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Are organosilicon surfactants safe for bees or humans?

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ABSTRACT

Organosilicon surfactants are the most potent adjuvants available for formulating and applying agricultural pesticides and fertilizers, household cleaning and personal care products, dental impressions and medicines. Risk assessment of pesticides, drugs or personal care products that takes into account only active ingredients without the other formulation ingredients and adjuvants commonly used in their application will miss important toxicity outcomes detrimental to non-target species including pollinators and humans. Over a billion pounds of organosilicon surfactants from all uses are produced globally per year, making this a major component of the chemical landscape to which bees and humans are exposed. These silicones, like most "inerts", are generally recognized as safe, have no mandated tolerances, and their residues are largely unmonitored. Lack of their public disclosure and adequate analytical methods constrains evaluation of their risk. Organosilicon surfactants, the most super-spreading and -penetrating adjuvants available, at relevant exposure levels impair honey bee learning, are acutely toxic, and in combination with bee viruses cause synergistic mortality. Organosilicon surfactants need to be regulated as a separate class of "inerts" from the more common silicones. In turn, impacts of organosilicon surfactant exposures on humans need to be evaluated. Silicones in their great diversity probably represent the single most ubiquitous environmental class of global synthetic pollutants. Do honey bees, a model environmental indicator organism, forewarn of hidden risks to humans of ubiquitous silicone exposures?

1. Introduction

Modern pesticide and drug delivery technology has greatly benefited from discovery of super -penetrating, -spreading and -wetting surfactants to potentiate the active ingredient against targeted pests and diseases (Green and Beestman, 2007; Hazen, 2000). Among the most widely used class of surfactants to attain the needed penetration of plant (Forster and Kimberley, 2015) and animal (Whitehead et al., 2007) cuticles or achieve the necessary level of surface tension reduction or cleaning power are the organosilicon surfactants.

Organosilicon surfactants are a class of silicone-based copolymers containing a hydrophobic methylated oligosiloxane backbone and a hydrophilic polyalkoxylate (ethoxylate and propoxylate) chain. By adjusting the polyalkoxylate/oligosiloxane ratio, desired surface tension and solubility properties can be obtained for numerous applications.

Due to its variety in chemical structure and surfactant properties, organosilicon surfactants enjoy wide utility in a diversity of applications ranging from carriers that enhance drug steroids (Sastry et al., 2017) to tank additives that allow the globally-dominant herbicide glyphosate to penetrate via the stomata of plants (Basi et al., 2014). These are among the most potent in the arsenal of penetration enhancers available to deliver veterinary and human drugs either transdermally (Karande et al., 2005) or orally (Whitehead et al., 2007).

In agricultural applications, the organosilicon surfactants most often have tri- and tetra- siloxane backbones to maintain good water solubility. It was the early recognition of the very low critical micelle concentration (Hill, 1992), superspreading (He et al., 1993) and superwetting (Hill et al., 1994) properties of the three primary trisiloxane surfactant (TSS) products; methoxy-capped TSS (CAS 27306-78-1), hydroxy-capped TSS (CAS 67674-67-3) and acetoxy-capped TSS (CAS 125997-17-3) that has led to their numerous commercial applications as super surfactants. Organosilicon surfactants are also the strongest class of the commercial adjuvants used in spray tanks to enhance the efficacy of pesticide, plant growth regulator and fertilizer applications (Mullin et al., 2015, 2016), and may play an important role in increasing pesticide exposure and

Abbreviations: TSS, trisiloxane surfactant; LC-MS, liquid chromatography-mass spectrometry; GC–MS, gas chromatography–mass spectrometry; MSDS, material safety data sheet; SDS, safety data sheet; CCD, colony collapse disorder; D4, octamethyl cyclotetrasiloxane.

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risk for honey bees due to their modern agriculture and urban uses (Benuszak et al., 2017; McArt et al., 2017).

In general, adjuvants and co-formulants greatly enhance the pesticidal efficacy and inadvertently the non-target effects of the active ingredient. At environmentally relevant levels, these co-formulants significantly enhance the acute toxicities of the active ingredient residues (Mullin et al., 2015). Organosilicon surfactants are the most potent tank adjuvants and super-penetrants available to growers. Based on the California Department of Pesticide Regulation data for agrochemical applications to almonds (CDPR, 2017), there has been increasing use of adjuvants, particularly organosilicon surfactants, during bloom when two-thirds of USA honey bee colonies are present. Increased tank-mixing of these with fungicides and insect growth regulators may be associated with recent USA honey bee declines (Mullin et al., 2016). Spray tank adjuvants are largely assumed to be biologically inert and are not registered by the US-EPA, leaving their regulation and monitoring to individual states (US EPA, 2017).

2. Organosilicon surfactants harm honey bees

Honey bees are sensitive to toxic effects of widespread co-formulants used in agrochemicals (Ciarlo et al., 2012; Zhu et al., 2014; Fine et al., 2017). Effects include learning impairment for adult bees and oral toxicity for larvae and adults. Multi-billion pounds of formulation ingredients from all uses are released into US environments, making this an important component of the chemical landscape to which bees are exposed. Most inerts are generally recognized as safe, have no mandated tolerances, and their residues are unmonitored. The majority of studies documenting pesticide effects on honey bees are performed without the full formulation or other relevant spray adjuvant components used in environmental applications of the toxicant. Organosilicon surfactants are used worldwide as adjuvants and can compose up to 2% (20,000 ppm) of the spray tank mix (Mullin, 2015). All organosilicon surfactant adjuvants tested (Dyne-Amic®, Syl-Tac®, Sylgard 309®, and Silwet L-77®) have been shown to impair honey bee olfactory learning much more than other nonionic surfactant adjuvants, while crop oil concentrates were inactive (Ciarlo et al., 2012). However, spray tank adjuvants are currently under-regulated in the USA at the federal level (US EPA, 2017).

Six of the most commonly used adjuvants in California almonds were analyzed by liquid chromatography-mass spectrometry (LC-MS) (Mullin et al., 2016). Dyne-Amic®, Kinetic HV®, Silkin®, Silwet L-77®, Sylgard 309®, and Syl-Tac® consisted mostly of hydroxy-capped, methoxy-capped and acetoxy-capped TSS (Chen and Mullin, 2015). The three dominant TSS in commercial spray adjuvants, when fed orally at 100 ppm (0.01%) in sugar water to adult honey bees over 10 days, greatly reduced their survival rates (Fig. 1). Experimental details are described in supplementary material.

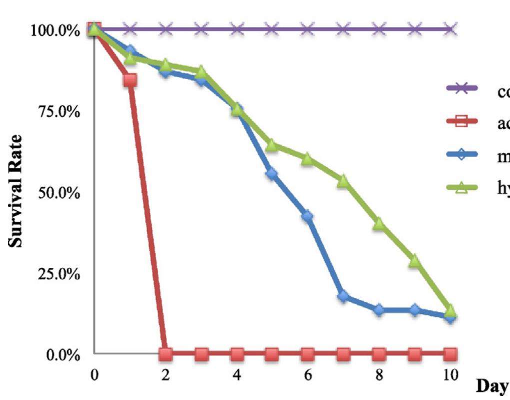

Fig. 1. Survival rates of adult honey bees fed on 100 ppm methoxy-capped TSS, hydroxy-capped TSS or acetoxy-capped TSS mixed in their sucrose/water (w/w, 50/50) diet for 10 days.

Among nonionic surfactants, we found the TSSs > alkylphenol polyethoxylates and fatty amine polyethoxylates in toxicity to adult honey bees (Fig. 2), and larvae are usually much more susceptible to these "inert" or "inactive" ingredients than adult honey bees (Zhu et al., 2014; Fine et al., 2017). Experimental details are described in supplementary material.

Thus, although organosilicon surfactants are considered the 'gold standard' of formulant and adjuvant detergents, they are also among the most toxic classes of surfactants used in agriculture to adult honey bees. While this is the case with most insects and other taxa (Mullin et al., 2016), exceptions have been found where tallow amines and other polyethoxylated surfactants are more toxic to fish (Haller and Stocker, 2003) and more genotoxic to bacteria (Nobels et al., 2011).

One possible management practice to mitigate bee exposures to agrochemicals is to resort more to bee-friendly organic agriculture, however this is not likely for spray adjuvants since the most toxic organosilicon surfactants are presently Organic Materials Review Institute-certified for organic use in the USA (OMRI, 2017).

Chronic feeding of honey bee larvae with 10 ppm Sylgard 309® (primarily acetoxy-capped TSS) using a sterile in vitro assay elicits little to no toxicity alone (Fine et al., 2017). However, a combination of the Sylgard 309® and a bee virus inoculum containing IAPV, BQCV, DWV and SBV (organosilicon surfactant + Virus) killed 68 ± 4% of the larvae before the adult stage, with highest mortality occurring around the time of pupation (Fine et al., 2017). This augments examples of a link between bee disease and pesticides (Sánchez-Bayo et al., 2016), except this time a formulant and not the active ingredient is implicated. The mechanism of the observed toxicity is unknown, but a Toll-7 ortholog was significantly downregulated relative to other virus exposed larvae. In *Drosophila melanogaster*, Toll-7 is a surface receptor that triggers an antiviral pathway (Nakamoto et al., 2012). Organosilicon surfactants are used to transform grape plantlets with *Agrobacterium* (Lizamore and Winefield, 2015), and thus may aid movement of pathogens or similarly sized particles into bee tissues. However, it is not known whether the concentration of organosilicon surfactant used in this work (10 ppm) could have caused increased membrane penetration. Regardless, Toll-like-receptors and their role in innate immunity are conserved in vertebrate taxa (Roach et al., 2005), and exposure to organosilicon surfactants may have parallel consequences for plants and other animals including humans.

3. Lack of analytical methodology for silicones and organosilicon surfactants

Silicones, also named organosilicons, siloxanes or polysiloxanes in the literature, as a very diverse suite of high production volume chemicals, probably overall represent the single most ubiquitous environmental class of global synthetic pollutants (Wang et al., 2013; Rücker and Kümmerer, 2015). Silicon, after oxygen, is the second most abundant element comprising 28% of the earth's crust (Jolly, 1966). Sand or silica, silicic acid and diverse silicate salts, the natural forms of silicon, are rare but essential components of animals and plants, and can be at elevated levels in plants to enhance mechanical strength and resist herbivore damage (Reynolds et al., 2009). Nanoparticle silica is incorporated at up to 1% in foodstuffs such as cake mixes and cappuccino and at 19% in toothpaste (Yang et al., 2016). This abundant mineral resource provides an economic route to the diverse silicones and organosilicon surfactants of commerce, which are all xenobiotic (Horii and Kannan, 2008; Mojsiewicz-Pieńkowska et al., 2016). While the inert and highly lipophilic silicone products have been used in commerce for well over a half-century, the organosilicon surfactants are a more recent innovation of the last 30 years (Penner et al., 1999).

Analytical methods for silicone compounds have lagged well behind the diversity and breadth of silicone technologies in commercial use. Although already the major organometallic compounds produced and