Chlorinated Byproducts of Neonicotinoids and Their Metabolites: An Unrecognized Human Exposure Potential?

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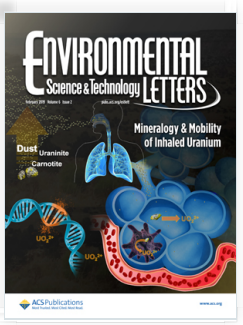

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Abstract

We recently reported the initial discovery of neonicotinoid pesticides in drinking water and their potential for transformation through chlorination and alkaline hydrolysis during water treatment. The objectives of this research were: (1) to determine if neonicotinoid metabolites are relevant to drinking water exposure and (2) to identify the products formed from chlorination of neonicotinoids and their metabolites. Desnitro-imidacloprid and imidacloprid-urea, two known metabolites of imidacloprid, are documented for the first time in drinking water. Desnitro-imidacloprid was present above the lower level of detection (0.03 ng/L) in 67% of samples (six of nine) from drinking water systems but detectable in all samples (up to 0.6 ng/L). Although concentrations of desnitro-imidacloprid were lower than concentrations of the parent neonicotinoids, desnitro-imidacloprid exhibits significantly greater mammalian toxicity than imidacloprid. Using LC-HR-ToF-MS/MS analysis of results from laboratory experiments, we propose structures for novel transformation products resulting from the chlorination of clothianidin, imidacloprid, desnitro-imidacloprid, imidacloprid-urea, and hydrolysis products of thiamethoxam. Formation of chlorinated neonicotinoid byproducts occurs at time scales relevant to water treatment and/or distribution for the imidacloprid metabolites ($t_{1/2}$ values from 2.4 min to 1.0 h) and thiamethoxam hydrolysis products (4.8 h). Neonicotinoid metabolites in finished drinking water and potential formation of novel disinfection byproducts during treatment and/or distribution are relevant to evaluating the exposure and potential impacts of neonicotinoids on human health.