Neonicotinoids are now the third most abundantly used insecticides worldwide and account for over 80% of the seed treatment market. They are used for pest management on hundreds of crops in agriculture, horticulture, and forestry. Neonicotinoids are also used to control insect pests in pets such as dogs, as well as in livestock and in aquaculture. These insecticides are registered for use in over 120 countries, with global production of 20,000 tonnes of active substance per year in 2010. Their widespread use has been prompted by the belief that they are “safer alternatives” to replace more hazardous organophosphate and carbamate insecticides.

Neonicotinoids are found ubiquitously in surface waters and on soils and other surfaces. Some studies report that, at authorized rates of usage, detected levels frequently exceed the lowest observable adverse effect concentrations (NOEC) for numerous nontarget species, whereas other studies have measured environmental levels less than the NOEC. Such issues result in grave concern regarding the potential impacts on pollinators such as honey bees, leading to reviews on the usage of such chemicals. In 2013, the European Commission moved to restrict three neonicotinoids, including imidacloprid, and regulatory reviews and some control actions have taken place or are taking place in some U.S. states and in Canada, e.g., refs 2 and 7.

Numerous questions have been raised about the risks posed by neonicotinoids and imidacloprid in particular, which is the most commonly used neonicotinoid pesticide (Figure 1). Such questions include the environmental persistence and potential toxicity of degradation products of specific neonicotinoids. Kiffe Aregahegn and Dorit Shemesh, from the groups of Barbara Finlayson-Pitts and R. Benny Gerber, have conducted careful and insightful experiments and theoretical analysis that shed new light on these questions and also raise new concerns. Their key findings are 3-fold. First, their experiments showed that imidacloprid is not particularly persistent; second, a transformation product is one that has been shown by others to have greater toxicity than the imidacloprid parent compound, and this transformation product is likely to be persistent; and third, the photolytic reaction of imidacloprid produces a potent greenhouse gas.

In more detail, the authors measured the quantum yields and investigated the transformation imidacloprid experiences from photolysis as a thin solid film on artificial surfaces. Unique insights into the mechanisms were provided by molecular dynamics and ab initio calculations. They found that imidacloprid has a photolytic lifetime of approximately 16 h at the Earth’s surface at midlatitudes (40°N latitude at noon in early April). Under these conditions, the photolytic quantum yields for loss of imidacloprid are \((1.6 \pm 0.6) \times 10^{-3}\) (1s) at 305 nm and, for comparison, \((8.5 \pm 2.1) \times 10^{-3}\) (1s) at 254 nm.

The second major finding was that the photolytic degradation of imidacloprid produces two main compounds, a urea derivative known as IMD-UR and a desnitro derivative (DN-IMD). IMD-UR and DN-IMD are produced in a ratio of 80:20, respectively. Aregahegn and Shemesh et al. provided evidence that both of these photoproducts are more stable—resisting photodegradation under ambient conditions. Further concerns arise because DN-IMD has been reported to have a higher binding affinity than the product.

What if the environmental risks of neonicotinoids like imidacloprid are only the beginning of the story (Environmental Science & Technology)?

Figure 1. MP2/cc-pVDZ optimized structure of imidacloprid. Reprinted with permission from ref 8. Copyright 2016 American Chemical Society.
First, their experiments showed that imidacloprid is not particularly persistent; second, a transformation product is one that has been shown by others to have greater toxicity than the imidacloprid parent compound, and this transformation product is likely to be persistent; and third, the photolytic reaction produces a potent greenhouse gas.

parent compound for nicotinic acetylcholine receptor sites, which are implicated in mammalian toxicity.9

The third major result of this study is the first measurements of gas-phase products from photolysis of imidacloprid. Surprisingly, the sole gas-phase product is nitrous oxide, N₂O, rather than NO₂ expected from cleavage of the −NO₂ group in imidacloprid. Quantum chemical calculations provided insight into the N₂O production. Briefly, absorption of light leads to initial cleavage of the −NO₂ group. However, NO₂ becomes trapped in the solid and recombines with the other fragment that was generated during photolysis. This releases significant energy that drives intramolecular reactions that form N₂O.

Production of nitrous oxide is important since it is a potent greenhouse gas with a global warming potential more than 250 times higher than that of CO₂ assuming a 20 year time scale. N₂O is also a significant contributor to stratospheric ozone depletion. The authors calculated that photolysis of the total tonnage of imidacloprid produced annually would yield 1900 t as nitrogen. This yield is small relative to all anthropogenic N₂O emissions,10 however releases could be locally significant and of comparable magnitude to those attributed to abiotic reactions of ammonium nitrate fertilizer in North America.11

The regulatory community tasked with adjudicating the future use of imidacloprid will appreciate these findings. It opens the door for additional studies of the other atmospheric fates of imidacloprid such as reactions with ozone and the hydroxyl and nitrate radicals. The research of Areghagen and Dorit Shemesh et al. also begs for future work on the photochemistry and atmospheric reactions of other neonicotinoid pesticides, as well as the environmental prevalence and ecotoxicological effects of the neonicotinoid transformation products like DN-IMD. And last but not least, the findings of the production of a potent greenhouse gas, in conjunction with the other results, serve to remind us how complex a web of adverse impacts is posed by our widespread use of synthetic chemicals and the need to work to foresee complications from their use.

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Notes
The author declares no competing financial interest.

REFERENCES

(1) Jeschke, P.; Nauen, R.; Schindler, M.; Elbert, A. Overview of the status and global strategy for neonicotinoids. J. Agric. Food Chem. 2011, 59, 2897−908.
(2) van der Slaa, J. P.; Amaral-Rogers, V.; Belzuneces, L. P.; Bijleveld van Lexmond, M. F. I. J.; Bonnatin, J.-M.; Chagnon, M.; Downs, C. A.; Furlan, L.; Gibbons, D. W.; Giorio, C.; Girolami, V.; Goulson, D.; Kreutzweiser, D. P.; Krupeck, C.; Liess, M.; Long, E.; McField, M.; Mineau, P.; Mitchell, E. A. D.; Morrissey, C. A.; Noone, D. A.; Pisa, L.; Settele, J.; Simon-Delso, N.; Stark, J. D.; Tapparo, A.; Van Dyck, H.; Van Praagh, J.; Whitehorn, P. R.; Wiemers, M. Conclusions of the Worldwide Integrated Assessment on the risks of neonicotinoids and fipronil to biodiversity and ecosystem function. Environ. Sci. Pollut. Res. 2015, 22, 148−154.
(3) Simon-Delso, N.; Amaral-Rogers, V.; Belzuneces, L. P.; Bonnatin, J. M.; Chagnon, M.; Downs, C.; Furlan, L.; Gibbons, D. W.; Giorio, C.; Girolami, V.; Goulson, D.; Kreutzweiser, D. P.; Krupeck, C.; Liess, M.; Long, E.; McField, M.; Mineau, P.; Mitchell, E. A. D.; Morrissey, C. A.; Noone, D. A.; Pisa, L.; Settele, J.; Stark, J. D.; Tapparo, A.; Van Dyck, H.; Van Praagh, J.; Van der Slaa, J. P.; Whitehorn, P. R.; Wiemers, M. Systemic insecticides (neonicotinoids and fipronil): trends, uses, mode of action and metabolites. Sci. Pollut. Res. 2015, 22, 5−34.
(4) Jeschke, P.; Nauen, R. Neonicotinoids—from zero to hero in insecticide chemistry. Pest Manage. Sci. 2008, 64, 1084−1098.
(5) Bonnatin, J.-M.; Giorio, C.; Girolami, V.; Goulson, D.; Kreutzweiser, D. P.; Krupeck, C.; Liess, M.; Long, E.; Marzaro, M.; Mitchell, E. A. D.; Noone, D. A.; Simon-Delso, N.; Tapparo, A. Environmental fate and exposure; neonicotinoids and fipronil. Environ. Sci. Pollut. Res. 2015, 22, 35−67.
(6) Stewart, S. D.; Lorenz, G. M.; Catchot, A. L.; Gore, J.; Cook, D.; Skinner, J.; Mueller, T. C.; Johnson, D. R.; Zawislak, J.; Barber, J. Potential exposure of pollinators to neonicotinoid insecticides from the use of insecticide seed treatment in the Mid-Southern United States. Environ. Sci. Technol. 2014, 48, 9762−9769.
(7) Anderson, J. C.; Dubetz, C.; Palace, V. P. Neonicotinoids in the Canadian aquatic environment: A literature review on current use products with a focus on fate, exposure, and biological effects. Sci. Total Environ. 2015, 505, 409−422.
(8) Areghagen, K. Z.; Shemesh, D.; Gerber, R. B.; Finlayson-Pitts, B. J. Photochemistry of thin solid films of the neonicotinoid imidacloprid on surfaces. Environ. Sci. Technol. 2017, DOI: 10.1021/acs.est.6b04842.
(9) Chao, S. L.; Casida, J. E. Interaction of imidacloprid metabolites and analogs with the nicotinic acetylcholine receptor of mouse brain in relation to toxicity. Pestic. Biochem. Physiol. 1997, 58, 77−88.
(10) Tian, H.; Lu, C.; Ciais, P.; Michalak, A. M.; Canadell, J. G.; Saikawa, E.; Huntzinger, D. N.; Gurney, K. R.; Sitch, S.; Zhang, B.; Yang, J.; Bousquet, P.; Bruhwiler, L.; Chen, G.; Dlugokencky, E.; Friedlingstein, P.; Mello, J.; Pan, S.; Poulet, L.; Prinn, R.; Saunois, M.; Schwalm, C. R.; Worsley, S. C. The terrestrial biosphere as a net source of greenhouse gases to the atmosphere. Nature 2016, 531, 225−232.
(11) Rubasinghege, G.; Spak, S. N.; Stanier, C. O.; Carmichael, G. R.; Grassian, V. H. Abiotic mechanism for the formation of atmospheric nitrous oxide from ammonium nitrate. Environ. Sci. Technol. 2011, 45, 2691−2697.