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Review

# Neonicotinoid contamination of global surface waters and associated risk to aquatic invertebrates: A review

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## ABSTRACT

Neonicotinoids, broad-spectrum systemic insecticides, are the fastest growing class of insecticides worldwide and are now registered for use on hundreds of field crops in over 120 different countries. The environmental profile of this class of pesticides indicate that they are persistent, have high leaching and runoff potential, and are highly toxic to a wide range of invertebrates. Therefore, neonicotinoids represent a significant risk to surface waters and the diverse aquatic and terrestrial fauna that these ecosystems support. This review synthesizes the current state of knowledge on the reported concentrations of neonicotinoids in surface waters from 29 studies in 9 countries world-wide in tandem with published data on their acute and chronic toxicity to 49 species of aquatic insects and crustaceans spanning 12 invertebrate orders. Strong evidence exists that water-borne neonicotinoid exposures are frequent, long-term and at levels (geometric means = 0.13 μg/L (averages) and 0.63 μg/L (maxima)) which commonly exceed several existing water quality guidelines. Imidacloprid is by far the most widely studied neonicotinoid (66% of the 214 toxicity tests reviewed) with differences in sensitivity among aquatic invertebrate species ranging several orders of magnitude; other neonicotinoids display analogous modes of action and similar toxicities, although comparative data are limited. Of the species evaluated, insects belonging to the orders Ephemeroptera, Trichoptera and Diptera appear to be the most sensitive, while those of Crustacea (although not universally so) are less sensitive. In particular, the standard test species *Daphnia magna* appears to be very tolerant, with 24–96 hour $LC_{50}$ values exceeding 100,000 μg/L (geometric mean > 44,000 μg/L), which is at least 2–3 orders of magnitude higher than the geometric mean of all other invertebrate species tested. Overall, neonicotinoids can exert adverse effects on survival, growth, emergence, mobility, and behavior of many sensitive aquatic invertebrate taxa at concentrations at or below 1 μg/L under acute exposure and 0.1 μg/L for chronic exposure. Using probabilistic approaches (species sensitivity distributions), we recommend here that ecological thresholds for neonicotinoid water concentrations need to be below 0.2 μg/L (short-term acute) or 0.035 μg/L (long-term chronic) to avoid lasting effects on aquatic invertebrate communities. The application of safety factors may still be warranted considering potential issues of slow recovery, additive or synergistic effects and multiple stressors that can occur in the field. Our analysis revealed that 81% (22/27) and 74% (14/19) of global surface water studies reporting maximum and average individual neonicotinoid concentrations respectively, exceeded these thresholds of 0.2 and 0.035 μg/L. Therefore, it appears that environmentally relevant concentrations of neonicotinoids in surface waters worldwide are well within the range where both short- and long-term impacts on aquatic invertebrate species are possible over broad spatial scales.

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**Contents**

## 1. Introduction

### 1.1. Background on neonicotinoids

Neonicotinoids belong to the group of nitroguanidine systemic insecticides frequently applied to crops as soil and seed treatments at planting to protect seedlings from early-season root and leaf-feeding pests, as well as via later season foliar treatments. Imidacloprid-containing products now dominate the insecticide market and are registered for use on more than 140 different crops in 120 countries (Jeschke and Nauen, 2008). The neonicotinoid class of insecticides was first developed and registered in the early 1990s, partly in response to ongoing pest resistance, concerns over cumulative exposure from organophosphorous and carbamate insecticides, and increasing evidence linking impaired neural development in children to cholinesterase-inhibiting insecticides (Eskenazi et al., 1999). Following on the industry success of imidacloprid, development and sale of other neonicotinoid insecticides with similar chemistries rapidly followed after 2000, specifically acetamiprid, clothianidin, dinotefuran, nitenpyram, thiacloprid and thiamethoxam among others, under various trade names. Neonicotinoids now represent the largest selling class of insecticide and seed treatments on the global market (Jeschke et al., 2010).

Due to their systemic activity, improved rain fastness, and convenience of use as a seed treatment, neonicotinoids are extremely popular for pest control on a broad range of crops (Elbert et al., 2008; Main et al., 2014; USGS, 2012). However, they exhibit chemical properties that enhance environmental persistence and susceptibility to transport into aquatic ecosystems through runoff and drainage of agricultural areas (Armbrust and Peeler, 2002). Recent reports suggest toxic residues of imidacloprid and other neonicotinoids have been detected in water bodies and researchers in the Netherlands have found correlative links to reduced aquatic insect populations (Van Dijk et al., 2013) and insectivorous farmland birds (Hallmann et al., 2014). However, in most countries there is a general lack of systematic environmental monitoring data for neonicotinoids in surface waters and until recently, analytical procedures were often insufficient to report the low concentrations known to cause harm to aquatic invertebrates.

Neonicotinoids are successful insecticides largely because the acute toxicity to mammals is lower than its replacements, they are extremely toxic to most insect pests and can be conveniently used as a systemic seed or in furrow treatment to protect seedling crops from piercing-sucking and chewing insects. All neonicotinoids bind agonistically to the post-synaptic nicotinic acetylcholine receptors (nAChR) in the invertebrate central nervous system, thus competing with the natural neurotransmitter acetylcholine (ACh). Toxicity studies with arthropods suggest that the binding to these receptors is long-lasting (Tennekes, 2010a), and lethal effects are typically delayed (Beketov and Liess, 2008a) such that repeated or chronic exposure can lead to cumulative effects over time (Tennekes and Sánchez-Bayo, 2013). For many aquatic invertebrates with long larval aquatic stages, exposure to neonicotinoids is expected to be prolonged due to either repeated pulse events and/or low level chronic exposures. Many invertebrates are extremely sensitive to these compounds, including non-target aquatic species (Alexander et al., 2007; Beketov and Liess, 2008a; EFSA, 2013; Liess and Beketov, 2011; Pestana et al., 2009; Roessink et al., 2013; Sánchez-Bayo and Goka, 2006; Stoughton et al., 2008) and terrestrial pollinators such as bumble bees and honey bees (Decourtye and Devillers, 2010; Sanchez-Bayo and Goka, 2014; Whitehorn et al., 2012). Consequently, the persistence and movement of neonicotinoids into aquatic ecosystems could pose a risk to sensitive aquatic invertebrates upon which vertebrate wildlife depend for food (Gibbons et al., 2014; Goulson, 2013; Tennekes, 2010b). The objective of this review is to summarize the available data on different neonicotinoid concentrations in surface waters worldwide and to cohesively synthesize and compare these values to the growing body of data from laboratory, field and mesocosm studies on the concentrations observed to cause lethal and sub-lethal toxicity to aquatic invertebrates. Finally, based on probabilistic analyses, we provide recommended aquatic invertebrate effect thresholds to aid in the development of appropriate water quality reference values for the range of neonicotinoids.

### 1.2. Chemical properties and environmental fate

All neonicotinoids exhibit high water solubility that makes them amenable for use as systemic insecticides. In addition, they also have long half-lives in soil and in water, where they are resistant to hydrolysis at neutral or acidic pH and under anaerobic conditions; although some of them are subject to rapid photodegradation under favorable conditions (i.e. shallow waters with greater light penetration; Table 1). Their chemical properties, particularly their high water solubility and partitioning properties (low log $K_{OW}$) and low soil adsorption (log $K_{OC}$), promote movement of these insecticides through surface and subsurface runoff (CCME, 2007; EFSA, 2008) and result in extended persistence under simulated environmental conditions (Tisler et al., 2009). Local environmental conditions can modify the persistence of neonicotinoids in water (e.g., increasing pH and turbidity enhances persistence) (Sarkar et al., 2001). The major transport routes to aquatic ecosystems include surface runoff after rain events (Armbrust and Peeler, 2002), soluble or insoluble fractions transported via snowmelt (Main et al., 2014), leaching into groundwater (Lamers et al., 2011) with associated subsurface discharge into wetlands and other surface waters (PMRA, 2001), talc and graphite dust associated with seeding drills at the time of planting (Krupke et al., 2012; Nuyttens et al., 2013), decay of systemically treated plants in water bodies (Kreutzweiser et al., 2008), and deposition of