

Environmental Toxicology

Are Green Household Consumer Products Less Toxic than Conventional Products? An Assessment Involving Grass Shrimp (*Palaemon pugio*) and *Daphnia magna*

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Abstract: Although it is generally assumed that green household consumer products (HCPs) contain individual compounds that are less toxic and/or more degradable than conventional HCPs, little research on this topic has been conducted. In our assessments, larval grass shrimp (*Palaemon pugio*) were used in a biodegradation study and juvenile freshwater cladocerans, *Daphnia magna*, were used in a photodegradation study. In each study, organisms were exposed to nondegraded and degraded treatments consisting of one green HCP and two conventional HCPs in six different categories (laundry detergent, dish detergent, mouthwash, insecticide, dishwasher gel, and all-purpose cleaner). Sensitivity to these products were assessed using 48-h static acute toxicity tests, and the median lethal concentrations (LC50s) then compared using an LC50 ratio test. For grass shrimp, only one green HCP (insecticide) was less toxic than both conventional HCPs. In one category (laundry detergent), the green HCP was the more toxic than either conventional HCP. Following a biodegradation treatment, none of the green product formulations became less toxic, whereas 44.4% of the conventional HCPs demonstrated decreased toxicity. For daphnids, green HCPs in three categories (dish detergent, insecticide, and all-purpose cleaner) were less toxic than both conventional products tested. Following a photodegradation treatment, two green product formulations (dish detergent and dishwasher gel) became less toxic (33.3%), whereas 87.5% of the conventional HCPs demonstrated decreased toxicity. The present study demonstrates that green HCPs are not necessarily less toxic and/or more degradable than their conventional counterparts. These results also suggest that the toxicity and degradability of end-product formulations need to be considered in the overall framework for green product evaluation. *Environ Toxicol Chem* 2022;41:2444–2453. © 2022 The Authors. *Environmental Toxicology and Chemistry* published by Wiley Periodicals LLC on behalf of SETAC.

Keywords: Acute toxicity; Degradation; LC50; Mortality; Consumer products

INTRODUCTION

Household consumer products (HCPs) are a diverse group of commercially available formulations used for a variety of specific applications around the home and for personal use (e.g., laundry detergents, dish detergents and gels, toothpaste and mouthwash, insecticides, all-purpose cleaners, etc.; Trantallidi et al., 2015). On a global scale, household cleaning products alone represented a market size of \$221.32 billion in 2020, following an 18.2% increase related to demand associated with the

COVID-19 pandemic (Fortune Business Insights, 2021), and it has been estimated that 2 billion kg are used annually (Sobrinho-Figueroa, 2018). Relative to other consumer products, such as pharmaceuticals, HCPs have not received as much attention regarding their potential environmental impacts (Gray et al., 2020; Kim & Carlson, 2007; Kolpin et al., 2002). Unlike pharmaceuticals, HCPs are typically not ingested by humans and therefore do not undergo enzymatically mediated metabolic alteration. As a result, large quantities of HCPs, especially cleaning products, enter the aquatic environment largely unaltered through the release of wastewater effluent and degraded sewage infrastructures (Ternes et al., 2004; Woodling et al., 2006).

Previous studies have documented the toxicity of individual compounds found in HCPs to aquatic organisms (reviewed by Brausch & Rand, 2011). For example, exposure to benzophenone, 1,4-dichlorobenzene, and benzyl paraben resulted in increased mortality, reduced reproduction, retarded growth,

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Published online 8 September 2022 in Wiley Online Library (wileyonlinelibrary.com).

DOI: 10.1002/etc.5435

and physical deformities (Brausch & Rand, 2011; Brooke et al., 1984; Buccafusco et al., 1981; Dougherty et al., 2010). The use of surfactants in HCP formulations is also a cause of concern for aquatic organisms due to the acute and chronic toxicity associated with exposure. Anionic surfactants have been documented to induce an inflammatory response and oxidative stress in aquatic organisms (Renaud et al., 2014; Susmi et al., 2010), whereas cationic surfactants can act as endocrine disruptors in aquatic organisms (Koerner et al., 1998). The mixture toxicity of HCPs, including the toxicity of commercial formulations, remains an area of limited research (Warne & Schifko, 1999). Thus, further research is warranted due to the limited evidence that mixtures can cause adverse effects in aquatic organisms, resulting in lower reproduction, developmental abnormalities, and histopathological alterations (Van Gestel et al., 2016; Galus et al., 2013). Furthermore, limited evidence suggests that individual compounds combined with surfactants in product formulations can result in synergistic outcomes (Tsui & Chu, 2004).

To reduce the environmental impacts related to the manufacturing and disposal of HCPs, several companies are marketing “green” product formulations as an alternative to conventional formulations. Green products are those manufactured utilizing green chemistry, which is the design of products that reduce or eliminate hazardous substances across the entire life cycle of the product from initial design to ultimate disposal. The green HCP industry has become big business for both manufacturers and retailers alike. The global marketplace for products made using green chemistry, which includes bio-based chemicals, green polymers, and less-toxic chemical formulations, is expected to grow from \$11 billion in 2015 to \$100 billion by 2020 (Forsgren, 2020). Among the many tenants of modern green chemistry proposed by Anastas and Warner (1998), several are directly relevant to HCPs and include the generation of substances that possess little to no toxicity to humans and the environment, and the design of chemical products that breakdown into innocuous degradation products at the end of their designed functionality.

Although product formulations manufactured using green chemistry are often marketed as “eco-friendly” and their labels often make claims referring to the product formulation being less toxic and/or more degradable, rarely have these claims been tested or verified independently. As such, it is not universally accepted by consumers that green HCPs are inherently better for the environment. For example, in 2008, 48% of consumers believed that green products were better for the environment. By 2012, this number decreased to 36% (Walker, 2012). Despite consumer skepticism, in 2018 over 50% of consumers 16–54 years old were willing to pay more for green products (Global Web Index, 2018).

Given that the labelling of HCPs, including green product formulations, does not need to disclose individual compounds due to proprietary considerations (Steinemann, 2009), the environmental impacts associated with their use and disposal, especially relative to conventional product formulations, remains largely unknown (Jones et al., 2001). Therefore, the present study aimed to determine (1) if green HCP formulations are less

toxic than their respective conventional counterparts to commonly used aquatic test organisms, the freshwater cladoceran *Daphnia magna* and estuarine daggerblade grass shrimp (*Palaemon pugio*), and (2) if green HCPs are less toxic following a biodegradation treatment (grass shrimp) and photodegradation treatment (*Daphnia*). Based on labelling claims and the tenants of green chemistry, we hypothesize that green HCPs are less toxic compared to their conventional counterparts both before and after degradation.

The present study represented the culmination of two independent research experiences. The choice of species, products, and degradation treatments were at the discretion of the researchers. The two studies are presented together here to highlight how HCPs and degradation treatments impact sensitive aquatic species.

METHODS AND MATERIALS

Experimental overview

The toxicity of green and conventional HCPs was assessed in six different HCP categories using a series of 48-h acute toxicity tests involving larvae of the estuarine daggerblade grass shrimp, *Palaemons pugio*, and juveniles of the freshwater cladoceran, *Daphnia magna*. The products used in the assay were those that were commercially available for consumers. For each species, data analysis was designed to compare (1) the toxicity of one green HCP in each of the different consumer product categories to that of two conventional HCPs, and (2) the toxicity of green and conventional HCPs before and after a degradation treatment.

For grass shrimp, we conducted a biodegradation treatment that involved adding activated sludge (0.83%) to each stock solution. It has been previously established that activated sludge is an effective method of removing a variety of pollutants from wastewater (reviewed by Buttiglieri & Knepper, 2007). We used activated sludge in these treatments due to reports that sludge can decrease concentrations of ionic and nonionic surfactants by >95% and a variety of organochloride pesticides from between 75% and 91% (Buttiglieri & Knepper, 2007).

For daphnids, the degradation treatment involved exposing stock solutions to simulated sunlight in the laboratory for 30 consecutive days to induce photodegradation. Photodegradation has been extensively reported in the literature as an effective method of degrading pharmaceuticals and household products in surface waters (reviewed by Boreen et al., 2003). For example, surfactants, including linear alkyl benzene sulfonate, alkylphenol ethoxylates, and quaternary ammonium surfactants, were found to be effectively degraded by UV radiation (reviewed by Rebello et al., 2014).

Test organisms: Larval grass shrimp

Larval grass shrimp were obtained from gravid adult grass shrimp collected from Leadenwah Creek (Wadmalaw Island, South Carolina, USA). Adult shrimp were acclimated in the

laboratory in 37.9-L tanks at 24 °C, 20‰ salinity, and a 14:10-h light: dark cycle for 72 h. Shrimp were fed Tetramin Fish Flakes and newly hatched brine shrimp (*Artemia*). Following acclimation, gravid females were placed in brooding traps to allow larvae (zoea) to hatch and escape without interference (Key et al., 2007). Larvae from at least five females were pooled for all tests to minimize genetic differences. Larvae used in toxicity tests were <48 h old.

Test organisms: Juvenile *Daphnia magna*

Daphnids were purchased from Science Kit and Boreal Laboratories. Daphnids were held in the laboratory in 5-L aquaria using moderately hard reconstituted freshwater (61–120 mg CaCO₃/L; US Environmental Protection Agency [USEPA], 2002). Daphnids underwent a 48-h acclimation period prior to subculturing offspring. Offspring were collected and subcultured in 1000-ml holding beakers. Prior to each assay, juvenile daphnids were removed from their holding beaker and transported to a separate beaker, where they underwent a 24-h starvation period.

HCPs

Six green product formulations were utilized across the two studies, each representing a different consumer use category (i.e., all-purpose cleaner, dish detergent, mouthwash, insecticide, laundry detergent, and dishwasher gel). For product comparisons, the acute toxicity of each green product was compared to that of two conventional products from within that same use category. The two conventional products in each category (i.e., conventional products #1 and #2) were the same products used in both the grass shrimp and daphnid assays, with the exception of the all-purpose cleaner category, where two different conventional product formulations were tested for grass shrimp (indicated as “conventional products #3 and #4”). For the degradation studies (described below *Biodegradation study*), the toxicity of all HCPs (both green and conventional products) was compared pre- and postdegradation.

The concentrations used in the two studies were comparable to those reported to enter the environment. Indiscriminate use of household products releases these compounds and their metabolites into the environment. These compounds are ubiquitously present in all waters (surface, ground, and wastewaters) at concentrations ranging from ng/L to µg/L (Okoye et al., 2022). For example, nonionic surfactants were reported in the waters of Long Island Sound (USA) ranging from 1.4 to 4.5 µg/L (Lara-Martín et al., 2014) and the Krka River estuary (Croatia) ranging from <0.02 to 1.3 µg/L (Kvestak & Ahel, 1994). All HCPs used in the present study were purchased from grocery stores in Charleston, SC and reflect those that are readily available to consumers nationwide. The brand names of the HCPs utilized in present study are not included. The labels on all green products clearly indicated that they were being marketed as an eco-friendly alternative. All green products had leaves, flowers, or plants on their label, and

many included the terms “Earth” and “Green” directly in the product name. Other common claims made on green product labels included “ingredients derived from natural products, including essential oils and coconut-based cleaners,” “contains plant-based surfactants,” “plant-based biodegradable cleaning ingredients,” and “safe for family and environment.”

Biodegradation study

Solutions (600 ml total) of biodegraded green and conventional HCPs were obtained by diluting each HCP with moderately hard reconstituted freshwater (61–120 mg CaCO₃/L; US Geological Survey, 2018), then adding activated sludge (5 ml). The amount of HCP added to each solution represented the amount required to create a solution that was 10-fold higher than that required for the highest treatment in the acute toxicity tests. Activated sludge was collected from Plum Island wastewater treatment plant and refrigerated (~4 °C) until use. Activated sludge used in solutions was <1-week-old. Solutions with activated sludge were mixed for 3 h. Following mixing, particulate matter was allowed to settle out overnight. The supernatant was then collected and diluted with brackish water to form test solutions for the acute toxicity tests (see below *acute toxicity assays*). Control solutions for the biodegradation acute toxicity tests were prepared in the same manner as described previously except no HCP was added to the solution.

Photodegradation study

Solutions (600 ml total) of photodegraded green and conventional HCPs were obtained by diluting each HCP with moderately hard reconstituted freshwater (61–120 mg CaCO₃/L; USEPA, 2002), then placing solutions under a bank of fluorescent bulbs designed to simulate natural sunlight for 30 consecutive days. As described previously, the amount of HCP added to each solution represented the amount required to create a solution that was 10-fold higher than that required for the highest treatment in the acute toxicity tests. Fluorescent bulbs (Vision) used in the present study have a spectral distribution very similar to that of natural sunlight (color rendering index = 91). Ultraviolet-A (320–400 nm) and UV-B (292–330 nm) were quantified using a Macam Photometrics Model UV-203 IP-67 radiometer. All solutions were exposed to a light regime consisting of a UV-A intensity of $211.0 \pm 7.0 \mu\text{W}/\text{cm}^2$, a UV-B intensity of $9.8 \pm 2.4 \mu\text{W}/\text{cm}^2$, and a 16:8-h light: dark photoperiod. Beakers containing these solutions were replenished daily with moderately hard freshwater to maintain 600 ml of solution volume to ensure HCPs were not concentrated due to evaporation. Control solutions for the photodegradation acute toxicity tests were prepared in the same manner as described previously except no HCP was added to the solution.

Acute toxicity assays

The toxicity of each HCP to larval grass shrimp and juvenile daphnids was examined using two 48-h static acute toxicity

tests. One toxicity test was conducted using solutions of HCP directly from the product bottle. A second toxicity test was conducted using HCP solutions following a degradation treatment: a biodegradation treatment (activated sludge [0.83%]) for grass shrimp and a photodegradation treatment for daphnids (described in the section *Biodegradation study* and *Photodegradation study*). Stock solutions for each assay were obtained by mixing either the HCP directly from the product container or degraded HCP solutions with filtered brackish water for grass shrimp or moderately hard reconstituted freshwater for daphnids. Other test solutions were produced by serially diluting each stock solution. Preliminary range finder assays were conducted first to determine the concentrations necessary for the definitive assays (Fielder et al., 1992; Organisation for Economic Co-Operation and Development, 2003). Based on the results from the range finder assays, five concentrations and a control (0% HCP) for the definitive assays were tested. Test solutions were produced by serially diluting (50% dilution) the stock solution. For both grass shrimp and daphnids, test chambers (crystallizing dishes; 180 ml) contained 10 animals and 150 ml of product solutions or control water. There were three replicate chambers per treatment or control. Mortality was monitored and recorded at 24 and 48 h, and water quality measurements were recorded at the beginning and end of the definitive assays (Table 1). Although each degradation treatment represents an independent study that assessed toxicity using different degradation methods and species, the overarching hypothesis we wished to test across both was whether green or nongreen consumer products were toxic to aquatic invertebrates before and after degradation compared to conventional counterparts. Due to the complexity of active ingredients among the various products, it was beyond the scope of the present study to conduct chemical analyses to measure active ingredients.

Statistical analysis

All statistics were performed using SAS Studio (SAS Institute, 2018). Probit analysis was used to determine median lethal concentrations (LC50) and their associated 95% confidence intervals for the acute toxicity tests. Differences among LC50 values were tested using an LC50 ratio test (Wheeler et al., 2006) with a Bonferroni correction. Comparisons were made among all HCPs within a product category, both directly out of the container (pre-degradation) and post-degradation to determine if the green HCP was less toxic than the conventional HCPs. Comparisons were also made for each HCP

TABLE 1: Water quality measurements of reconstituted freshwater (daphnids) and filtered brackish water (grass shrimp) used during the present study (mean \pm SE)

Daphnids DO (mg/L)	Conductivity (μ S/cm)	pH
5 \pm 0.16	477 \pm 17.5	7.7 \pm 0.09
Grass shrimp DO (mg/L)	Salinity (ppt)	pH
6.6 \pm 0.08	29.2 \pm 0.20	7.7 \pm 0.04

DO = dissolved oxygen; SE = standard error.

pre- and post-degradation to determine how the degradation treatment influenced its toxicity. All values are reported as μ l HCP/L.

RESULTS AND DISCUSSION

Results from our assays demonstrated green and conventional HCPs were acutely toxic to both grass shrimp and daphnids (Tables 2 and 3). Differences in toxicity between products were likely influenced by interactions among various compounds within the product formulations, where their interactions could be antagonistic, additive, or synergistic. It was beyond the scope of the present study to identify the primary drivers of toxicity in each product or to delineate their interactions within the product formulation. Instead, we focus holistically on product formulation (as a single environmental contaminant) and discuss in general terms possible individual compounds in each product category that could be primarily responsible for the observed toxicity. For the two studies reported, we also observed differences in the responses between larval grass shrimp and juvenile daphnids. Differences were most likely the result of the different degradation processes, design, and matrixes (freshwater vs. brackish water). For example, DeLorenzo et al. (2009) found that the toxicity of xenobiotics, particularly pesticides, was lower in conditions with higher salinity concentrations. Below we report the LC50s for each product category across both studies. Average control mortalities in the biodegradation and photodegradation study were 6.1% and 6.2%, respectively.

Laundry detergents

Similar trends were observed in toxicity for both grass shrimp and daphnids (Tables 2 and 3). For the nondegraded HCPs, the toxicity of the green product was similar to that of conventional product #2; both of these HCPs were approximately 4-fold more toxic than conventional product #1. Following the biodegradation treatment, the green product became 1.5-fold more toxic to grass shrimp, whereas conventional products #1 and #2 became 2.3- and 5.4-fold less toxic, respectively (Table 2). The biodegraded green product was the most toxic HCP to grass shrimp. Following the photodegradation treatment, the toxicity of the green product did not change for daphnids, whereas the photodegraded conventional products #1 and #2 became 2.4- and 1.4-fold less toxic, respectively (Table 3). The photodegraded green product had similar toxicity to the photodegraded conventional product #2 to daphnids, whereas photodegraded conventional product #1 was the least toxic product.

Compared to other product categories, laundry detergents were among the most toxic HCPs tested. Individual compounds in the green product formulation differed from that of the conventional counterparts in that the green product contained sodium lauryl sulfate (anionic surfactant) and laureth-6 (surfactant). Conventional counterparts contained less toxic anionic surfactants such as alcohol ethoxysulfate, benzene

TABLE 2: Toxicity of green household products and two conventional product formulations to larval grass shrimp before and after biodegradation treatment

Category	Products tested	Nondegraded LC50 (95% CI)	Biodegraded LC50 (95% CI)	Biodegraded Relative toxicity	LC50 ratio test (p value of Z-test)
Laundry detergent	Green	20.0 (17.3–23.5)	13.7 (12.0–15.6)	Increase, 1.5x	<0.0001
	Conventional #1	86.5 (63.6–113.0)	200.5 (146.5–272.4)	Decrease, 2.3x	<0.0001
	Conventional #2	24.1 (–21.8–50.0)	129.1 (79.9–182.3)	Decrease, 5.4x	0.0124
	Product comparison	G C2 C1 G vs. C1 G vs. C2 C1 vs. C2	G C2 C1 G vs. C1 G vs. C2 C1 vs. C2		<0.0001; <0.0001 0.7719; <0.0001 0.0525; 0.0639
Dish detergent	Green	115.1 (95.6–142.5)	108.4 (89.7–132.1)	No difference	0.6600
	Conventional #1	163.6 (139.0–195.0)	133.5 (106.6–166.5)	No difference	0.1310
	Conventional #2	55.6 (45.6–69.7)	42.6 (37.2–50.3)	Increase—1.3x	0.0342
	Product comparison	C2 G C1 G vs. C1 G vs. C2 C1 vs. C2	C2 G C1 G vs. C1 G vs. C2 C1 vs. C2		0.0062; 0.1395 <0.0001; <0.0001 <0.0001; <0.0001
Mouthwash	Green	10,250 (8969–12,056)	8187 (6214–10,537)	No difference	0.1194
	Conventional #1	1920 (1516–2392)	629.6 (434.9–803.6)	Increase, 3.6x	<0.0001
	Conventional #2	19,508 (16,538–21,984)	9906 (8294–12,374)	Increase, 2.0x	<0.0001
	Product comparison	C1 G C2 G vs. C1 G vs. C2 C1 vs. C2	C1 G C2 G vs. C1 G vs. C2 C1 vs. C2		<0.0001; <0.0001 <0.0001; 0.2306 <0.0001; <0.0001
Insecticide	Green	14.6 (11.1–20.2)	12.7 (10.2–15.8)	No difference	0.4473
	Conventional #1	0.337 (0.274–0.434)	0.493 (0.353–0.689)	Decrease, 1.5x	0.0088
	Conventional #2	0.127 (0.083–0.176)	0.223 (0.174–0.290)	Decrease, 1.8x	0.0083
	Product comparison	C2 C1 G G vs. C1 G vs. C2 C1 vs. C2	C2 C1 G G vs. C1 G vs. C2 C1 vs. C2		<0.0001; <0.0001 <0.0001; <0.0001 <0.0001; <0.0001
Dishwasher gel	Green	36.9 (–16.2–71.0)	42.6 (16.6–65.3)	No difference	0.8068
	Conventional #1	375.3 (317.8–450.0)	757.8 (515.8–992.0)	Decrease, 2.0x	<0.0001
	Conventional #2	541.3 (432.0–692.4)	1204 (880.7–2062)	Decrease, 2.2x	0.0002
	Product comparison	G C1 C2 G vs. C1 G vs. C2 C1 vs. C2	G C1 C2 G vs. C1 G vs. C2 C1 vs. C2		<0.0001; <0.0001 <0.0001; <0.0001 <0.0001; <0.0001
All-purpose cleaner	Green	730.0 (–441.7–1091)	1241 (1077–1469)	No difference	0.1291
	Conventional #1	5994 (4382–7963)	12,428 (10,867–14,373)	Decrease, 2.0x	<0.0001
	Conventional #2	1182 (–87.8–1871)	2896 (2198–3964)	Decrease, 2.5x	0.0170
	Product comparison	G C2 C1 G vs. C1 G vs. C2 C1 vs. C2	G C2 C1 G vs. C1 G vs. C2 C1 vs. C2		<0.0001; <0.0001 0.3233; <0.0001 <0.0001; <0.0001

Units are in μL . For product comparisons, products are listed in order of decreasing toxicity (i.e., most toxic product listed first). Products sharing the same line have toxicity that is not significantly different from each other.

C1 = conventional product #1; C2 = conventional product #2; CI = confidence interval; G = green product; LC50 = median lethal concentration; N/A = not available.

Level of significance for nondegraded versus biodegraded comparisons is $p \leq 0.05$.

Level of significance for product comparisons is $p \leq 0.0167$ due to multiple comparisons (Bonferroni correction).

TABLE 3: Toxicity of green household products and two conventional product formulations to juvenile daphnids before and after a photodegradation treatment

Category	Products tested	Nondegraded LC50 (95% CI)	Photodegraded LC50 (95% CI)	Photodegraded, relative toxicity	LC50 ratio test (p value of Z-test)
Laundry detergent	Green	23.2 (19.3–30.4)	30.6 (23.5–40.2)	No difference	0.1658
	Conventional #1	77.2 (51.1–105.4)	184.0 (140.0–300.0)	Decrease, 2.4X	<0.0001
	Conventional #2	19.3 (12.8–26.3)	27.3 (21.3–42.2)	Decrease, 1.4X	<0.0001
Dish detergent	Product comparison	G C2 C1 G vs. C1 G vs. C2 C1 vs. C2	G C2 C1 G vs. C1 G vs. C2 C1 vs. C2		<0.0001; <0.0001 0.4290; 0.5184 <0.0001; <0.0001 0.0059
	Green	114.7 (80.3–148.9)	187.5 (146.6–239.0)	Decrease, 1.6X	0.9997
	Conventional #1	33.7 (N/A)	30.2 (16.3–42.2)	No difference	<0.0001
Mouthwash	Conventional #2	34.4 (29.1–41.3)	116.4 (87.2–188.8)	Decrease, 3.4X	<0.0001
	Product comparison	C1 C2 G G vs. C1 G vs. C2 C1 vs. C2	C1 C2 G G vs. C1 G vs. C2 C1 vs. C2		<0.0001; <0.0001 <0.0001; 0.0349 0.9997; <0.0001 0.0071
	Green	249.9 (199.0–318.3)	224.4 (184.6–277.4)	Increase, 1.1X	<0.0001
Insecticide	Conventional #1	7021 (5078–11,373)	621.7 (N/A)	Increase, 11.3X	<0.0001
	Conventional #2	7735 (5554–9978)	25,297 (13,500–47,000)	Decrease, 3.3X	<0.0001
	Product comparison	G C1 C2 G vs. C1 G vs. C2 C1 vs. C2	G C1 C2 G vs. C1 G vs. C2 C1 vs. C2		<0.0001; <0.0001 <0.0001; <0.0001 <0.9987; <0.0001 <0.0001
Dishwasher gel	Green	388.3 (270.8–750.4)	186.1 (137.6–244.3)	Increase, 2.1X	<0.0001
	Conventional #1	4.77 (2.51–6.78)	0.36 (0.29–0.46)	Increase, 13.3X	<0.0001
	Conventional #2	8.23 (5.12–12.0)	0.13 (0.09–0.18)	Increase, 63.3X	<0.0001
All-purpose cleaner	Product comparison	C1 C2 G G vs. C1 G vs. C2 C1 vs. C2	C2 C1 G G vs. C1 G vs. C2 C1 vs. C2		<0.0001; <0.0001 <0.0001; <0.0001 <0.0001; <0.0001 <0.0001
	Green	3.16 (2.90–5.78)	36.9 (28.5–71.0)	Decrease, 11.7X	<0.0001
	Conventional #1	556.0 (N/A)	373.9 (316.4–453.3)	Increase, 1.5X	<0.0001
All-purpose cleaner	Conventional #2	124.1 (50.0–250.0)	551.4 (453.3–648.3)	Decrease, 1.4X	<0.0001
	Product comparison	G C2 C1 G vs. C1 G vs. C2 C1 vs. C2	G C1 C2 G vs. C1 G vs. C2 C1 vs. C2		<0.0001; <0.0001 <0.0001; <0.0001 <0.0001; <0.0001 <0.0001
	Green	1645 (1105–2,160)	360.0 (253.3–470.0)	Increase, 4.6X	<0.0001
All-purpose cleaner	Conventional #3	150.9 (113.2–188.0)	1861 (1535–2363)	Decrease, 12.3X	<0.0001
	Conventional #4	599.5 (452.2–761.4)	3645 (2676–7702)	Decrease, 6.1X	<0.0001
	Product comparison	C3 C4 G G vs. C3 G vs. C4 C3 vs. C4	G C3 C4 G vs. C3 G vs. C4 C3 vs. C4		<0.0001; <0.0001 <0.0001; <0.0001 <0.0001; <0.0001 <0.0001

Units are in μL product/L. For product comparisons, products are listed in order of decreasing toxicity (i.e., most toxic product listed first). Products sharing the same line have toxicity that is not significantly different from each other.

C1 = conventional product #1; C2 = conventional product #2; CI = confidence interval; G = green product; LC50 = median lethal concentration; N/A = not available.

Level of significance for nondegraded versus biodegraded comparisons is $p \leq 0.05$.

Level of significance for product comparisons is $p \leq 0.0167$ due to multiple comparisons (Bonferroni correction).

sulfonic acid, and alcohol sulfates (Dowden & Bennett, 1965; Mohammed, 2007; Warne & Schiffko, 1999). Furthermore, conventional counterpart #1 contained biodegradable surfactants, which likely explains the lower toxicity compared to the other products. Surfactants make up approximately 15%–40% of all detergent compounds (Zhang, 2007). Decades-long research has identified surfactants as toxic substances to aquatic organisms (Salmani et al., 2021). Based on this, it is likely that surfactants were at least partially responsible for the acute toxicity observed in the HCPs tested in the laundry detergent category. Surfactant contributions to overall toxicity may be lessened in the environment due to secondary wastewater treatment, which can remove more than 90% of surfactants, and the presence of organic matter and sediments, which can alter their bioavailability (Warne & Schiffko, 1999).

Dish detergents

The green product was significantly more toxic to grass shrimp than conventional product #1 and significantly less toxic than conventional product #2 (Table 2). For daphnids, the green product was significantly less toxic than both conventional products #1 and #2 (Table 3). Following the biodegradation treatment, the toxicity of the green product and conventional product #1 did not change relative to that of the nondegraded product to grass shrimp (Table 2). By contrast, conventional product #2 became 1.3-fold more toxic. Following the photodegradation treatment, the photodegraded green product and conventional product #2 became 1.6- and 3.4-fold less toxic to grass shrimp (Table 3). The toxicity of photodegraded conventional product #1 did not change relative to that of the nondegraded product. The photodegraded green product had similar toxicity to the photodegraded conventional product #2 to daphnids, and both were less toxic than photodegraded conventional product #1 (Table 3).

The green product contained ingredients unique and relative to that of the two conventional products. Among those were coconut-based cleaning agents, sodium lauryl, and alkyl dimethylamine. The conventional counterparts contained anionic and nonionic surfactants that have been documented to cause mortality in daphnia (alcohol ethoxy sulfate, sulfate, benzene sulfonic acid, alcohol sulfates, and alcohol ethoxylate; Dowden & Bennett, 1965; Warne & Schiffko, 1999). The sensitivity of daphnia to these compounds might explain why the LC50s were lower in the exposures with daphnids compared to grass shrimp. It is of note that none of the tested biodegraded dish detergent products became less toxic. One explanation is that perhaps these approximately 15-h biodegradation treatments (3 h of product mixing, then overnight settling) was simply not enough time to allow for significant degradation of the surfactants used in dish detergents. Another explanation may be the quality of the activated sludge used in this assay. Previous studies have indicated that the quality of activated sludge can vary widely, with some samples demonstrating low colonization, poor biological depuration, and poor biological activity, resulting in a sludge that is ineffective at degrading

compounds (Madoni, 1994; Papadimitriou et al., 2007). Because we were using fresh (<1 week old) activated sludge for each product category, it is possible that sludge quality varied from one product category to the next. Certainly, further research on this topic is warranted.

Mouthwash

The green product was significantly less toxic to grass shrimp than conventional product #1 but significantly more toxic than conventional product #2 (Table 2). Daphnids were 40-fold more sensitive to the green product than grass shrimp. Compared to conventional products #1 and #2, the green product formulation was approximately 30-fold more toxic to daphnids (Table 3).

Following the biodegradation treatment, the green product did not change its toxicity relative to the nondegraded product to grass shrimp. By contrast, the conventional products #1 and #2 became 3.6- and 2.0-fold more toxic, respectively (Table 2). Following the photodegradation treatment, the toxicity of the green product significantly increased 1.1-fold relative to the nondegraded green product. Conventional product #1 became 11.3-fold more toxic, whereas conventional product #2 became 3.3-fold less toxic following the photodegradation treatment. The photodegraded green product was significantly more toxic than the photodegraded conventional products (Table 3).

Compared to other product categories, mouthwashes, in general, were the least toxic category of HCPs tested. The only exception was the relatively high toxicity observed in the green product formulation to daphnids. It is important to note that the green product contained zinc chloride in its formulation, which has been documented to cause acute toxicity in *D. magna* at concentrations ranging from 0.7 to 11 mg/L (Ergonul et al., 2012). While this is higher than the exposure levels used in the present study, its mixture with other compounds could have resulted in a potentiated effect where higher toxicity was observed in the green product. Zinc adsorption has also been reported to increase with salinity, making the compound less available (Chesne & Kim, 2014). Thus, the presence of sodium chloride in the brackish water explained the lower toxicity in the grass shrimp assays. Along with zinc, sodium hydroxide is toxic to daphnids (55 mg/L; Oberdoster et al., 2006). However, in a mixture, the combination can yield a synergistic effect, resulting in higher mortality at lower concentrations.

Insecticides

All three insecticides were more toxic to grass shrimp than daphnids. The green product was significantly less toxic to grass shrimp than both conventional products #1 and #2 (43.3- and 115-fold, respectively; Table 2). For daphnids, the green product was also significantly less toxic than conventional products #1 and #2 (81.4- and 47.2-fold, respectively; Table 3). Following the biodegradation treatment, the toxicity of the green product did not change relative to the

nondegraded product to grass shrimp, and it remained the least toxic HCP in this category (Table 2). By contrast, conventional products #1 and #2 became 1.5- and 1.8-fold less toxic, respectively. Following the photodegradation treatment, the toxicity of the green product became 2.1-fold more toxic to daphnids (Table 3). Conventional products #1 and #2 also became significantly more toxic (13.3- and 63.3-fold, respectively; Table 3). The photodegraded green product remained the least toxic photodegraded HCP in this category. Both conventional counterparts contained either bifenthrin or lambda-cyhalothrin as active ingredients. These compounds are acutely toxic to aquatic organisms at doses as low as 0.32–0.39 µg/L (Barata et al., 2006; Mokry & Hoagland, 1990). The green product contained cyfluthrin, whose LC50 is 0.52 mg/L, which is less toxic than bifenthrin or lambda-cyhalothrin (Brausch & Smith, 2009). It is of note that toxicity increased following photodegradation, which may have been the result of photoactivation and photomodification, where exposure to UV light increases toxicity, as seen with polycyclic aromatic hydrocarbons (Fu et al., 2012).

Dishwasher gel

For grass shrimp and daphnids, the green product was the most toxic among tested dishwasher gels (Tables 2 and 3). The nondegraded green product was 10.2- and 14.7-fold more toxic than conventional products #1 and #2. Following the biodegradation treatment, the toxicity of the green product did not change relative to the nondegraded product to grass shrimp, and it remained the most toxic biodegraded HCP in this category (Table 2). Conventional products #1 and #2 became 2.0- and 2.2-fold less toxic following the biodegradation treatment, respectively. In daphnids, the nondegraded green product was 11.7-fold more toxic than in grass shrimp. The green product was 177.6- and 39.3-fold more toxic than conventional products #1 and #2, respectively (Table 3). Following the photodegradation treatment, the green product became 11.7-fold less toxic to daphnids, whereas conventional product #1 became 1.5-fold more toxic and conventional product #2 became 1.4-fold less toxic (Table 3). The photodegraded green product remained the most toxic photodegraded HCP tested in this category.

The product formulations for each of the products differed in composition. Similar to the laundry detergent, the green product contained laureth-6, a more toxic surfactant than the compounds used in the conventional counterparts (alcohol ethoxylate and sodium salts). The presence of laureth-6 may have been the driver that influenced toxicity, because the

green product consistently was more toxic among experiments both pre- and postdegradation.

All-purpose cleaner

The toxicity of the green product varied between the grass shrimp and daphnids. For grass shrimp, the green product had similar toxicity to conventional product #2, and both were significantly more toxic than conventional product #1 (Table 2). Following the biodegradation treatment, the toxicity of the green product did not change, whereas the toxicity of conventional products #1 and #2 decreased 2.0- and 2.2-fold, respectively (Table 2). For daphnids, the green product was significantly less toxic than either conventional product #3 or #4 (Table 3). Following the photodegradation treatment, the toxicity of the green product increased 4.6-fold, whereas the toxicity of the conventional products #3 and #4 decreased 12.3- and 6.1-fold, respectively (Table 3). The photodegraded green product was significantly more toxic than either of the photodegraded conventional products.

Similar to that which was observed with the photodegraded green insecticide, the toxicity of the all-purpose green product increased following the photodegradation treatment. This suggests that photomodified and/or photoreactive compounds were produced which increased the toxicity of the product. The green product also contained biodegradable preservatives, which may have ameliorated the toxicity, albeit not significantly, of the biodegraded product. It is of note that all four conventional products tested in the all-purpose cleaner category exhibited significantly decreased toxicity following their respective degradation treatment. That same trend was not exhibited by the green product.

Despite claims that these eco-friendly or “green” products are less toxic and more degradable than conventional counterparts, findings from the present study suggest that this is not always the case. Our biodegradation study found that 50% of the green products were less toxic than their conventional counterparts when exposed to grass shrimp. None of the green products demonstrated decreased toxicity following biodegradation treatment (Table 4). However, 44% of the conventional counterparts decreased in toxicity follow degradation. Following biodegradation 67% of the green products became less toxic than at least one of the conventional counterparts (Table 4).

In the photodegradation study, 50% of the green products were less toxic than their conventional counterparts, yet only 33% of the green products became less toxic after degradation (Table 4). Following photodegradation, 87.5% of the

TABLE 4: Percentage of products tested meeting each of the present study criteria

Study criteria	Grass shrimp (%)	Daphnids (%)
Green products less toxic than conventional products before degradation	50	50
Green products demonstrating decreased toxicity following degradation treatment	0	33.3
Conventional products demonstrating decreased toxicity following degradation treatment	44.4	87.5
Green product less toxic than at least one conventional product after degradation treatment	66.7	50

conventional counterparts became less toxic and 50% of the green products became less toxic compared to their conventional counterparts (Table 4).

SUMMARY AND CONCLUSION

In our HCP comparisons for grass shrimp, only one green product formulation (insecticide) was less toxic than conventional products. The toxicity of most green product formulations in other categories was similar to at least one of the two comparative products. The major exception was the green product in the dishwasher gel category, which was among the most toxic HCPs tested across all categories. For daphnids, green products in three categories (dish detergent, insecticide, and all-purpose cleaner) were less toxic than both conventional products tested. The green product in the laundry detergent category had similar toxicity to one of the conventional products, while the green product in the mouthwash and dishwasher gel categories had toxicity that was higher than that of both conventional products tested. Based on the LC50s reported for green and conventional counterparts in Tables 3 and 4, if placed in the USEPA toxicity scale, each product tested would be classified as extremely toxic (Appendix A, USEPA, n.d.).

Following the biodegradation treatment, none of the green products became less toxic to grass shrimp. The toxicity of the photodegraded laundry detergent became more toxic relative to the nondegraded product. By contrast, the decreased toxicity of those comparative products subjected to the biodegradation treatment was observed in four of the six product categories. Following the photodegradation treatment for daphnids, two green product formulations (dish detergent and dishwasher gel) became less toxic. By contrast, the photodegraded green product in the laundry detergent category had similar toxicity to the nondegraded product. Green products exposed to the photodegradation treatment in the mouthwash, insecticide, and all-purpose cleaner categories were more toxic than the nondegraded product.

Despite manufacturer claims and consumer assumptions that green HCPs are less toxic and more degradable than conventional HCPs, these results suggest this is not always the case. More work should be dedicated to understanding how these products may impact nontarget organisms in the environment. There remains the need to understand the interactions among compounds within these product formulations and how they influence toxicity. Our results demonstrate that the end-product formulations of green products were not necessarily less toxic before or after degradation treatments, suggesting that consumer skepticism over manufacturer claims is justified. One of the green products tested in the present study (in the dish detergent category) had received the USEPA's Design for the Environment certification, and it was the least toxic HCP in that category to daphnids. We also observed a decrease in toxicity for that product following photodegradation treatment. Based on this limited observation, we suggest that there may be an opportunity for more effort to educate consumers about the Design for the Environment

certification and how they may look for it on product labels so that they may make informed decisions regarding green product purchases.

Acknowledgments—The present study was conducted as part of the Citadel Undergraduate Research Experience (CURE). Funding for this project was provided through a Faculty Research Grant from The Citadel Foundation to J. Weinstein.

Disclaimer—The authors have no relevant financial or nonfinancial interests to disclose.

Author Contributions Statement—**Austin D. Gray:** Investigation; Data curation; Validation; Writing—original draft; Writing—review & editing; Visualization; Formal analysis. **Jonté Miller:** Investigation; Validation; Formal analysis. **John Weinstein:** Conceptualization; Resources; Supervision; Software; Writing—review & editing.

Data Availability Statement—Raw data and LC50 information can be accessed at FigShare at https://figshare.com/articles/dataset/Gray_Greenstudy_raw_data/20235879.

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