



NEONICOTINOIDS AND WATER: Nature drowned in pesticides



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A. The risks to aquatic organisms and their definition in environmental quality standards

A.a. Impact of Imidacloprid on aquatic organisms.

A group of Australian-German-Canadian researchers from the public and private sectors collected and published in 2014 data on Neonicotinoid (NN) concentrations recorded in surface waters, as well as data on their impact on non-targeted aquatic invertebrates.

From the data of 29 separate studies, carried out in 9 countries, emerges a ubiquitous contamination of aquatic environments from NN. In about 50% of cases, Imidacloprid (IMI) shows the highest detection frequency rate compared to all NN substances.

Compared to all the NN concentration measurements, in all the studies, researchers calculated that the geometric mean of the individual averages, both of 130 ng / l, and the maximum of 630 ng / l. To characterize the impact of NN, the authors are based on 214 studies, covering a total of 49 aquatic species (insects and crustaceans / 12 orders of invertebrates).

IMI is involved in 66% of these studies.

Using a probabilistic (SSD) approach, the authors recommend NN contamination threshold values not exceeding 35 ng / l in the annual average and 200 ng / l in the pollution peak, to avoid long-lasting effects on various aquatic species. In all the aforementioned 29 monitoring studies, these thresholds are exceeded in 74% and 81% of cases respectively.



Morrissey, C.A. et al. (2014). *Neonicotinoid contamination of global surface waters and associated risk to aquatic invertebrates: A review.* Environment International 74 (2015) 291–303

From a recent meta-analysis based on environmental contamination data collected in 11 countries: the average of the measured presence of IMI is 730 ng / l, the maximum value stands at 320,000 ng / l.

Compared to the acute toxicity data for aquatic organisms (LD50), the SSD / LD50 distribution - adapted by the authors in the light of their bibliographic references - shows that, for example in two states (Sweden and Maryland in the USA), contamination causes an environmental damage affecting a little more than 40% of aquatic organisms, particularly insects and crustaceans. (LD50 = following exposure to the toxic, death of half the population of the species concerned).

The authors conclude that the decline of many invertebrate populations is likely to irreversibly influence the structure and function of aquatic ecosystems. And even beyond, since terrestrial vertebrates and amphibians feed mainly on insects and other aquatic invertebrates, they too are already affected by it. The authors launch a heartfelt appeal, unheard to date, so that the contamination of aquatic environments from NN is considered adequately and that it stops basing the aquatic eco-toxicology on erroneous and / or archaic precepts, of which the dossiers for authorisations (Marketing Authorisations) of pesticides abound.

Other publications warn about the consequences of the decline of some aquatic species in various ecosystems.



Sánchez-Bayo, F.; Goka, K. and Hayasaka, D. (2016) *Contamination of the Aquatic Environment with Neonicotinoids and its Implication for Ecosystems*.

Front. Environ. Sci. 4:71. doi: 10.3389/fenvs.2016.00071

Several related studies indicate that a concentration of IMI of 13 ng / l may cause a decline in macro-invertebrate populations, and that of 20 ng / l that of insectivorous birds



- Van Dijk, et al(2013) *Macro-Invertebrate Decline in Surface Water Polluted with Imidacloprid*. PLoS ONE 8(5): e62374. doi:10.1371/journal.pone.0062374



Hallmann, C.A. et al (2014) *Declines in insectivorous birds are associated with high neonicotinoid concentrations*, Nature 9 juli 2014 DOI: 10.1038/nature13531



VanderSluijs, J.P. et al. (2015) : *Conclusions of the Worldwide Integrated Assessment on the risks of neonicotinoids and fipronil to biodiversity and ecosystem functioning*. Environ.Sci.Pollut.Res. 22,148– 154. doi:10.1007/s11356-014-3229-5



Pisa L, et al. (2014): *Effects of neonicotinoids and fipronil on non-target invertebrates*. Environ Sci Pollut Res. doi:10.1007/s11356-014-3471-x



Chagnon M, et al. (2014): *Risks of large scale use of systemic insecticides to ecosystem functioning and services*. Environ Sci Pollut Res. doi:10.1007/s11356-014-3277-x

Spreading neonicotinoids in water is especially dangerous for bees and other NN sensitive pollinators:

- A bee colony collects and brings between 30 and 50 litres of water in the beehive every year. If this water is contaminated, it entails a serious danger for the whole colony.
- Surface and ground waters are a source of irrigation for many crops and crop edges. Because of the systemic nature of the neonicotinoids, if a plant absorbs contaminated water, the pesticide spreads throughout the plant, thus becoming within the reach of the pollinators.

A.b. The definitions of the threshold values in aquatic eco-toxicity - fresh waters: RAC-MA in chronic exposure and RAC-CMA in Acute exposure

Netherlands:

In the face of ever higher levels of IMI in water since 2003, the CTGB, the agency responsible for pesticide authorisation, has determined in 2008 the reference threshold value of aquatic eco-toxicity for chronic exposure from 13 to 67 ng / l! In 2014, against further data, Dutch eco-toxicologists proposed a more restrictive threshold value than before 2003: RAC-MA = 8.3 ng / l.

For acute exposure, the threshold value remained RAC-CMA = 200 ng / l.



Smit, C.E. (2014) *Water quality standards for imidacloprid, Proposal for an update according to the Water Framework Directive*, RIVM Letter report 270006001/2014

Canada:

RAC-MA = 230 ng / l, radically put into question in the context of the new eco-toxicological evaluation. The trend is to move towards the latest European standards.

Sweden:

RAC-MA = 13 ng/l

Switzerland:

Recent Proposal: **RAC-MA = 2,3 ng/l** et **RAC-CMA = 100 ng/l**

France:

The average annual concentration identified to protect water column organisms has been reported in RAC-MA = 200 ng / l (from a study that was conducted by the Bayer laboratories, and which has never been published) and RAC- CMA = 300 ng / l (This study was carried out in 1991 by a private American laboratory on behalf of Bayer, who can then claim ownership of it.

In Europa:

Since 2014, the European Food Safety Authority (EFSA) has provisionally identified, pending confirmation of the conclusions of the Dutch studies: RAC-CMA = 9 ng / l (under Tier2) RAC-CMA provisional = 98 ng / l (under Tier2))



EFSA, 2014. *Conclusion on the peer review of the pesticide risk assessment for aquatic organisms for the active substance imidacloprid*. EFSA Journal 2014;12(10):3835, 49 pp.

It is interesting to note that:

- The JRC (Joint Research Center), invested by the Commission, has established an NQE on chronic exposure to aquatic organisms exposed to NN: imidacloprid = 9 ng / l, thiamethoxam = 140 ng / l, clothianidin = 130 ng / l, thiacloprid = 50 ng / l, acetamiprid = 500 ng / l.
- The European Chemicals Agency (ECHA) has just revised the decline of IMEC PNEC for freshwater: PNEC = 4.8 ng / l ECHA is based on the eco-toxicological studies of Roessink and al. 2013, concerning a species of ephemeral, applying an extrapolation factor of 5.



Roessink, I. et al. (2013) *The neonicotinoid imidacloprid shows high chronic toxicity to mayfly nymphs*. Environ Toxicol Chem 32,1096-1100.

B. The presence of Imidacloprid in fresh water, ascertained by agencies, scientists or structures responsible for monitoring their quality.

B.a. Surface water: rivers, stretches of water.

Netherlands:

In 2003, the Netherlands found significant IMI pollution of their surface water in greenhouse surrounding areas, orchards, bulb crops. The annual figures of this pollution, year after year, confirm the very high frequency of exceedances of the aquatic environmental standards.

Since May 2014, management measures have been introduced, researchers from the Centre for Environmental Sciences (Leiden) have been able to promptly observe:

- A drop of 90 centile (some aberrant values have been avoided because greenhouse growers have invested in waste water treatment equipment).
- a limited downward trend of the 75 centile and median and middle values.
- Annual averages that remain well above the PNEC standards = 8.3 ng / l, now applicable in the Netherlands.



Tamis, W.L.M, et al. (2016) *Analyse van imidacloprid in het oppervlaktewater tot en met februari 2016*. Institute of Environmental Sciences (CML)

Belgium:

The Flemish Agency for the Environment (VMM) launched in 2014 a first campaign to measure 3 neonicotinoids (Imidacloprid, Clothianidin, Thiamethoxam) in 92 points of the surface water network, with LOQ = 10 ng / l.

The results indicate that in this case IMI is the most problematic substance:

- **100% of the validated sampling points (4 measurements / year min.) have an average annual concentration higher than the PNEC - Imidacloprid standard: 8 ng / l in Belgium. In these validated points, the average annual concentration reaches more than 171 ng / l.**
- **17% of the validated sampling points (4 measurements / year min) present a maximum concentration in the year that exceeds the MAC threshold of Imidacloprid: in Belgium of 200 ng / l. The IMI has been ascertained up to 680 ng / l.**



Vlaamse Milieumaatschappij (2015), *Neonicotinoïden in oppervlaktewater – Resultaten campagne 2014*.

In the 2014 Annual General Report of the Environmental Surface Water Quality Agency, list 1 shows that Imidacloprid is the most problematic pesticide. Let us note that these results correspond to the samplings carried out in 2014, the first year of the "European moratorium on NN".



Vlaamse Milieumaatschappij (2015), *Pesticiden in oppervlaktewater en RWZI's in 2014*

Italia:

In 2014, the national agency Ispra (Institute for the protection of the environment and research), based on data from regions and environmental organizations, found that Imidacloprid is ranked second among the most frequently discovered active ingredients in 2012 in Italy, both in surface and deep waters. The molecule was particularly present in the underground waters of Sicily. In terms of frequency it is the substance with the highest rate of exceeding limits in groundwater. In addition, even higher contamination peaks were recorded near Padua, Veneto, an area of intensive agriculture, particularly maize.



Paris, P. et al.(2014) *Rapporto nazionale pesticidi nelle acque*. Istituto Superiore per la Protezione e la Ricerca Ambientale.

California (USA):

The Department of State Pesticide Authorization (CDPR) has undertaken the monitoring of Imidacloprid in several watercourses. Out of 23 sites sampled in 2010 and 2011, especially during the irrigation period, the analysis results of the 75 samples are such:

- **89% of IMI measurements are > 10 ng/l.**
- **19% of IMI measurements are > 1050 ng/l** (at the time, threshold value for toxicity)

The authors conclude that under the irrigation conditions in California, IMI can be transported to rivers, thus damaging the aquatic fauna.



Starner, K. et al. (2012) *Detections of the Neonicotinoid Insecticide Imidacloprid in Surface Waters of Three Agricultural Regions of California, USA, 2010–2011*. Bull Environ Contam Toxicol 88:316–321

Maryland (USA):

The apiculture research laboratory, connected to the US Department of Agriculture, has carried out analyses of the water sampled in different environments: residential, urban, agricultural, nurseries, farms, open field crops. In total 18 sites were sampled, according to 6 samples per site, made according to the case in a river, a ditch, a drainage, in puddles, in ponds or other basins. These 108 water points had in common the presence of hives less than 700 m, and it was therefore possible that they were visited by bees.

With a very high LOQ (of the order of 200-300 ng / l, following the ELISA technique), the authors found that 21% (23/108) of the water samples contained IMI at levels > 200 ng / l, with maximum values for a nursery water reserve (27,000 ng / l), a pond in a golf course (25,000 ng / l) and a river near cattle breeding (19,000 ng / l).



Johnson, J.D et al. (2014) *A survey of imidacloprid levels in water sources potentially frequented by honeybees (Apis mellifera) in the Eastern USA*. Water Air Soil Pollut 225:2127

USA (National):

US Geological Survey has looked for neonicotinoids in river waters:

- in a "national" study, 38 rivers were monitored in 24 states + Puerto Rico, between November 2012 and June 2014.

- 10 additional rivers have been added, with particular characteristics: significant rainfall episodes (Iowa), or proximity to important urban areas compared to the surface of the basin, both close to ecologically fragile areas, or to a waste water treatment plant.

At least 1 NN was found (for LOD = 2 ng / l) in 53% of samples, as well as in 63% of 48 sampled rivers. With a rate of 37%, IMI was the most frequently detected NN in the "national" study. The maximum concentration was 140 ng / l. Its presence has been related to the importance of the urban area compared to the basin. In Iowa, 6 rivers were sampled between mid-June and early July 2014, following rains and floods: the average IMI concentration was 19 ng / l.



Hladik, M.L . et al. (2015) *First national-scale reconnaissance of neonicotinoid insecticides in streams across the USA*. Environ. Chem. 13(1) 12-20 <http://dx.doi.org/10.1071/EN15061>

Worldwide:

A meta-analysis to take stock of the risks from NN for aquatic organisms. Made with data on exposure to NN residues in the aquatic matrix, recently published worldwide.

Based on data from 31 publications in 11 countries, the authors found that:

- up to 6 NN are commonly found in aquatic environments around the world.
- IMI is the most frequently detected NN; the average of all IMI measurements is 730 ng / l, significantly higher than that of the other NNs (the maximum detected level of IMI was recorded in the Netherlands: 320,000 ng / l).
- the very high average is mainly explained by the numerous results from the Netherlands and Sweden (the effect of water discharged from the greenhouses). The 25th and 75th centiles are respectively 25 ng / l and 2,200 ng / l.



Sánchez-Bayo, F. et al. (2016) *Contamination of the Aquatic Environment with Neonicotinoids and its Implication for Ecosystems* Front. Environ. Sci. 4:71. doi: 10.3389/fenvs.2016.00071

Another meta-analysis produced by the Worldwide Integrated Assessment on the risks of neonicotinoids and fipronil to biodiversity and ecosystem functioning, cites other bibliographic sources, which clarify the exposure to systemic insecticides (including IMI), especially in aquatic environments.



Bonmatin, J-M. et al. (2014) : *Environmental fate and exposure; neonicotinoids and fipronil*. Environ Sci Pollut Res. doi:10.1007/s11356-014-3332-7

B.b. Underground water

Quebec:

The Ministry of the Environment tried to understand which of all pesticides and nitrates used for growing potatoes were likely to contaminate the waters of surrounding domestic wells. 79 wells were sampled, between 1999-2001. Although the use of the molecule is recent in Canada (1996), IMI has already been detected in 35% of the 79 wells (the maximum detection frequency among all the pesticides sought).

- The maximum concentrations detected were 6400 ng / l, 18 ng / l, 400 ng / l and 2 ng / l respectively for IMI and its metabolites urea, guanidine and olefin.
- The median concentrations were 38 ng / l, 3 ng / l, 4 ng / l and 2 ng / l respectively for IMI and its metabolites urea, guanidine and olefin



Giroux, I. (2003), *Rapport : "Contamination de l'eau souterraine par les pesticides et les nitrates dans les régions en cultures de pommes de terre"*. Direction du suivi de l'état de l'environnement, Min. de l'environnement du Gouvernement du Québec.

State of New York (USA):

Following a monitoring conducted by Bayer on 1 agricultural well in 1998 for 5 months, 3 years after its first use authorization, IMI has been shown to pollute the groundwater defined as shallow. Furthermore, the EPA has committed itself to seeking IMI in the waters of almost 2000 wells.

The Department of Environmental Conservation focused on Long Island, where drinking water most often comes from underground aquifers. Already in 2000 (the first use of IMI in 1995), it was found that IMI polluted these waters. Between 2000 and 2011, out of 179 sites, IMI was quantified 1000 times, with a maximum of 407,000 ng / l.

During this monitoring period, depending on the year: the 75th centile is located between 800 and 3300 ng / l in monitored catchment basins, between 350 and 1300 ng / l in private wells, between 230 and 450 ng / l in water distributed to the public (while the European health standard is <100 ng / l) In the last year of monitoring, the averages were 1000, 450 and 275 ng / l respectively.



Bureau of Pest Management Pesticide Product Registration Section, (2015), *Long Island Pesticide Pollution Prevention Strategy Active Ingredient Assessment*.

In Wisconsin (USA):

In 2008-2012, the Department of Agriculture conducted NN monitoring of 23 pumping stations in groundwater.

On the 67 positive analyses (IMI, CLO, TMX), 30 are of IMI: the mean (+/- SD) is 790 (+/- 830 ng / l) (min 260 / max 3340 ng / l). In 2013, the maximum concentration was 1590 ng / l.

The same study also analyses the mobility of NN (in this case TMX) in the soil, according to how the NN (leaf, granules or liquid in the row) is applied in the crop of potatoes, and even if it depends on irrigation. Opportunity that shows that irrigation water pumped from a source full of NN, "recycles" somehow the NN on the crop.



Huseth, A.S. et al. (2014) *Environmental fate of soil applied neonicotinoid insecticides in an irrigated potato agroecosystem*. PLoS One ; 9(5): e97081.

France:

IMI is not a substance object of a particular research in metropolitan underground waters, despite a high GUS score (a score of 3.76 which corresponds to a high mobility / percolation potential in soils).

Monitoring in the catchment basin may reveal significant levels of IMI. So, 09.02.2016, for the sources of Roumois (North of the Eure), the water captured in Moulineaux which supplies the municipalities of the metropolis of Rouen in Normandy and the Varas basin that feeds Roumois, the IMI has been dosed at 348 ng / l.

IMI is present in the groundwater of 5 DOM, with a frequency of quantification (LOQ = 0.1 ng / l) higher for Mayotte (83%) and La Reunion (56%), and an average of 39 %. The average of the levels is about 1.7 ng / l, and their maximum towards 93 ng / l.



Lopez,B. et al. (2013) *Recherche de contaminants organiques dans les eaux souterraines des DOM en 2012- 2013* BRGM

B.c. Urban water: rainfall / waste water

California (USA):

In a California Department of Pesticide Management study, Southern California rainwater was analysed between mid-2014 and mid-2015. For IMI, 73 percent of the 40 rainwater samples were the same or higher than 50 ng / l (= LOQ), without however reaching the California threshold of 1050 n / l (now in question).



Department of Pesticide Regulation (2016) *Ambient Monitoring Report*

In the region of San Francisco, California, in the waters in and out of wastewater treatment plants, in 2015 the IMI was present in all the samples, respectively between 58-310 ng / l and 84-310 ng /. The author points out that **wastewater is discharged into the San Francisco Bay with an IMI content 60 times PNEC (here, 4.8 ng / l).**

USA (National):

In the United States, the incoming and outgoing waters of 13 conventional wastewater treatment plants were analysed to understand their NN load. Upon entry, the IMI and ACE substances (and one of its metabolites) were regularly ascertained, the CLO was found intermittently.

A conventional water treatment plant does not significantly eliminate the IMI and in a limited way the ACE:

- for IMI: entry at (60.5 ng / l ± 40.0), exit at (58.5 ng / l ± 29.1)
- for ACE (e - N-desmethyl): entry at (2.9 ng / l ± 1.9); output at (2.3 ng / l ± 1.4). The study on a single example of a swamp designed to treat wastewater has shown that it does not eliminate IMI (neither ACE nor CLO).

Extrapolating from the 13 factories studied, the authors calculate that in the United States, the wastewater treatment plants could release each year in the environment, the equivalent of 1000 - 3400 kg of IMI



Sadaria, A.M. et al. (2016) *Mass Balance Assessment for Six Neonicotinoid Insecticides During Conventional Wastewater and Wetland Treatment : Nationwide Reconnaissance in United States Wastewater*. Environ. Sci. Technol. 50, 6199–6206.

France:

The effluents of the two main treatment plants of the Bordeaux agglomeration were sampled, between May 2012 and March 2013, for the research of about 50 active substances. IMI is in 2nd place of the highest concentrations: 40-50 ng / l. As already reported previously, IMI is, in fact, refractory to the treatment of the purification plant.



Cruz, J.M. (2015) *Etude de la contamination par les pesticides des milieux eau, air et sols : développement de nouveaux outils et application à l'estuaire de la Gironde*. Thèse Université de Bordeaux.