| Fall, 2012 (harvest) | Barley | 13 | 8 | 1.1 | 7 | 1.1 | 7 |
| Canola | 35 | 20 | 5.4 | 32.6 | 2 | 30.9 |
| Oats | 3 | 33 | 4.2 | 12 | ND | ND |
| Peas | 5 | 40 | 5.3 | 16 | ND | ND |
| Wheat | 15 | 0 | ND | ND | ND | ND |
| Grassland | 9 | 22 | 13.5 | 101 | ND | ND |
| Overall | 80 | 16 | 4 | 101 |  | 30.9 (5%) |
| Spring, 2013 (pre-seeding) | Barley | 16 | 94 | 74.9 | 212 | 53.2 | 157 |
| Canola | 51 | 98 | 53.1 | 178 | 38.5 | 173 |
| Oats | 3 | 100 | 60.7 | 102 | 16.9 | 20.4 |
| Peas | 6 | 100 | 33.3 | 60.6 | 33.3 | 60.6 |
| Wheat | 9 | 89 | 41.4 | 85.3 | 21.4 | 30.7 |
| Grassland | 5 | 0 | ND | ND | ND | ND |
| Overall | 90 | 91 | 52.7 | 212 |  | 173 (87%) |

Table 3. Summary of reported surface and ground water concentrations of clothianidin

| **Chemical** | **Year** | **Location** | **Water body** | **Land use** | **Detection Limit (μg/L)** | **Mean concentration (μg/L)** | **Max Concentration (μg/L)** | **Detections** | **Source reference** |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Clothianidin | 2012 | Quebec, Canada | Rivers | Agricultural (Corn and soybean) | NA | NA | 0.37 | NA | Giroux 2014 pers comm |
| Clothianidin | 2013 | Sydney, Australia | Rivers | Agricultural (vegetable and horticultural crops) | 0.017 | 0.06 ± 0.13 | 0.42 | 53% | Sanchez-Bayo and Hyne 2014 |
| Clothianidin | 2012-13 | Quebec, Canada | Ponded water on fields | Agricultural (corn)-during and post seeding | 1.0 | 4.6 | 55.7  | 92–100% | Samson-Roberts *et al*. (submitted)  |
| Clothianidin | 2012-13 | Saskatchewan, Canada | Prairie wetlands | Agricultural (canola, cereals, grasslands) | 0.0012 | 0.004 – 0.077\* | 3.1 | 5–87% | Main *et al.* 2014 |
| Clothianidin | 2009-10 | Osaka, Japan | Estuaries and rivers | Urban, rice upstream | 0.00062 | 0.0032 | 0.012 | 100% | Yamamoto *et al*. 2012 |
| Clothianidin | 2011-12 | Wisconsin | Leachate (irrigation water) | Agricultural (potato, row crops-irrigated) | 0.02 | 0.056 | 0.225 | NA | Huseth and Groves 2014 |
| Clothianidin | 2008-2012 | Wisconsin | Groundwater | Agricultural (potato, row crops) | NA | 0.62 | 3.43 | 25% | State of Wisconsin Dept. of Agriculture Trade and Consumer Protection (in Huseth and Groves 2014) |
| Clothianidin | 2013 | Iowa, USA | Rivers | Agricultural | 0.0062 | 0.008\*\* | 0.257 | 75% | Hladlik *et al.* 2014 |

NA: not available; ND: not detected \*Reported as total neonicotinoids. Author reports total as dominantly clothianidin and thiamethoxam.\*\*Reported as the median, below method detection limit

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1. Mean, Median, and Standard Deviation (Stdev) were estimated using the Kaplan-Meier method for censored datasets (Helsel 2012). [↑](#footnote-ref-2)