

Neonicotinoid Insecticides: State of Knowledge of Their Potential Impacts on Aquatic Organisms

The purpose of this fact sheet is to provide an overview of the characteristics of neonicotinoid insecticides registered in Canada, to describe their presence and fate in the St. Lawrence River and its tributaries, and to outline their toxicity in non-target aquatic organisms.

Neonicotinoid insecticides were discovered in the 1980s and were introduced into the market a decade later. Since then, their use has become extremely widespread around the world, notably in response to the increasing resistance of insect pests to traditional insecticides such as organophosphates, carbamates and pyrethroids. Neonicotinoids are systemic insecticides that, unlike insecticides that remain on the surface of treated foliage, are absorbed by the plant and transported throughout its tissues, including the foliage, stems, roots, flowers, pollen and fruit. The parent compounds of neonicotinoids and their metabolites circulate in the plant's tissues, protecting the plant from numerous insect pests (Bonmatin et al. 2015). When an insect pest comes into contact with the insecticide or ingests part of the treated plant, the neonicotinoid acts on its central nervous system (Bonmatin et al. 2015), quickly leading to paralysis and subsequently its death.

Due to their broad spectrum of action, neonicotinoids can affect not only insect pests but also non-target organisms such as bees. Non-target organisms can be exposed to these insecticides by direct contact with contaminated dust or with the insecticide itself on vegetation, or by ingesting a plant that has absorbed the insecticide.

Given their persistence in soils, high solubility in water and low lipophilicity (affinity for lipids), neonicotinoids are likely to be found in runoff and to be transferred from agricultural fields to aquatic environments (Figure 1). Consequently, non-target aquatic organisms may be susceptible to exposure to these pesticides. The presence of neonicotinoids in aquatic environments could therefore represent a risk to the health of these ecosystems.

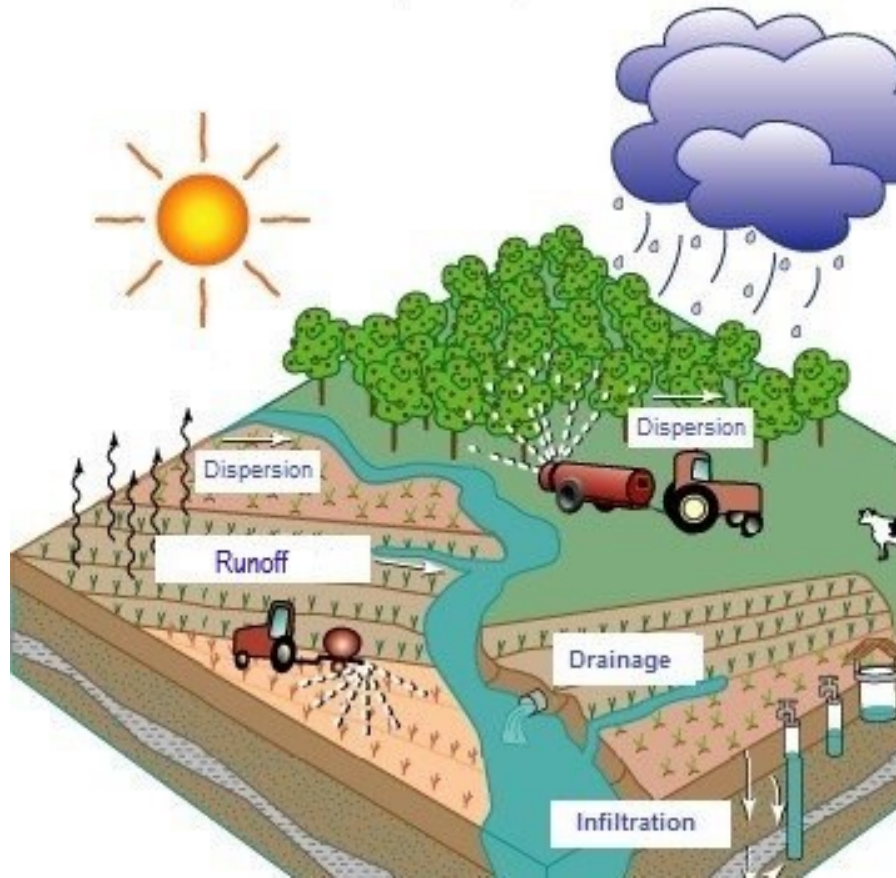


Figure 1– Fate of pesticides in the environment

The main neonicotinoids

Imidacloprid was one of the earliest neonicotinoids to be synthesized. It was first registered for use in the United States in 1992 and in Canada in 1995. Imidacloprid was initially marketed to control the Colorado potato beetle (Anderson et al. 2015), and has since been used in foliar and soil drench applications to fight insect pests of tomatoes, potatoes, field lettuce and a number of greenhouse plants. Imidacloprid is also effective against sucking insects, whiteflies, termites and turfgrass insects and is used as a seed coating for mustard, canola, corn, rapeseed and soybean crops.

Thiamethoxam and clothianidin were registered in Canada in 2000 and 2003, respectively (Uneme 2011). They are used as seed treatments, mainly for corn and soybeans. They are also registered for use in spray form on a wide variety of crops. In the case of clothianidin, different formulations are employed as seed coatings or to control insect pests of pome and stone fruits, potatoes and turfgrass. Various thiamethoxam formulations are used to curb lawn grub beetles, notably the European chafer, June beetle, masked chafer and the Japanese beetle.

Thiacloprid was essentially developed to control aphids and whiteflies. Acetamiprid is also used to control these sucking insects on leafy vegetables, cole crops, citrus fruits, cotton and ornamental plants.

Although nitenpyram is sometimes used on crops, its main application is controlling external parasites of livestock and pets in veterinary medicine.

Physico-chemical characteristics

Insecticides in the neonicotinoid family have low volatility (cf. vapour pressure in Table 1) and, consequently, may only be present in gaseous state for a brief period after spraying. Neonicotinoid insecticides range from soluble to very soluble in water, depending on the pH, water temperature, and the formulation of the insecticide when applied. Neonicotinoids are only slightly lipophilic, if at all (K_{ow} ¹, Table 1). Owing to these properties, neonicotinoids tend to be highly mobile in the environment.

Table 1 – Selected physico-chemical properties of neonicotinoids

	Molecular weight (g/mol)	Vapour pressure (mmHg at 25°C)	Solubility (mg/l)	log K_{ow}	log K_{oc}
Acetamiprid	222.7	4.4×10^{-5}	2,950 – 4,200	0.80	2.12 – 2.43
Clothianidin	249.7	9.8×10^{-10}	340	0.91	1.78
Imidacloprid	255.7	3.0×10^{-12}	510	0.57	2.19 – 2.90
Nitenpyram	270.7	8.2×10^{-12}	590,000	- 0.66	3.92
Thiacloprid	252.7	6.0×10^{-12}	184	1.26	3.67
Thiamethoxam	291.7	4.95×10^{-11}	4,100	- 0.13	1.84

Sources: Carbo et al. 2008, PPDB 2012, Morrissey et al. 2015, Jeschke et al. 2011

Fate in soil

In soils, neonicotinoids tend to bind to organic matter and clay particles (Bonmatin et al. 2015, Liu et al. 2002, Anderson et al. 2015) and to persist for several months or even several years after application. Researchers have measured neonicotinoids in soils one or two years after coated seeds were planted (Bonmatin et al. 2015, Gupta and Gajbhiye 2007). It should be noted that metabolites or degradation products may compete with neonicotinoids for adsorption on organic matter or clay, enhancing mobility of neonicotinoids (Liu et al. 2002). Neonicotinoid residues from the previous year were detected in spring in runoff and tile drain water samples on the edge of corn fields in Saint-Samuel, Quebec (Chrétien et al. 2017).

¹ K_{ow} = octanol-water partition coefficient. It provides an indication of a compound's hydrophilic or hydrophobic (lipophilic) nature. A very high value for log K_{ow} indicates greater solubility in octanol than in water, reflecting its lipophilic nature. Conversely, a low value for log K_{ow} signifies that the compound is hydrophilic.

Half-life in soils

The rate of degradation of each pesticide can be expressed by its half-life (DT_{50}). At the end of this period, half of the initial quantity of the pesticide remains in place, while the other half has been eliminated through various degradation processes, which can involve biological organisms (bacteria, fungi) as well as physico-chemical processes (light, temperature).

The half-lives of neonicotinoids in soil varies considerably among pesticides and among studies and depends on many factors, such as soil texture, the presence of organic matter, pH, the incidence of UV rays, temperature and soil water content. The cold soil temperatures frequently encountered in Canada are associated with longer half-lives (Main et al. 2014). Similarly, dry conditions are associated with a significantly longer half-life for acetamiprid (Gupta and Gajbhiye 2007).

Substance	Half-life in soil (days)
Acetamiprid	2 to 450
Clothianidin	13 to 6,931
Imidacloprid	27 to 1,250
Nitenpyram	1 to 15
Thiacloprid	3 to over 1,000
Thiamethoxam	7 to 335

Sources: Morrissey et al. 2015, Cloyd and Bethke 2011, Goulson 2013, Main et al. 2014

Given their persistence and half-life in soils, neonicotinoids have a high potential to be transferred to surface water and groundwater. Clothianidin, imidacloprid and thiamethoxam are classified as having high leaching potential and nitenpyram as having possible leaching potential (Pesticide Properties Data Base 2012). However, acetamiprid, nitenpyram and thiacloprid break down more easily in the soil, thus reducing their risk of being transferred to aquatic environments.

Fate in water

The fate of neonicotinoids in aquatic environments depends on many environmental factors (e.g., water pH and temperature, presence and composition of organic matter, and incidence of UV rays) and physical, chemical and biological processes (e.g., dissolution, photodegradation, adsorption on organic matter, sedimentation, and biodegradation). Hydrolysis appears to play a minor role in the fate of neonicotinoids in surface water, while photodegradation plays a major role, except for acetamiprid and thiacloprid (Bonmatin et al. 2015, PPDB 2012). It should be noted that the extent of photodegradation depends on many factors (e.g., wavelength and water penetration of solar radiation, water turbidity) and can therefore vary depending on the environment.

Furthermore, these substances tend to bind to organic matter and clay particles (Bonmatin et al. 2015), allowing them to settle and accumulate in sediments. Their half-life in sediments ranges from 28 days (thiacloprid) to 130 days (imidacloprid; PPDB 2012).

Environmental concentrations

In Quebec, neonicotinoids have been systematically monitored since 2012. A permanent pesticide monitoring network consisting of 10 stations, along with rotating surveys in certain rivers, was established to determine changes in pesticide concentrations in St. Lawrence tributaries located near target crops. Between 2015 and 2017, clothianidin was detected in an average of 91% of 360 surface-water samples, while thiamethoxam was found in 98% of the samples; the samples were taken from four streams draining agricultural areas dominated by corn and soybean cultivation. Levels of both clothianidin and thiamethoxam exceeded the chronic aquatic life criterion (CALC; 0.0083 µg/l) (see box below) in 91% and 90% of samples, respectively (Giroux 2019). Neonicotinoids were also detected in streams in areas where vegetable crops (Giroux 2017) and potatoes (MELCC 2020) are grown, as well as in areas with orchards (Giroux 2017). Nearly 100% of samples taken from streams in potato- and vegetable-growing areas were found to contain clothianidin, thiamethoxam and imidacloprid. Levels of these neonicotinoids exceeded the CALC value in over 94% of samples in vegetable-growing areas and in over 70% of samples in potato-growing areas. In streams in areas with orchards, neonicotinoids were detected in 10% to 60% of samples, exceeding the CALC value in 8% to 44% of samples. During monitoring in Lake Saint-Pierre in 2014 and 2015, thiamethoxam was detected in 67% to 100% of water samples and clothianidin was detected in 33% to 90% of samples, varying by station and year (Giroux 2018). Among the Lake Saint-Pierre samples, 10% to 55% had thiamethoxam levels exceeding the CALC value, and 10% to 44% had clothianidin levels exceeding the CALC value. Neonicotinoids have also been detected in groundwater in Quebec, particularly in individual wells in potato-growing areas (Giroux and Sarrasin 2011). Neonicotinoid pesticides were detected in over 50% of wells sampled near potato fields. The maximum concentrations measured were 6.1 µg/L for imidacloprid, 2.5 µg/L for thiamethoxam and 1.6 µg/L for clothianidin (MELCC 2020, Giroux and Sarrasin 2011).

According to data from the literature, high concentrations of neonicotinoids have been measured in surface water samples collected near treated fields and from adjacent ditches. Significantly higher concentrations are found immediately after application, but the compounds can still be detected for weeks following their use.

Criteria for the protection of aquatic life

The Canadian Council of Ministers of the Environment (CCME) has developed guidelines for certain neonicotinoids, as has the Ministère de l'Environnement et de la Lutte contre les changements climatiques (MELCC). To protect all aquatic organisms in an ecosystem, thresholds are established on the basis of sublethal effects recorded in the most sensitive group of organisms. It should be noted that the CCME is currently reviewing these guidelines to take account of the results of scientific studies conducted since 2007.

Substance	CALC ^{1,2} (µg/L)	CWQG ³ freshwater (µg/L)	CWQG ³ saltwater (µg/L) ²
Acetamiprid	-	-. ⁵	-
Clothianidin	0.0083	-. ⁵	-
Imidacloprid	0.0083	0.23 ^{4,5}	0.65 ^{4,5}
Nitenpyram	-	-. ⁵	-
Thiacloprid	-	-. ⁵	-
Thiamethoxam	0.0083	-. ⁵	-

Sources: MELCC 2019, CCME 2007

¹: Aquatic life protection criteria (chronic effects) adopted by MELCC

²: These criteria apply to the combined levels of the following neonicotinoids: clothianidin, imidacloprid and thiamethoxam.

³: Canadian Water Quality Guidelines for the Protection of Aquatic Life

⁴: Draft recommendations

⁵: Recommendations under development / review

Toxicity to aquatic organisms

To our knowledge, no studies have been conducted that specifically evaluate the toxicity to aquatic organisms of neonicotinoids in the St. Lawrence River and its tributaries. However, the effects of imidacloprid on aquatic invertebrates have been extensively studied around the world, which is not the case for the other neonicotinoids. The information available is summarized in the following sections.

Aquatic plants and algae

According to the available data, the neonicotinoids found in the St. Lawrence River and its tributaries are not present in sufficient concentrations to affect the growth of exposed aquatic plant species. Median effective concentrations (EC₅₀) of between 106 mg/L and 740 mg/L have been measured in aquatic plants and algal communities exposed to imidacloprid (Tisler et al. 2009, SERA 2015). Concentrations range from 10 mg/L to > 121 mg/L for clothianidin (DeCant and Barrett 2010), from 45 mg/L to 60.6 mg/L for thiacloprid (EPA 1992), over 90 mg/L for thiamethoxam (EPA 1992) and over 1 mg/L for acetamiprid (EPA 1992).

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Aquatic invertebrates

According to most of the available studies, aquatic invertebrates are particularly sensitive to neonicotinoids at concentrations representative of those found in the St. Lawrence River, although sensitivity can vary among taxon, as well as within taxa.

Among the species evaluated, mayflies and caddisflies (Figure 2) were the most sensitive, for all effects combined. Indeed, the sensitivity of these insects was several orders of magnitude greater than that of species commonly used for standard toxicity tests, such as the water flea (daphnid) *Daphnia magna*. In the mayfly *Baetis rhodani*, the concentration lethal to 50% of organisms exposed to imidacloprid over a 48-hour period (LC₅₀ 48 h) was only 8.49 µg/L, compared to 7,000 µg/L for *D. magna* (Beketov and Liess 2008a).

The importance of mayflies and caddisflies

Mayflies and caddisflies are two extremely important groups of invertebrates in freshwater ecosystems, with aquatic larval stages that live and forage in rivers, ponds and ditches. Immature mayflies feed on detritus, diatoms and algae, making them invaluable decomposer organisms in aquatic systems. In addition, mayflies and caddisflies serve as prey species for many species of fish, birds, bats, reptiles and amphibians. Consequently, any disturbance to their populations can affect the food resources of their predators.



Figure 2 – Larval and adult stages of caddisfly (a) and mayfly (b)

Indeed, neonicotinoid exposure can cause mortality in many species of aquatic invertebrates, at concentrations that vary greatly among species and according to the organism's development stage (larva vs. juvenile vs. adult; Osterberg et al. 2012). Along with these acute effects, various sublethal effects have also been documented in aquatic invertebrates exposed to neonicotinoids.

For example, a decrease in feeding rates has been demonstrated in invertebrates exposed to varying concentrations of neonicotinoids. This phenomenon has been documented in stoneflies in the family Pteronarcyidae and in larval crane flies in the family Tipulidae exposed to 12 µg/L of imidacloprid in the water (Kreutzweiser et al. 2008). For comparison purposes, this concentration is lower than the concentration causing mortality in these species, i.e., 130 µg/L (Kreutzweiser et al. 2008). Note that exposed individuals may continue to exhibit feeding inhibition even after the end of exposure (Alexander et al. 2007).

Neonicotinoid exposure can also reduce the reproductive success of aquatic invertebrates, which can ultimately lead to population declines. For example, a decline in the density of nymphs of mayflies in the genera *Epeorus* and *Baetis* was observed following chronic exposure (20 days) to 0.8 µg/L of imidacloprid (Alexander et al. 2008). In that study, no *Epeorus* sp. male emergence occurred at imidacloprid concentrations of 0.25 µg/L and 0.8 µg/L (Alexander et al. 2008).

Indirect toxic effects can also be observed in species that feed on aquatic invertebrates, since neonicotinoids can have an impact on prey abundance. Several studies have demonstrated that imidacloprid exposure can affect the growth and development of medaka (*Oryzias latipes*), a freshwater fish, in its natural environment, by indirectly affecting the insect populations on which the juveniles feed (Hayasaka et al. 2012, Sanchez-Bayo and Goka 2005). Although the concentrations measured in these studies were probably too low (\approx 0.001 mg/L to 0.05 mg/L) to have a direct toxic effect on medaka, they were high enough to reduce the abundance of its prey. Consequently, neonicotinoids could have broader impacts on aquatic food webs.

Lastly, avoidance behaviour is a common reaction by aquatic invertebrates to disturbances in their environment according to some studies. In the case of neonicotinoids, a study has documented downstream drift (i.e., the movement of organisms) in mayflies (*Baetis rhodani*), amphipods (*Gammarus pulex*) and black flies (*Simulium latigonium*) within two hours after exposure to imidacloprid, thiacloprid and acetamiprid, at all concentrations tested (Beketov and Liess 2008b). Imidacloprid exposure initiated drift in *Baetis rhodani* at concentrations equal to or greater than 1 µg/L. Another study has shown that benthic organisms may avoid sediments contaminated with neonicotinoids. Sardo and Soares (2010) demonstrated that the oligochaete *Lumbriculus variegatus* avoided sediments contaminated with imidacloprid at concentrations ranging from 0.05 mg/kg to 5.0 mg/kg. Although this type of behaviour may protect the individual organism, it can disrupt the population structure and ecological functions of the community.

Aquatic vertebrates

At relatively high concentrations, neonicotinoids can induce mortality in fish. Concentrations causing mortality in 50% of fish exposed during a 96-hour period (LC₅₀ 96 h) ranged from 83 mg/L to 236 mg/L for imidacloprid (Wang et al. 2017, Tisler et al. 2009, EPA 2012, SERA 2015), from 19.7 mg/L to over 104 mg/L for thiacloprid (EPA 1992), over 94 mg/L for clothianidin (DeCant and Barret 2010) and over 100 mg/L for thiamethoxam and acetamiprid (EPA 1992, Wang et al. 2018). According to the available data, neonicotinoid concentrations measured in the St. Lawrence River and its tributaries are well below these lethal concentrations.

As in aquatic invertebrates, sublethal effects have been observed in fish exposed to neonicotinoids at concentrations representative of those in the St. Lawrence River and its tributaries. Therefore, there is a potential for indirect effects in fish and amphibians associated with reduced numbers of prey (i.e., aquatic invertebrates). Direct sublethal effects have also been noted in aquatic vertebrates. For example, imidacloprid may increase oxidative stress in the zebrafish (*Danio rerio*), in turn reducing antioxidant enzyme activity. In addition, significant DNA damage has been reported with increased imidacloprid concentrations (Ge et al. 2015). According to some studies, the physiological stress observed in fish exposed to neonicotinoids could make them more

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susceptible to parasites. For example, Sanchez-Bayo and Goka (2005) demonstrated that imidacloprid exposure increases the risk of a massive infestation by a *Trichodina* ectoparasite in medaka near fields treated with this neonicotinoid.

Few studies have been conducted on neonicotinoid toxicity to amphibians. The only neonicotinoid for which median lethal concentrations are known in amphibians is imidacloprid, with LC₅₀ values ranging between 52 mg/L and 468 mg/L (Howard et al. 2003, Perez-Iglesias et al. 2014, Ruiz de Arcaute et al. 2014, Feng et al. 2004). Information on sublethal effects in amphibians is also limited. For example, Robinson et al. (2017) reported no significant effects on the size or body mass of wood frogs (*Lithobates sylvaticus*) exposed to different concentrations (up to 0.1 mg/L) of imidacloprid and thiamethoxam.

Conclusions

According to the studies consulted, neonicotinoids can persist in soils and can contaminate surface water and groundwater through transfer by runoff or percolation.

Despite limited data on some of these substances, the information compiled demonstrates that the neonicotinoids found in the St. Lawrence River and its tributaries could pose a risk to exposed aquatic organisms, particularly those that are highly sensitive to environmental concentrations of these substances. There are certain lines of research that could be pursued to further our understanding of neonicotinoids. For example:

- Few in-depth studies have been conducted on the sublethal and long-term effects of neonicotinoids, or their degradation products and metabolites, on aquatic organisms.
- Although the available data show that vertebrate communities are not significantly affected by exposure to neonicotinoids, there are few studies on their effects on larval and egg development or their multigenerational effects on vertebrates.
- Very few studies have evaluated the additive or synergistic effects of simultaneous exposure to several neonicotinoid at representative environmental concentrations. However, many non-target species are simultaneously exposed to neonicotinoids, as well as to other pesticides and contaminants present in the environment.
- To our knowledge, there have been no studies on the resilience of exposed aquatic organisms (i.e., on how aquatic communities recover following exposure to neonicotinoids).

The information compiled in this fact sheet demonstrates the importance of the continued monitoring of neonicotinoids in the aquatic environment (as MELCC is currently doing), both in their pure and metabolized forms. Non-target organisms exposed to neonicotinoids will also be monitored using integrative tools and methods when available (e.g., assessment of the health of benthic communities and toxicity tests using environmental water samples). The direct use of these tools in the field will allow the health of aquatic communities in agricultural watersheds to be evaluated.

Lastly, under the St. Lawrence Action Plan (SLAP), MELCC and Environment and Climate Change Canada (ECCC), have implemented knowledge acquisition projects to better define the risks associated with these pesticides, with the following objectives:

- Test the use of biomarkers of sublethal effects in conjunction with the measurement of pesticides and physico-chemical parameters in watercourses in watersheds that are the target of collaborative initiatives to improve agricultural practices;
- Evaluate the benefits of the implementation of new practices on the health of aquatic species by measuring biomarkers of sublethal effects in in-situ caged invertebrates and by conducting water toxicity tests in the laboratory;
- Study in vivo the effects of pesticides of interest on the biology of aquatic invertebrates, algae, plants, and fish, notably by exposing organisms to environmental concentrations of pesticides, individually and in combination, and by evaluating the sublethal effects linked to chronic pesticide exposure.

Since March 2018, MELCC has required prior agronomic justification and agronomic prescriptions for the purchase and application of neonicotinoids. These requirements apply to all types of uses, included coated seeds. In the urban environment, the sale and application of neonicotinoids for lawn maintenance purposes is prohibited, except for golf courses. These regulatory changes should help reduce the use of neonicotinoids, since they are now banned in urban environments and will only be used in agricultural environments when absolutely necessary. These measures will limit the exposure of non-target organisms, including pollinators and aquatic organisms, to neonicotinoids.

For more details on the new requirements on the use of neonicotinoids, see the web page on pesticide management practices, including the Pesticide Management Code: [Pesticides \(gouv.qc.ca\)](http://Pesticides(gouv.qc.ca)).

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