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Survey of Pesticide Products Sold in Retail Stores in Northern California, 2017

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Abstract

The California Department of Pesticide Regulation's (CDPR) Surface Water Protection Program (SWPP) staff conducted a survey of seven retail locations in Northern California to identify the active ingredients (AIs) in pesticide products currently available to the general public. Pesticide use by professional applicators is tracked in CDPR's Pesticide Use Reporting system (PUR); however, applications by residents are not. To get a more complete understanding of AIs in current use, it is important to track the changes in the residential pesticide market. AIs identified were categorized according to application site, use type, aquatic toxicity, and formulation. Results were compared to previous retail surveys and monitoring reports of ambient surface water sampling by CDPR. A total of 593 products and 168 AIs were identified. 2,4-D, dimethylamine salt (2,4-D), imidacloprid, MCPP-P, dimethylamine salt, and isopropylamine glyphosate were the most prevalent AIs. Four AIs (spinosad, tau-fluvalinate, prallethrin, pyrethrin) of outdoor use products not currently identified by CDPR's urban prioritization model based on reported use were noted as monitoring candidates based on consumer product sales and aquatic toxicity data. Pyrethroids were identified in the most number of indoor use products, implicating their potential as a source to wastewater. Personal care products are unlikely to serve as a source of pesticides of concern to either surface runoff or down-the-drain pathways. Information gained during this survey will be utilized to fill in data gaps on pesticide use patterns and source identification efforts.

1.0 Introduction

Pesticides have been detected in several watersheds receiving urban runoff throughout California [1-3]. Several pyrethroid insecticides and fipronil are of special concern, as concentrations detected in receiving waters often exceed aquatic toxicity thresholds for aquatic invertebrate species [4, 5]. The California Department of Pesticide Regulation (CDPR) is mandated by the California Food and Ag Code to protect the environment against deleterious effects of pesticides found in runoff. A clear understanding of pesticide sources and environmental pathways is critical for the development of effective mitigation strategies to reduce pesticide concentrations in runoff (Figure 1).

Urban runoff generated by rain events or irrigation practices has the potential to transport pesticides offsite into adjacent waterways [6]. Monitoring efforts have implicated applications made to outdoor urban landscapes as a major contributor to surface water pesticide concentrations [7, 8]. As part of the continuous evaluation process, CDPR has developed a model that prioritizes current-use pesticides for monitoring based on aquatic toxicity values and pesticide use reported to CDPR's Pesticide Use Reporting (PUR) database [9, 10]. Licensed applicators are required to submit use data on structural and landscape maintenance applications as monthly use reports to the PUR. Applications made by individual residents are not reported; therefore, this use pattern is not incorporated into the monitoring prioritization. It is essential to consider pesticides used by individuals to ensure pesticides of ecological concern are not overlooked through monitoring efforts.

There is a growing concern of the potential of pesticides to enter the waste stream through indoor applications and subsequent washing activities. Recent work has detected pyrethroid insecticides in wastewater effluent [11, 12]. The authors concluded that pesticides disposed down the drain contribute to substantial pesticide loading to the waste stream at concentrations that exceed toxicity thresholds for sensitive aquatic species [12]. Other research has found pyrethroids attached to dust collected within residential indoor dwellings [13]. There is currently very little information directly linking indoor pesticide use practices to wastewater concentrations. However, a recent study conducted by CDPR demonstrated the potential for flea control spot-on pet products to wash off at a rate that could account for the majority of measured fipronil concentrations detected at local municipal wastewater treatment plants [14].

The market is continually shifting with new products being introduced. It is imperative for regulatory agencies to have a clear understanding of products and active ingredients available to the public sector. Previous store surveys conducted by CDPR's Surface Water Protection Program (SWPP) focused on either outdoor or indoor-use products [15, 16]. For this study, CDPR surveyed seven large retail outlets in the Sacramento, California region for all pesticide products labelled for indoor, outdoor, and personal care use. Pet products were not addressed in this survey as the environmental pathway has been well established and the relevant active ingredients have already been identified in a past survey conducted by CDPR [14, 16]. This survey will assist CDPR identify pesticides of concern not identified in the prioritization model and provide data necessary for developing an environmental-pathway model of pesticides entering the waste stream. Ultimately, this information will assist regulatory agencies to develop effective mitigation strategies in the protection of aquatic ecosystems.

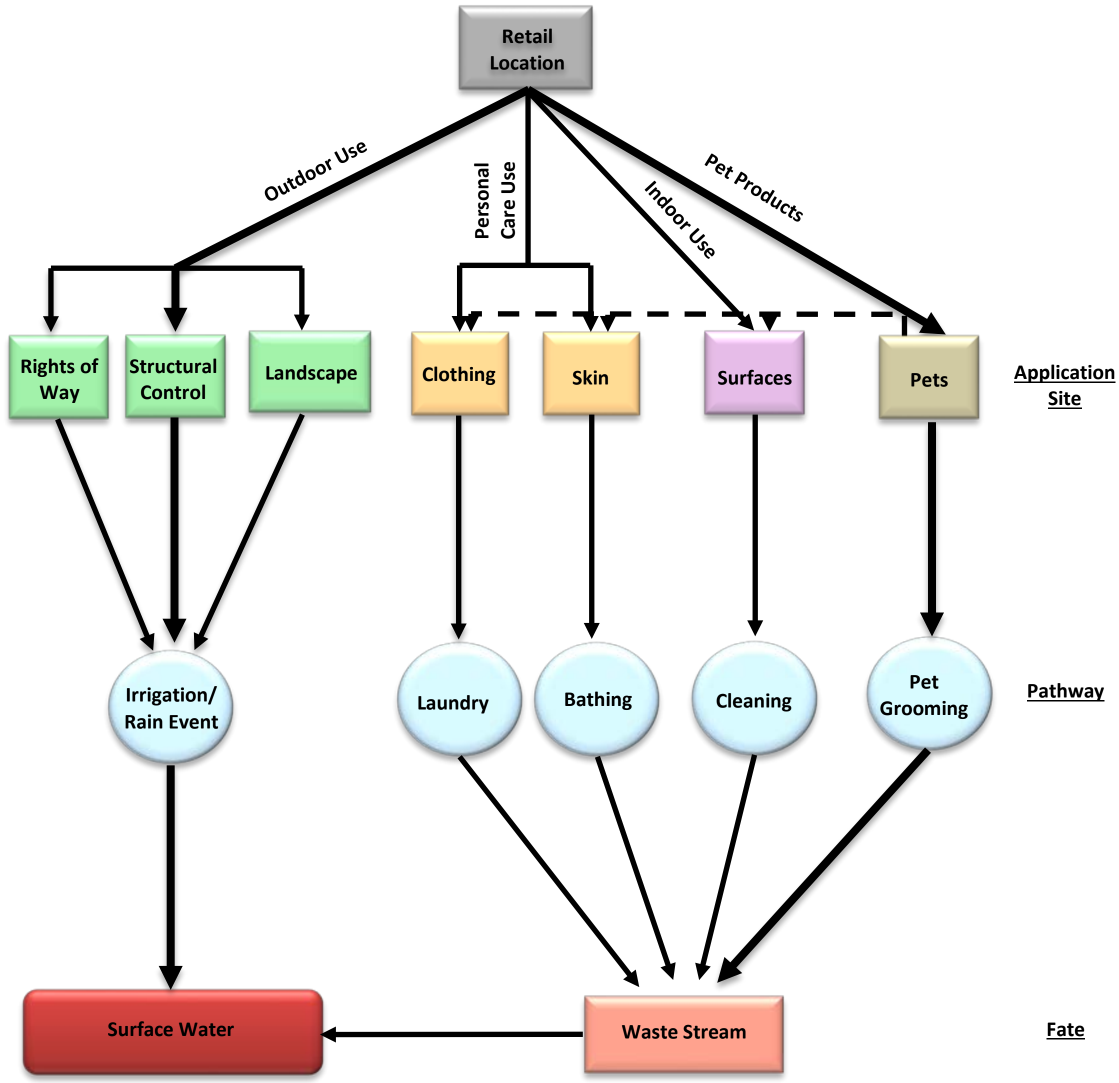

Figure 1. Conceptual model of potential environmental pathways for pesticides to enter surface waters. Darker lines indicate pathway supported by monitoring and/or research data. Dotted lines indicate indirect exposure route.

The specific objectives of conducting this store survey include:

1. Identify currently available pesticide products and associated active ingredients (AIs) available for residential use.
2. Evaluate products according to label application site.
3. Determine primary chemical classes by use patterns.

4. Evaluate environmental toxicity spectrum of AIs available in home use products.

5. Identify pesticides of concern not currently monitored by CDPR urban monitoring program.

6. Identify pesticides with potential to enter the waste stream.

2.0 Methods

A survey of pesticide products was conducted at seven retail locations in the Sacramento region in Northern California between March and May 2017. All products containing a pesticidal active ingredient (AI) were recorded, excluding pet care products. The following information was recorded for each product:

- Manufacturer Name
- Product Name
- Formulation
- Active Ingredients
- Percentage of Active Ingredients
- Application Site (indoor, outdoor, both, or personal care)

Volume was not considered a unique qualifier. Unique product numbers were obtained for products using the CDPR product label database. Pesticides determined by the US EPA to be of minimum risk to human health or the environment are exempt from registration by the Federal Insecticide, Fungicide, and Rodenticide Act; therefore, products containing only exempted AIs have no corresponding product numbers (Appendix 1).

Application site was determined directly from the label as registered for indoor use, outdoor use, or both. Products labeled for direct application to skin or clothing were designated as personal care use. Products labeled for both were counted in both the indoor and outdoor use categories, therefore represented in more than one analysis section below.

Active ingredients were assessed independently as products may contain more than one AI. AIs were categorized by classification and formulation. For simplicity, all herbicides were grouped together. Natural products include many low risk AIs including botanicals, animal derivatives, oils, soaps, and inorganic compounds. Product formulation type was also recorded (Appendix 2).

The reference toxicity values represent the minimum US EPA aquatic benchmark (BM) or a benchmark equivalent based on aquatic toxicity tests reported by the International Union of Pure and Applied Chemistry (Appendix 1). AIs were categorized from very low to very high toxicity (Table 1). AIs with no listed BM were assigned a toxicity value of “na”.

Table 1. Toxicity range values (μg/L) for AIs.

Toxicity Range (µg/L)	Category
> 1,000	Very Low Toxicity
101 - 1000	Low Toxicity
1.1 - 100	Moderate Toxicity
0.1 - 1	High Toxicity
< 0.1	Very High Toxicity

3.0 Results and Discussion

3.1 All Products

Five hundred ninety-three unique products and 168 AIs were identified at the seven retail locations surveyed (Appendix 3). The AI 2,4-D, dimethylamine salt was found in the most products (43), followed by imidacloprid (32), and MCPP-P, dimethylamine salt (32) (Figure 2). AIs used as insecticides and herbicides make up 56% of the AIs present (Appendix 4). There is a wide selection of available formulations, the most prevalent being ready-to-use, concentrate, and granule (54% combined) (Appendix 5). The AIs identified from all the products exhibited a wide range of aquatic toxicity, with an approximately similar number of very low and very high toxic AIs (Appendix 6).

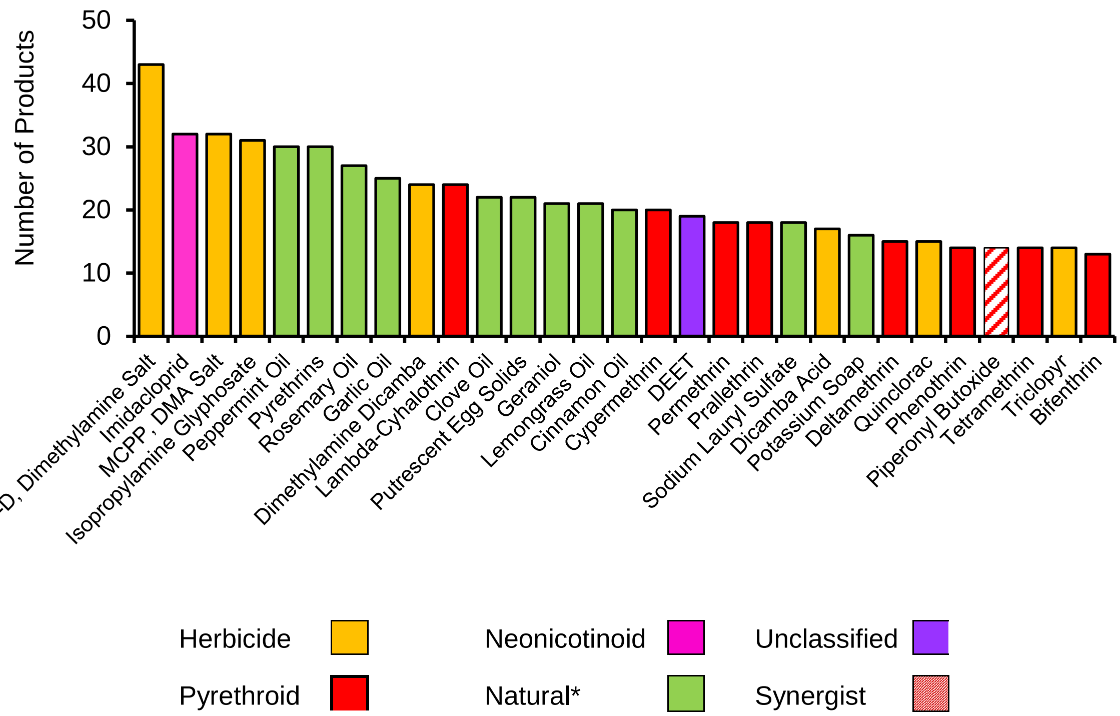

Figure 2. Number of products, designed for all use types categorized by chemical class. All herbicides classified together. Natural category includes oils, soaps, botanicals, animal derivatives, and inorganic classes.

3.2 Outdoor Products

Five hundred twenty-four products were designated for outdoor use containing 158 associated AIs (Appendix 3). The herbicides 2,4-D, dimethylamine salt (43), MCPP-P (32), and isopropylamine glyphosate (31) were found in the most number of products (Figure 3). The neonicotinoid imidacloprid is the most prevalent insecticide, found in 25 products. Several pyrethroids are also common in outdoor pest control products, including lambda-cyhalothrin (22), permethrin (15), deltamethrin (14), and bifenthrin (13). A store survey conducted in 2010 also identified glyphosate, 2,4-D, dimethylamine salt, dicamba, imidacloprid, lambda-cyhalothrin, bifenthrin and permethrin as the most frequent AIs found in outdoor use products [15]. This indicates that there has not been a drastic shift in the outdoor product market to other compounds since the previous survey. Insecticides are the most prevalent use type for outdoor products (34%), followed by herbicides (23%) and fungicides (13%) (Appendix 7). Ready to use (RTU), concentrates, and granules are the most common formulations (65%) (Appendix 8).

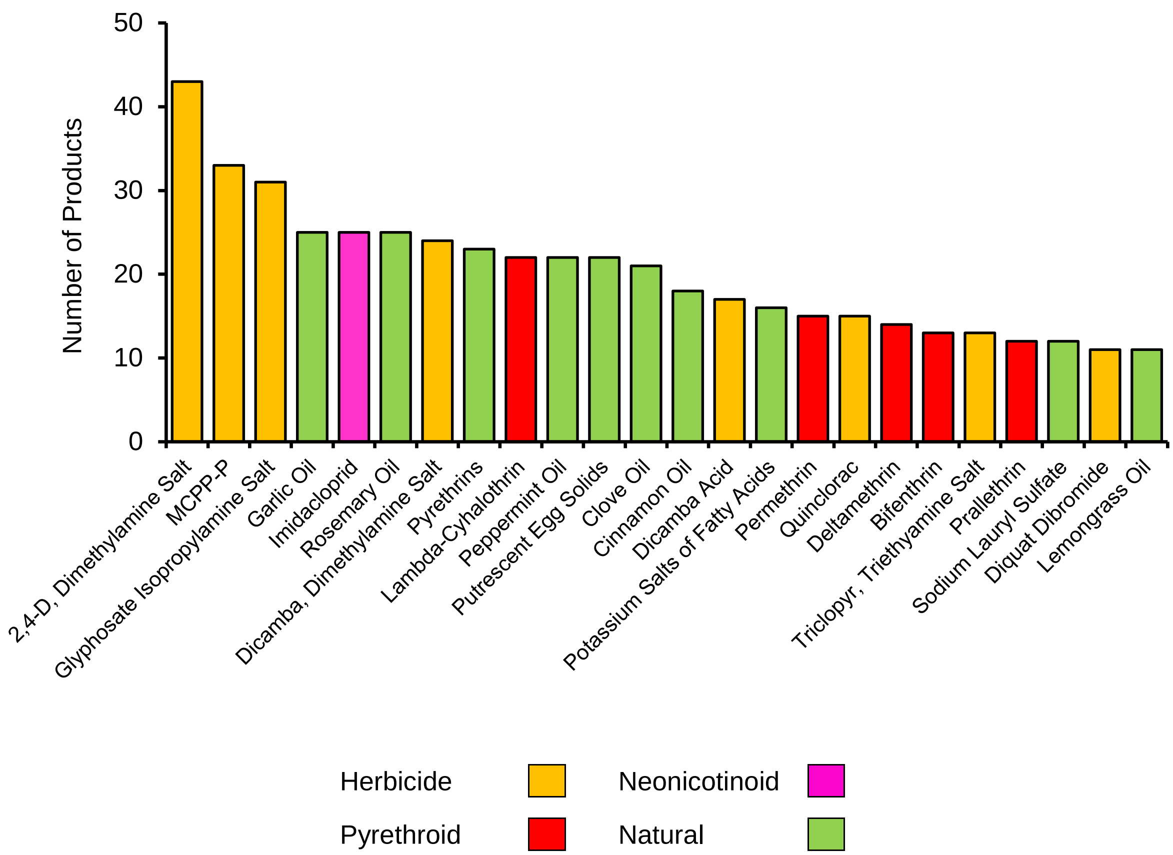

Figure 3. Number of products, designed for outdoor use categorized by chemical class. All herbicides classified together. Natural category includes oils, soaps, botanicals, animal derivatives, and inorganic classes.

Many of the AIs identified in products registered for outdoor use are frequently detected in California surface waters located within the region the surveys were conducted. CDPR detected

2,4-D in 93% of water samples collected in its ambient surface water monitoring of urban areas of Northern California between July 2015 and June 2016, making 2,4-D the most frequently detected pesticide [17]. Several other herbicides have been detected at high frequency, including dicamba (59%) and triclopyr (52%). Although bifenthrin was identified in fewer products than other pyrethroids, it is the most commonly detected insecticide with a detection frequency of 83%, followed by imidacloprid (44%) and permethrin (11%). Of the top five pyrethroids present in outdoor products, four (i.e., bifenthrin, lambda-cyhalothrin, permethrin, and deltamethrin) have been detected in surface waters above their respective minimum US EPA benchmarks (BM); [17]. Fipronil and diuron were not identified in any outdoor use product during this survey, but both are frequently detected in surface waters [17], indicating the sources of these AIs to surface water are primarily from outdoor applications by licensed applicators. Product formulations influence the fate and transport of pesticides. Pesticides applied to impervious surfaces around structures are more prone to offsite transport through irrigation and rainfall runoff [18, 19]. Fifty-eight percent of products were formulated as ready-to-use sprays or concentrates, which are more likely to be directly applied to impervious surfaces than granules or baits (Appendix 8).

The identified pesticides used in outdoor settings have a wide range of associated aquatic toxicity (Appendix 9). Aquatic BM values are incorporated into CDPR's Surface Water Monitoring Prioritization (SWMP) model [10]. Due to the lack of use data associated with consumer products, it is not possible to prioritize consumer-use AIs. However, it is critical to evaluate consumer-use AIs to ensure monitoring programs are not overlooking AIs with the potential to contaminate surface waters. Over two hundred outdoor use products were identified in the store surveys containing 14 AIs with associated high (0.11–1 ppb) or very high (≤ 0.1 ppb) aquatic toxicity BMs (Table 2 and Appendix 9). The model does not recommend five of the high-toxicity AIs for monitoring based on their physicochemical properties. Three AIs are only contained within bait products or repellent candles, which have limited exposure for offsite transport. For the six remaining AIs with high toxicity and runoff potential, a prioritization evaluation was conducted using product-sales data. The prioritization model was used to rank pesticides used for urban landscapes on a statewide basis. The five-year (2012–2016) average sales of the AI in products identified in this survey were added to the reported use of each AI. An inherent assumption to this approach is that the amount of consumer-use pesticide products sold during this period would approximate the use rate by non-professionals in urban areas. The prioritization rank was re-calculated using the adjusted use scores. CDPR's urban monitoring program utilizes a final prioritization value of nine as the recommended cutoff for monitoring [20]. Using the sales-enhanced use data, four of the AIs identified in the store surveys qualify for monitoring; spinosad, tau-fluvalinate, prallethrin, and pyrethrins. Prallethrin is currently undergoing method development to incorporate into future monitoring activities (Sue Peoples, personal communication, 2018).

Table 2. AIs with high associated toxicity identified in outdoor use products*.

Active Ingredient	DPR Number	Toxicity BM (ug/L)	REF	Monitored?	False?	Note
Avermectin B1	2254	0.17	OPP	N	n	all baits
Difenoconazole	5024	0.86	OPP	N	n	1 product, RTU
Hexaflumuron	3899	0.0555	OPP	N	n	1 product, bait
Indaziflam	5999	0.019	IUPAC	N	n	2 products, conc and RTU
Metofluthrin	5943	0.6	OPP	N	n	3 products, personal use or burn
Prallethrin	3985	0.65	OPP	N	n	18 products, sprays
Pyrethrins	510	0.86	OPP	N	n	30 products, sprays
Spinosad	3983	0.6	OPP	N	n	8 products, RTU and granules
Tau-Fluvalinate	2195	0.064	OPP	N	n	4 products (1)
Chlorothalonil	677	0.6	OPP	N	y	
Dichlorvos	187	0.0058	OPP	N	y	
Diquat Dibromide	229	0.75	OPP	N	y	
Halosulfuran-Methyl	3919	0.2	IUPAC	N	y	
Phenothrin (Sumithrin)	2093	0.47	OPP	N	y	

*Based on average sales data of products containing AIs (2012–2016). OPP = USEPA; IUPAC=International Union of Pure and Applied Chemistry

3.3 Indoor Products

One hundred forty products designated for indoor use containing 66 AIs were identified at the seven retail locations (Appendix 3). Insecticides make up the majority of indoor use products (56%), and 74% of products were formulated as aerosol spray (41), bait (32) or ready-to-use (31) (Appendices 10–11). Similar to outdoor uses, over 200 products were identified with AIs that have high or very high associated aquatic toxicity (Appendix 12).

Pyrethroids were found in the most number of products, including cypermethrin (19), followed by pyrethrins (15), and deltamethrin (14) (Figure 6). Pyrethroids are common AIs in aerosol sprays and fogger products (36%) (Appendices 3 and 11). Product formulation appears to be an important parameter for estimating pesticide availability for transfer to the waste stream. Keenan (2009) found cypermethrin evenly distributed on various surfaces throughout a test room after dispersing a fogger in the center of the room, with up to 30% available for transfer [21]. The authors estimated a much lower surface depositional pattern away from the application area for indoor perimeter , crack-and-crevice , and spot applications [22]. There is clear evidence that AIs applied indoors from home-use products are available for transfer; however, more research is needed to evaluate the wash-off potential of AIs dispersed on various surfaces within a structure.

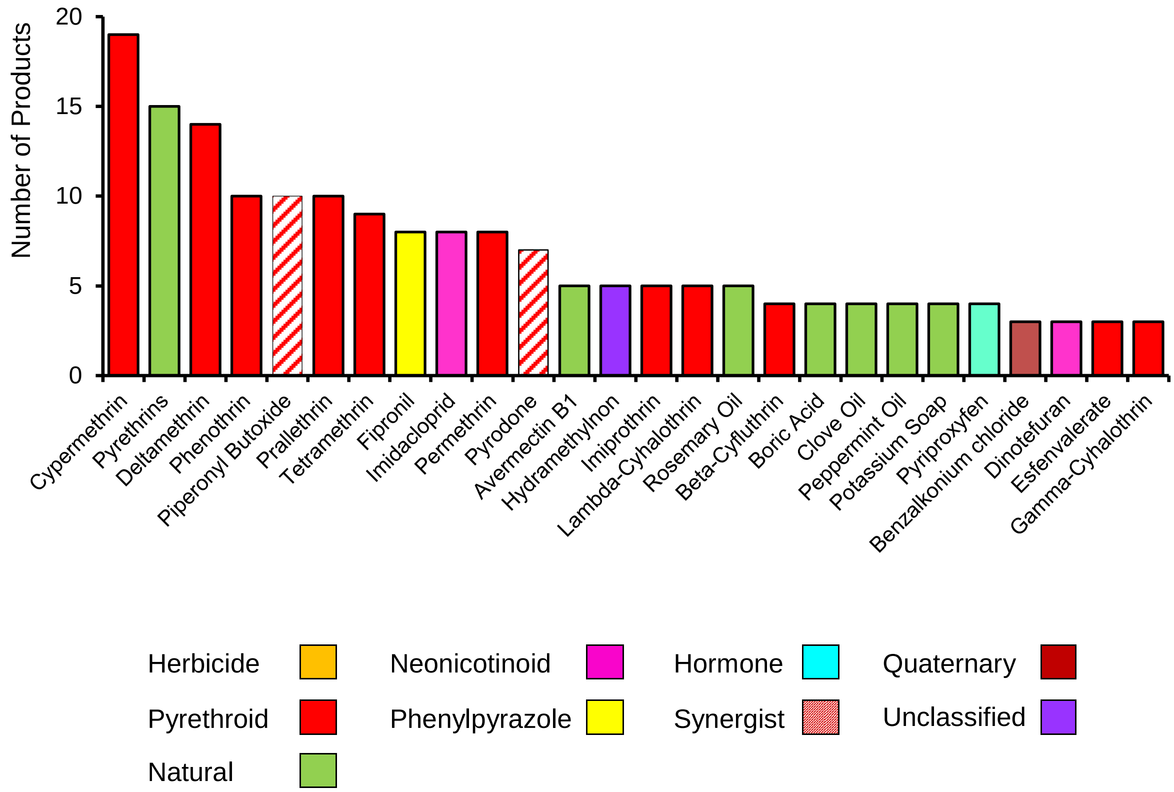

Figure 6. Number of products, designed for indoor use categorized by chemical class. All herbicides classified together. Natural category includes oils, soaps, botanicals, animal derivatives, and inorganic classes.

A recent study documented high levels of several pyrethroids, imidacloprid and fipronil in the influent of a wastewater treatment plant (WWTP) located in Northern California [23]. This study also collected samples at single-source locations within the sewershed, including a pet grooming business, pest control operator, and a commercial laundromat. Fipronil, permethrin and imidacloprid were all found at high levels at the pet grooming facility. This was expected, as these are all common AIs in pet flea-control, spot-on products [16]. However, the highest concentrations of cypermethrin were detected at the laundromat location. An evaluation of sales data of surveyed products revealed the average annual sales of cypermethrin in indoor products is approximately an order of magnitude greater than the second highest AI (Figure 7). Products containing cypermethrin are diverse, being formulated as aerosol sprays (41.2%), foggers (31.6%), ready-to-use (15.8%), and concentrates (5.7%). This finding supports the hypothesis that indoor use products have the potential to enter the waste stream through indoor applications and subsequent cleaning activities.

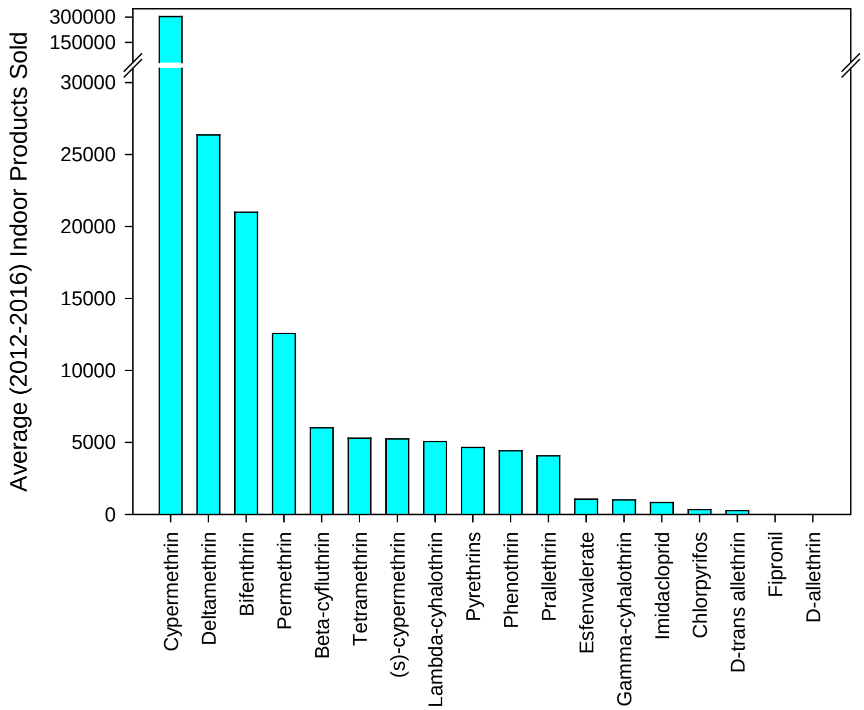

Figure 7. Average annual (2012–2016) active ingredients sold (lbs) in products registered for indoor use. AIs with <100 lbs sold not shown.

Fipronil and its degradates have also been detected in wastewater monitoring studies [24, 25]. This study found high levels of fipronil and its degradates in each 24-hr composite sample, and very little removal within the WWTP, highlighting the potential of wastewater effluent to serve as source of fipronil contamination to surface waters. A recent study found the majority of fipronil and degradates loading within the sewershed could be explained by the washing of pets treated with spot-on, flea-treatment products [14]. This hypothesis is further supported by the observation that fipronil was only identified in baits and gel indoor use products (Appendix 3).

3.4 Personal Care Products

Personal care products are labeled for outdoor use; however, users are instructed to apply the product directly to clothing or skin. Very little is known about the environmental fate of personal care products. It is conceptually possible that AIs within these products may enter the wastestream through cleaning and bathing activities. A total of 39 personal care products containing 21 associated active ingredients (AI) were identified at the seven retail locations surveyed (Appendix 3). DEET was found in the most products (15), followed by geraniol (11), and lemongrass oil (9) (Figure 8). AIs used as insecticides, repellents, and fungicides make up 75% of the AIs present (Appendix 13). Sixteen AIs are classified by the US EPA as minimum risk pesticides (Appendix 1). The pyrethroids permethrin and metofluthrin were identified in one personal care product each; all other products contained natural ingredients and repellents (Appendix 3). These two AIs are the only AIs found in personal care products with associated BMs of concern (Appendix 1, Appendix 14). It should be noted that outdoor sports stores were not included in this survey, however a cursury look at online websites revealed the availability of permethrin containing products registered as insect repellents for clothing and outdoor gear application are available at stores located within the survey area. It is unclear whether these products are registered for use in California, requiring a follow-up investigation by the CDPR Enforcement Branch. Therefore, it is unlikely that personal care products would be a significant contributor of pesticides with aquatic life BMs into the waste stream.

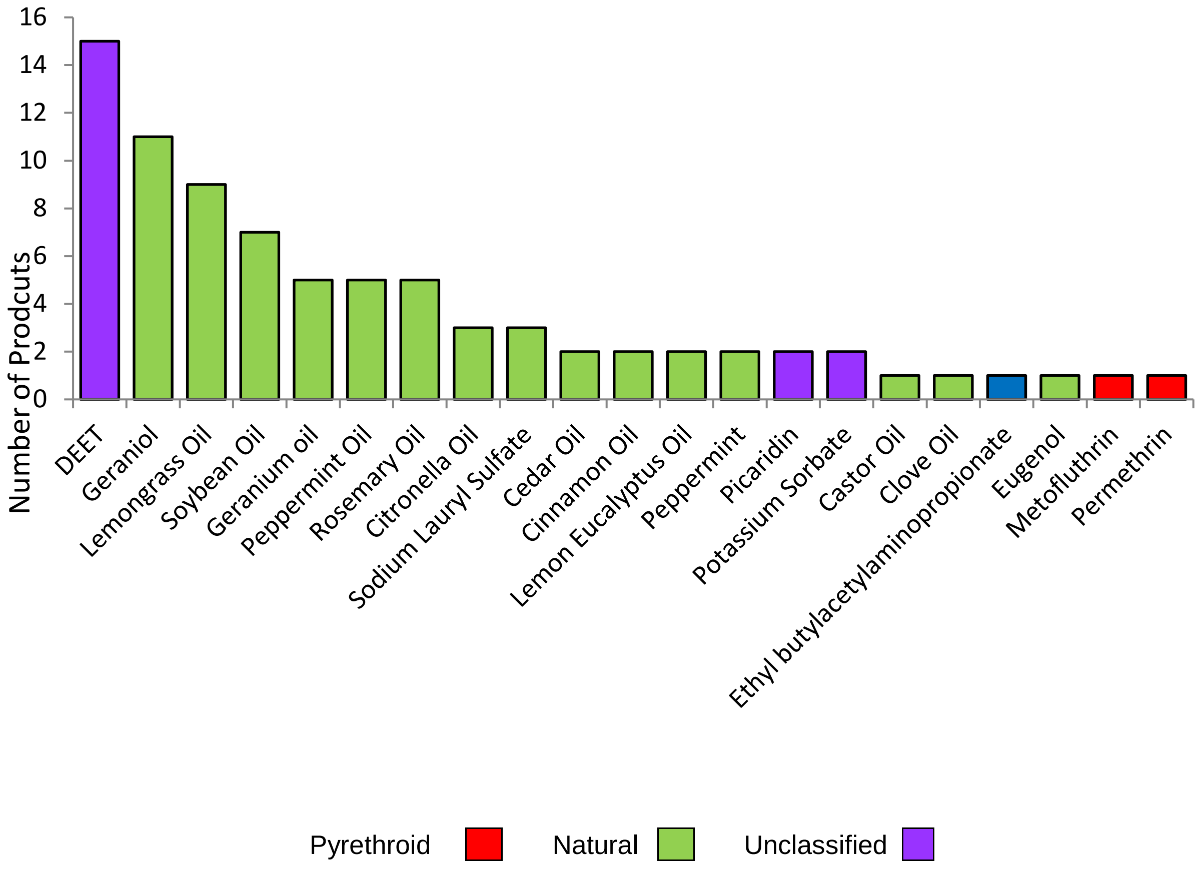

Figure 8. Number of products, designed for personal care use categorized by chemical class. All herbicides classified together. Natural category includes oils, soaps, botanicals, animal derivatives, and inorganic classes.

4.0 Conclusions

The evaluation of pesticide products available for homeowner use provides useful information on sources and environmental fate pathways. Personal care products are unlikely to serve as a source of pesticides of concern to either surface waters or the waste stream. Pyrethroid insecticides were identified as a potential concern in both outdoor and indoor use products, based on number of products and associated aquatic toxicity thresholds. Lambda-cyhalothrin, permethrin and bifenthrin are common AIs in products labeled for outdoor use; they are also detected at high frequencies in California surface waters. This product survey identified cypermethrin as the most common AI found in indoor use products; however, both cypermethrin (0%) and deltamethrin (24%) have very low associated detection frequencies in Northern California [17]. Cypermethrin has been identified as a major pesticide constituent in wastewater, indicating indoor use products as a likely source and a potential for cypermethrin exposure from treated wastewater discharge. More research is needed to identify indoor product formulations and application scenarios responsible for down-the-drain pesticide contributions. All but four AIs identified as an environmental concern in outdoor use products are currently monitored by CDPR SWPP. By comparing the findings from this product survey with regional monitoring results, one can infer certain application use patterns. For instance, the lack of fipronil and diuron in outdoor use products available for use by residents indicates these are AIs primarily found in professional use products. Other AIs, such as imidacloprid and bifenthrin are common in both. Future analysis of sales and use data is necessary to fully elucidate pesticide use questions such as proportions applied by professional applicators versus residential users.

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