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Letter

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Assessing Pesticide Application Contributions of Per- and Polyfluoroalkyl Substances (PFAS) in Agricultural Streams

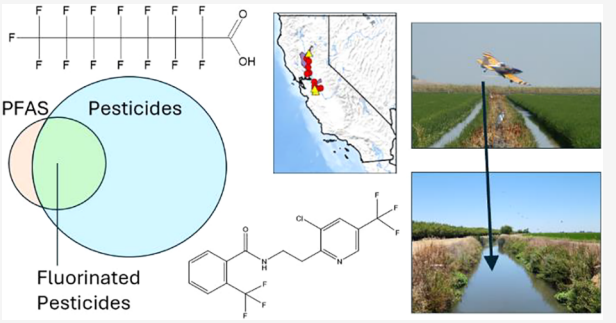
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ABSTRACT: Research has documented per-and polyfluoroalkyl substances (PFAS) to be prevalent in streams impacted by urban sources; less is known regarding PFAS contributions via pesticide applications, potentially from pesticide containers and/or "inert" ingredients not listed on pesticide formulation labels. To assess co-occurrence of pesticides and PFAS in agricultural streams, 10 streams were sampled in two agricultural valleys in northern California, USA during two periods of pesticide application (May and July of 2024). Water samples were analyzed for 183 pesticides and 57 PFAS. Sixty pesticides were detected: 23 herbicides, 18 insecticides, 18 fungicides, and 1 insecticide synergist. Detection frequencies (DFs) ranged from 0 to 100%, and concentrations ranged from nondetect (ND) to 782 ng/L (fluxapyroxad). Fourteen PFAS were detected: 6 perfluoroalkyl carboxylates (PFCAs), 5 perfluoroalkyl sulfonates (PFSAs), 2 PFCA/PFSA precursors, and 1 perfluoroalkyl phosphinate with DFs ranging from 0 to 60% (perfluorooctonoate [PFOA]) and concentrations ranging from ND to 20 ng/L (perfluorobutanoate [PFBA]). Co-occurrences of PFAS and pesticides were observed in 80% of the samples. Adopting the Organisation for Economic Cooperation and Development PFAS definition, pesticide applications are a likely source of instream PFAS. Examination of total organic fluorine and transformations to terminal and ultrashort PFAS could further elucidate pesticide contributions to environmental PFAS.



KEYWORDS: *per- and polyfluoroalkyl substances, fluorinated pesticides, pesticide applications, surface water, agricultural drainage*

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INTRODUCTION

Per- and polyfluoroalkyl substances (PFAS) are a class of thousands of fluorinated chemicals used in numerous commercial and industrial applications.[1] High use and stability of PFAS have resulted in widespread environmental occurrence and exposure on national and global scales.[2] In surface water systems, PFAS occurrence has been linked to urban sources including aqueous film forming foam activities, PFAS manufacturing facilities, wastewater treatment plants, and landfills.[3] There are sources of PFAS in less developed areas; the application of biosolids can lead to PFAS accumulation in soils, surrounding waters, and crops.[4−6] Another less studied source of PFAS is the application of pesticides,[7] which could pose risks to environmental and human health.[7−9]

Recent studies have documented PFAS in pesticide products[7,9,10] (Supporting Information Table S1). While concentrations of PFAS are generally in the ng/L range,[7] one study reported insecticide concentrations of perfluorooctanesulfonate (PFOS) ranging from 3.92 to 19.2 mg/kg.[10] Moreover, suspect screening and total oxidizable precursor (TOP) analyses showed that additional PFAS beyond the target analytes are also present in insecticide formulations.[10] PFAS in pesticide products, specifically perfluoroalkyl carboxylates (PFCAs), have been linked to fluorinated high-density polyethylene (HDPE) plastic containers.[7,11] Other potential sources that have not been tested but have been proposed are formulation solvents, manufacturing byproducts, and the unlisted, "inert" ingredients or adjuvants in the formulation.[7] Currently, fewer than 20 pesticide formulations have been tested; thus, the number of formulations that contain PFAS and the magnitude of PFAS concentrations are unknown.

Furthermore, the expanded definition of PFAS developed by the Organisation for Economic Cooperation and Development (OECD) defines PFAS as any compound that contains at least one perfluorinated methyl group ($-CF_3$) or a perfluorinated methylene group ($-CF_2-$), with some exceptions.[12] This definition includes many fluorinated pesticides, and the fluorinated pesticide market has grown substantially over the

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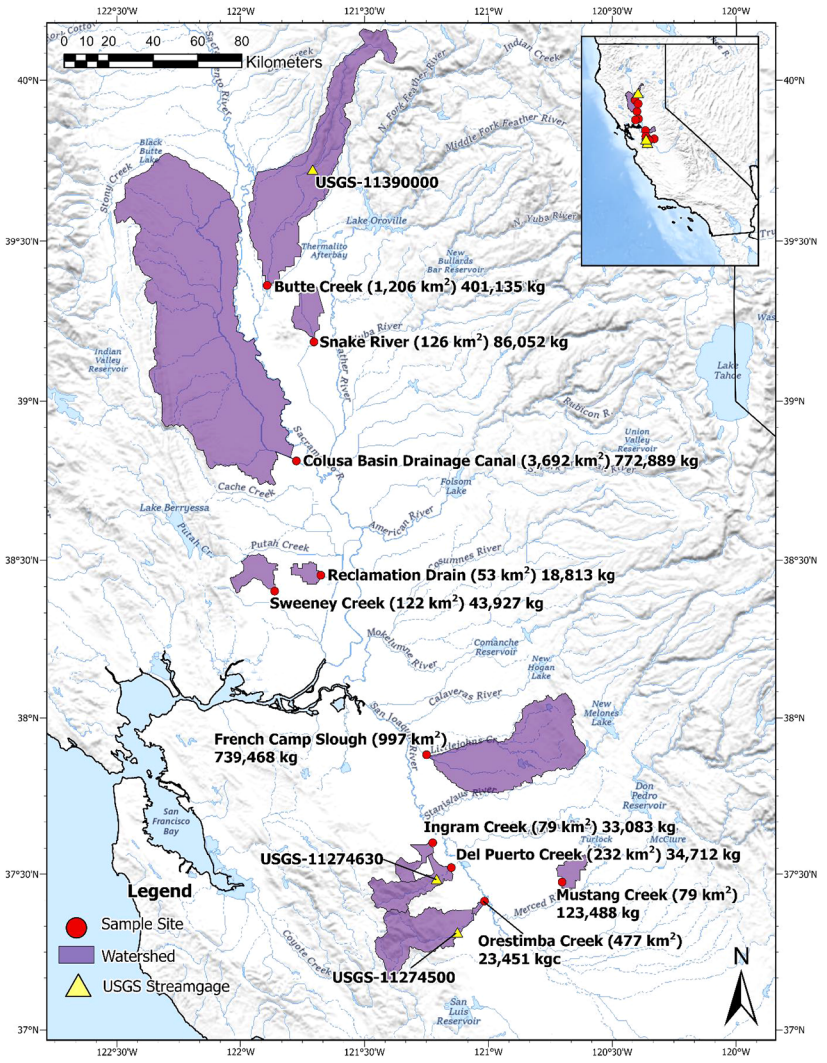


Figure 1. Distribution of 10 sites[22] sampled across the San Joaquin and the Sacramento Valleys. Numbers next to each site name represent the drainage area in square kilometers (km^2) and total annual kilograms (kg) of pesticides applied in each watershed.[20]

past 30 years, accounting for roughly 70% of the approved agrochemical market.[13] The properties that make fluorinated pesticides effective in agricultural productivity (stability, lipophilicity, and bioavailability) are the same properties that can lead to environmental persistence, bioaccumulation, and potential biomagnification.[14] Consequently, there are concerns around fluorinated pesticide effects on ecological and human health.[13,14] To provide clarity and to distinguish between types of PFAS in this work, the term "OECD fluorinated pesticide" will refer to fluorinated pesticides that are technically PFAS under the OECD definition, and the term "PFAS" will refer to nonpesticide compounds.

Pesticides have become indispensable in agriculture, and their use continues to increase globally.[15,16] Environmental PFAS occurrences and exposures resulting from pesticide applications represent knowledge gaps in the literature. The objective of this study was to evaluate pesticide applications as a source of PFAS in streams draining agricultural regions in California: San Joaquin Valley and Sacramento Valley. Sites across the San Joaquin Valley and Sacramento Valley were sampled for 183 pesticides and pesticide transformation products (TPs) and 57 individual PFAS[17] (Figure 1; Figures S1−S2; Tables S2; Tables S3 and S4). Study results can help researchers (1) understand the co-occurrence of pesticides and PFAS in agricultural streams, (2) determine if pesticide applications contribute to stream PFAS concentrations, (3) better characterize water quality effects from pesticide applications, and (4) help direct future PFAS research on source attribution.

MATERIALS AND METHODS

Site Selection

Site selection was based on two criteria: (1) minimal nonagricultural influences and (2) substantial application of methoxyfenozide, an active ingredient in the pesticide formulation Intrepid 2F (Figure S3). Recent research documented the presence of perfluorobutanesulfonate (PFBS) in Intrepid 2F at 350 ng/L[7]. To capture periods of methoxyfenozide application, sites (n = 10; Figure 1; Figures S1 and S2) were sampled in May and July (2024) to correspond with 2021 peaks in methoxyfenozide application, the most recent year of data available during study design[18] (Figure S4). The chosen sites/watersheds represented a diverse range of crop types (e.g., alfalfa, rice, tomatoes, and nuts) and pesticides applied[19,20] (Tables S5 and S6 and Table S7). The sum of all active ingredients applied in 2022 in the sampled watersheds ranged from 18813 to 772889 kg[20] (Figure 1; Table S5). Historical data (pesticide use and timing) showed similar broad patterns across years. Therefore, the assumption is that 2022

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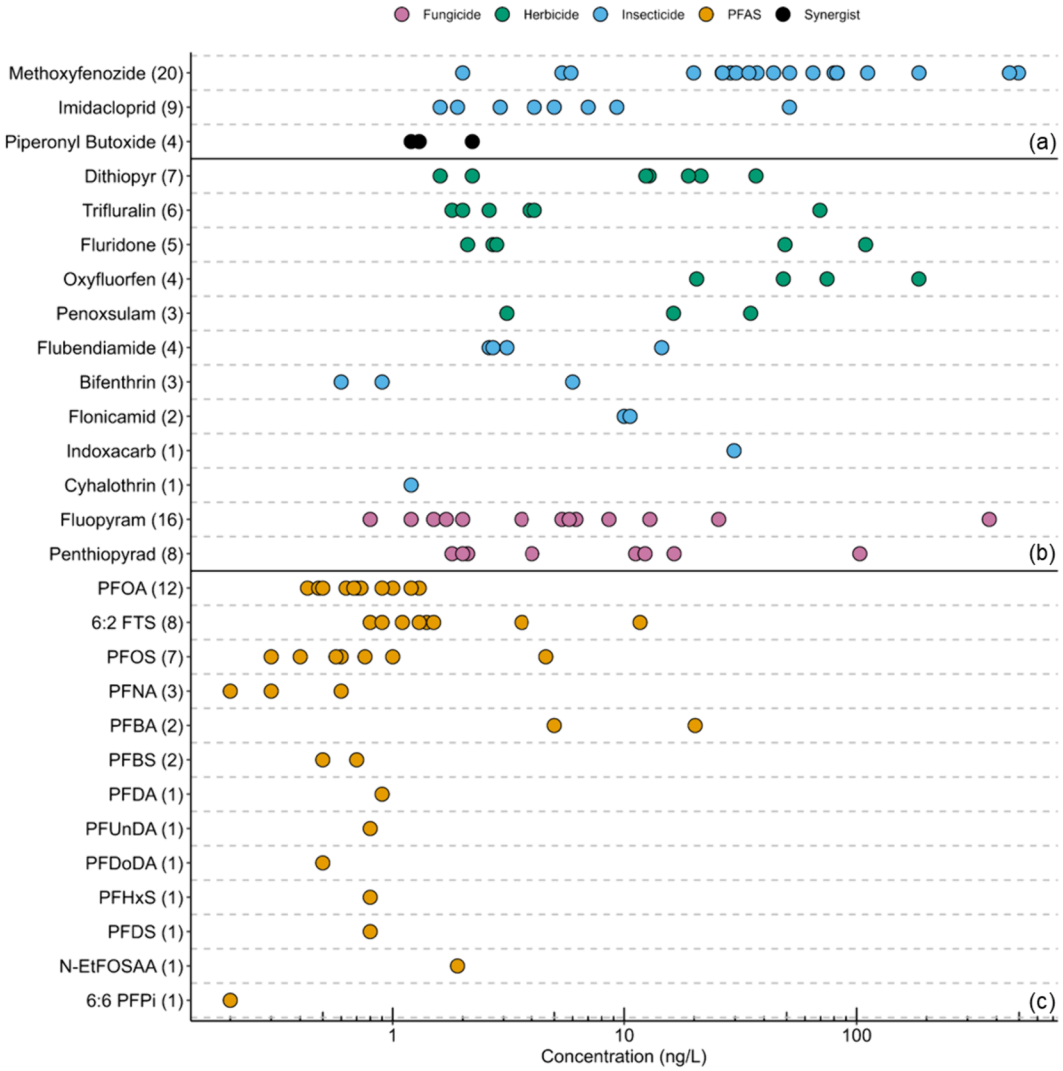


Figure 2. Concentrations (ng/L) of pesticide and PFAS detected across all sites and samples (n = 20). Compounds are grouped into three categories: (a) active ingredients in formulations that were linked to PFAS in Donley et al.,[7] (b) OECD fluorinated pesticide compounds, and (c) PFAS. The number in parentheses next to each compound indicates the number of detections, and concentrations of linear and branched PFAS reported in Table S3 were combined. [PFAS, per- and polyfluoroalkyl substances; OECD, Organisation for Economic Cooperation and Development.]

pesticide use data (the most recent year available) are representative of the 2024 pesticide data.

Hydrologic Setting

In May 2024, less than 2.5 cm of rainfall occurred across the San Joaquin Valley target counties the day before sampling and no rain occurred the day before sampling in the Sacramento Valley (Table S8). In July 2024, no rain occurred across all sampling counties the day before sampling[21] (Table S8). Generally, minimal rainfall occurred in both valleys the entire week before sampling. None of the sampling sites have a U.S. Geological Survey (USGS) streamgage, but three sites are downstream of active streamgages: Orestimba Creek (USGS streamgage 11274500), Del Puerto Creek (USGS streamgage 11274630), and Butte Creek (USGS streamgage 11390000) (Figure 1). Continuous streamflow data at Orestimba and Del Puerto Creeks showed that May sampling occurred along the falling limb of the hydrograph, coming off a small rainfall event, and July sampling occurred under baseflow to no flow conditions. Continuous streamflow data at Butte Creek showed seasonal reductions in streamflow from May through July and no major storm event during sampling.[22] These locations are heavily managed for agriculture; several drains, canals, and sloughs exist between the upstream gage and the sampling location. Statewide, rainfall was limited, conditions were dry, and runoff was likely minimal; collected samples represented primarily agricultural return waters (irrigation runoff and drainage).

Sampling and Analysis

Grab water samples were collected from the center of flow for pesticides and PFAS in 1 L amber glass bottles and 1 L HDPE bottles, respectively. For pesticides and PFAS, water was collected using a hand dip or weighted bottle/pole sampler method. For PFAS, roughly 1 mL was decanted immediately into six 2 mL polypropylene centrifuge tubes. Pesticide samples were processed following methods outlined in Gross et al.[23] with no deviations, and method detection levels (MDLs) ranged from 0.5 to 11 ng/L. Samples were filtered (0.7 μm glass fiber), extracted using an Oasis HLB cartridge, and analyzed using liquid chromatography−tandem mass spectrometry (LC-MS/MS) and gas chromatography−tandem mass spectrometry (GC-MS/MS). PFAS samples were analyzed following methods described in Gray et al.[24] but with modifications that expanded the target list and lowered the method reporting limits (MRL; 0.095−18 ng/L). Instead of direct injection, the method used online solid phase extraction (Oasis WAX cartridge) to concentrate PFAS and remove interferences followed by LC-MS/MS with isotope-dilution quantitation.[24,25] Quality assurance and quality control (QA/QC) for pesticide and

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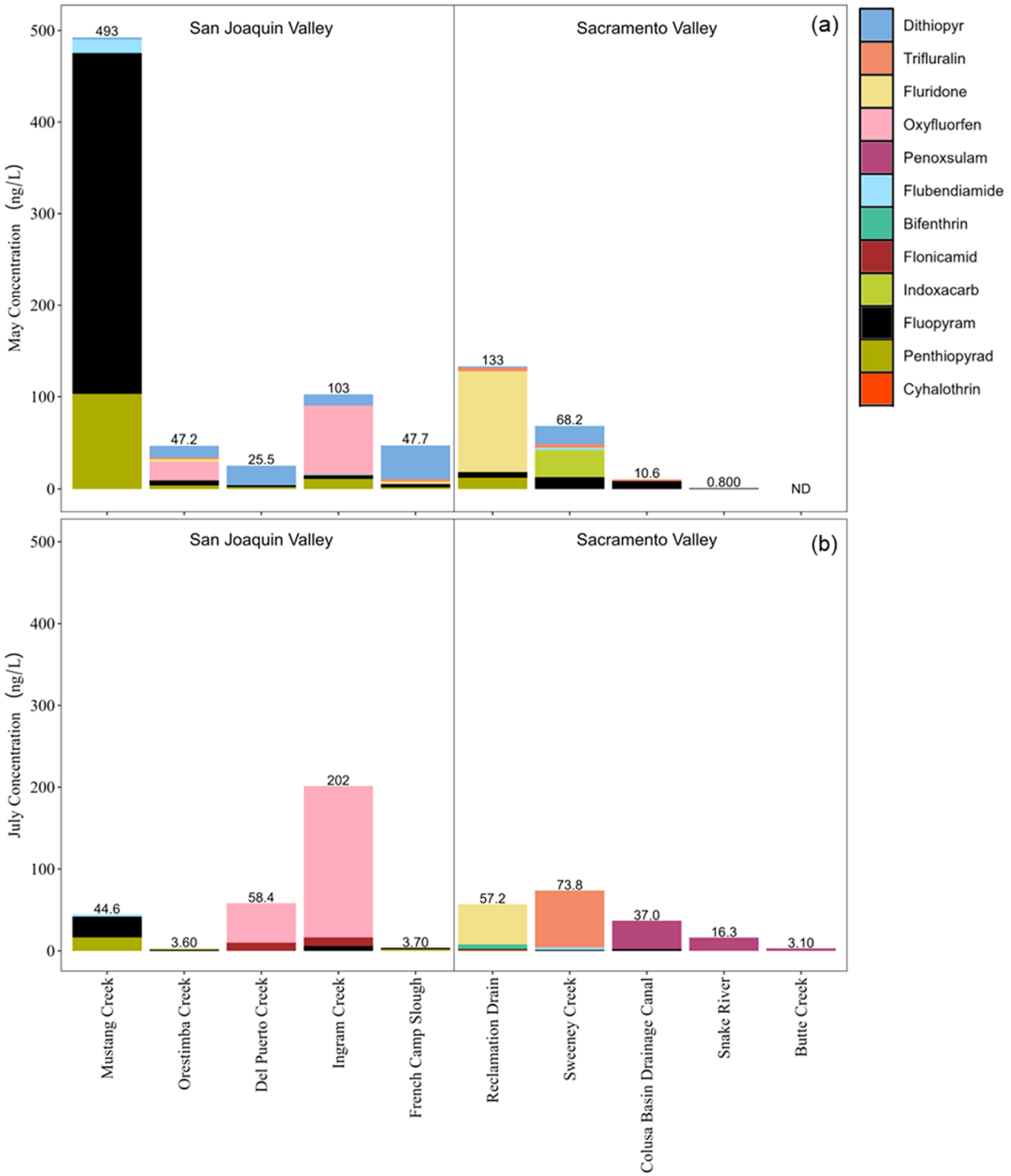


Figure 3. Concentrations (ng/L) of OECD fluorinated pesticides detected at each site during (a) May 2024 sampling and (b) July 2024 sampling. The number above each bar represents the total OECD fluorinated pesticide concentration (ng/L) for the detected compounds only [OECD, Organisation for Economic Cooperation and Development.]

PFAS methods included field blanks, replicates, and matrix spikes (Tables S3 and S4). For both methods, compounds were not detected in the field blanks. Additional method and QA/QC details are provided in the Supporting Information.

Statistical Analyses

Statistical analyses were conducted in RStudio version 2025.05.0.[26] Spearman correlations were run on compounds that had a ≥50% detection frequency. Nondetect (ND) pesticide values were replaced with 1/2 MDL, and nondetect PFAS values were replaced with 1/2 MRL.[27] Correlations were first evaluated across all sites, and then sites were broken up by valley (north—Sacramento Valley vs south—San Joaquin Valley) and sampling time frame (May versus July). Summary parameters were included for each site: total PFAS concentration, total pesticide concentration, total OECD fluorinated pesticide concentration, PFAS counts, pesticide counts, and pesticide use (kg) normalized by watershed area (km^2). Statistical significance was evaluated at $\alpha = 0.05$.

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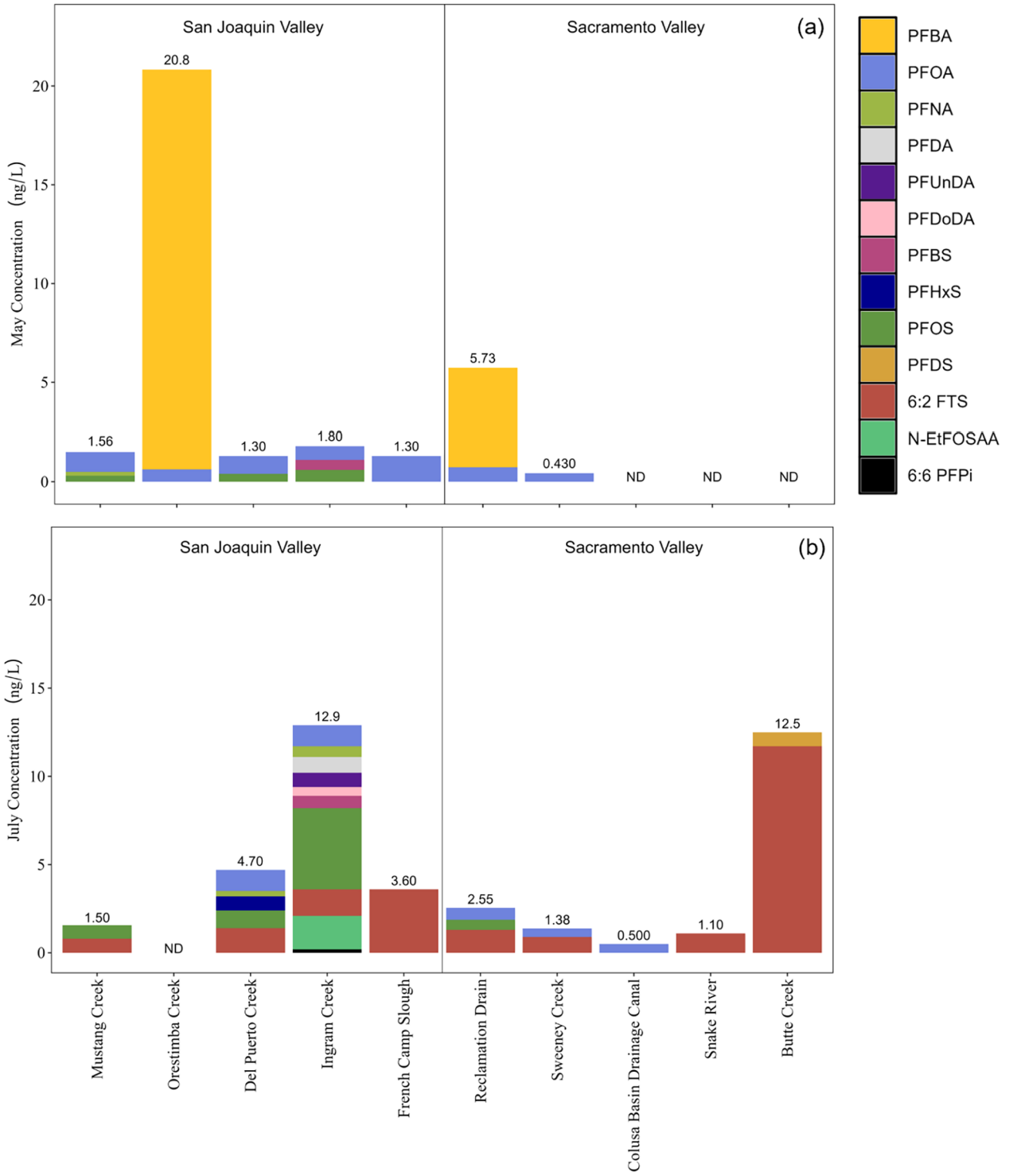


Figure 4. Concentrations (ng/L) of PFAS detected at each site during (a) May 2024 sampling and (b) July 2024 sampling. The number above each bar represents the total PFAS concentration (ng/L) for detected compounds only, and concentrations of linear and branched PFAS reported in Table S3 were combined. [PFAS, perfluoroalkyl and polyfluoroalkyl substances.]

RESULTS AND DISCUSSION

Sampling sites were chosen to represent intense agricultural activity and pesticide applications, and the results confirm that sites were substantially influenced by both. Correlations (Figures S5–S9), specifically across all sites (Figure S5), further confirmed this influence via a positive correlation between pesticide use per unit area and total pesticide concentration[20,28] (ρ = 0.47, and p = 0.03). A total of 60 unique pesticides and TPs were detected across all sites and samples: 23 herbicides, 18 insecticides, 18 fungicides, and 1 synergist (Figure S5). Detection frequencies (DFs) ranged from 5 to 100%. Methoxyfenozide, the insecticide targeted in site selection, and azoxystrobin (fungicide) had 100% DF (Figure S10). Three of the detected pesticides are active ingredients in formulations that have been associated with PFAS: methoxyfenozide (associated with PFBS), imidacloprid

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(DF 45%; PFOS and perfluorododecane sulfonate [PFDoDS]), and piperonyl butoxide (DF 20%; perfluorobutanoate [PFBA], perfluoropentanoate [PFPeA], perfluorohexanoate [PFHxA], perfluoroheptanoate [PFHpA], perfluorooctanoate [PFOA], perfluorohexane sulfonate [PFHxS], perfluoroheptane sulfonate [PFHpS], PFOS, 6:2 fluorotelomer sulfonate [6:2 FTS], and hexafluoropropylene oxide dimer acid [HFPO−DA]) (Figure 2; Table S1). Twelve (5 herbicides, 5 insecticides, and 2 fungicides) of the 60 pesticides detected were OECD fluorinated pesticides (Figure 2). The most frequently detected OECD fluorinated pesticide was fluopyram (DF = 80%), a broad-spectrum fungicide.

Concentrations of pesticides, including OECD fluorinated pesticides, varied by site and sample timing (Figure 3; Figure S11). The highest total pesticide concentration (3780 ng/L) and total OECD fluorinated pesticide concentration (493 ng/L) occurred at Mustang Creek (May) (Figure 3; Figure S11). High pesticide and OECD fluorinated pesticide concentrations at Mustang Creek were expected because this site (Figure S1) had the highest mass of pesticides applied per unit area (1567 kg/km^2) and the highest percentage of cropped area (82%) out of the 10 watersheds (Tables S5 and S6). The higher concentrations observed in May could be the result of spring applications to almond orchards near the site (61%; Table S6).

A total of 14 PFAS were detected in at least one water sample: 6 PFCAs, 5 perfluoroalkyl sulfonates (PFSAs), 2 PFCA/PFSA precursors, and 1 perfluoroalkyl phosphinate (Figure 2). The most frequently detected PFAS were PFOA (DF 60%), 6:2 FTS (DF 40%), and PFOS (DF 35%)-(Figure 2). The remaining 11 PFAS had three or fewer detections (Figure 2). Detection frequencies for PFAS were generally much lower than those for pesticides, but at least one PFAS was detected at each site, and 16 of the 20 (80%) samples collected contained both PFAS and pesticides (Figure 2; Figure 4; Figure S11).

Concentrations of PFAS also varied by site and sample timings (Figure 4). The highest total PFAS concentration (20.8 ng/L) was measured at Orestimba Creek in May (Figures 3 and 4; Table S4). The total PFAS concentration in this sample was mostly comprised of PFBA (20.2 ng/L). Even though this watershed is dominated by grassland/pasture (81%; Table S6), almonds and walnuts were growing adjacent to the sampling location (Table S7). Detections of PFBA at this site could be related to spring applications of pesticides to nut crops, a hypothesis that may explain why no PFAS were detected at this site in July. Another potential source of PFBA is the fluorinated pesticide containers; a 2021 U.S. Environmental Protection Agency (EPA) report showed that PFBA is the dominant PFAS in fluorinated HDPE rinsate.[7,11] There were no additional known PFAS sources identified in the upstream drainage area from the PFAS Analytics Tool[29] (Table S9; Figure S12), but California allows land application of biosolids.[30] This study focused on pesticide applications, but biosolids may also contribute PFAS to these watersheds.

The associations between PFAS and formulation active ingredients reported in the literature were investigated[7,9,10] (Table S1). Co-occurrence was observed for three formulation active ingredients and four PFAS (Tables S3 and S4). The active ingredient piperonyl butoxide was detected in water samples with 6:2 FTS (Snake River—July and Butte Creek—July) and PFOA (French Camp Slough—May and Colusa Basin Drainage Canal—July) (Tables S3 and S4); methoxyfenozide was detected with PFBS (Ingram Creek, May and July), and imidacloprid was detected with PFOS (Ingram Creek, May and July; Del Puerto Creek, May and July; and Reclamation Drain, July). The only compounds in Table S1 that met the detection frequency cutoff to be included in the correlation analyses were PFOA, PFOS, 6:2 FTS, methoxyfenozide, and imidacloprid (Figures S5−S9). The only correlation between these compounds was methoxyfenozide and PFOA in May samples (ρ = 0.64; p = 0.04) (Figure S6). This could indicate a relation between the application of Intrepid 2F (methoxyfenozide) and PFAS; however, this differs from the methoxyfenozide/PFBS relation noted in the literature.[7]

At first glance, pesticide applications were not a major contributor of PFAS to the environment, or at least PFAS measured in target methods[31] (e.g., EPA Method 1633); however, several important clarifications must be considered. If results are interpreted according to the global OECD definition of PFAS (e.g., to include certain fluorinated pesticides), then pesticide applications could (through runoff, drift, and other off-field transport processes) contribute to PFAS presence and persistence in the environment. As mentioned above, 12 of the 60 detected pesticides meet the OECD definition (Figure 3). In contrast to the target PFAS in Table S3 (maximum DF, 60%; maximum compound concentration, 20.2 ng/L), the OECD fluorinated pesticides were generally detected more frequently and at higher concentrations (maximum DF, 80%; maximum compound concentration, 372 ng/L) (Table S4; Figure 3).

If results are interpreted according to earlier definitions of PFAS (must contain at least a $-CF_3$),[32] there are still known PFAS contributions stemming from the degradation of certain fluorinated pesticides and other organofluorine compounds to the ultrashort PFAS trifluoroacetate (TFA).[33,34] Transformation to TFA has been documented for select fluorinated pesticides[35,36] and has been modeled or predicted for others based on structure.[33,37] Studies have documented the global distribution of TFA in the environment,[34] pesticides as a major TFA source in water,[33] and known and unknown environmental health concerns associated with environmental TFA.[34] Measurements and analyses of TFA and total organic fluorine (TOF) would likely yield a more complete assessment of pesticide applications as a PFAS source but were outside the scope of this study.

Finally, this study only measured 57 target PFAS out of the thousands, or, as one study reports, millions of PFAS that exist or could exist.[1,38] Thus, pesticide applications may be contributing other, unmeasured PFAS directly to streams. Furthermore, it is unclear if such unmeasured PFAS are degrading to ultrashort PFAS or oxidizing to terminal end products. Lasee et al.[10] measured PFAS in insecticide formulations pre- and postoxidation, with PFAS concentrations increasing postoxidation. This suggests that pesticide formulations contain unmeasured PFAS that could oxidize to PFCAs and PFSAs. Research analyzing pesticide formulations for PFAS, PFCA/PFSA precursors, and TOF is generally limited; additional research could help fill this information gap.

This study documents the co-occurrence of PFAS and pesticides in agricultural streams. Concentrations of detected PFAS (0.2−20 ng/L) were generally an order of magnitude lower than observed for detected pesticides (0.6−782 ng/L) and OECD fluorinated pesticides (0.6−372 ng/L). This study presents a limited data set but identifies pesticides as a potential PFAS source and can inform future PFAS source

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attribution research. Incorporating discharge measurements at each site could help determine seasonal differences in concentrations, and location data for biosolid applications could help discern pesticide versus biosolid contributions. Incorporating analyses of PFCA/PFSA precursors, nontarget PFAS, TOF, and ultrashort chain PFAS could help better characterize pesticide contributions to environmental PFAS. Finally, additional research is needed to better understand the scale of this source and potential effects related to simultaneous exposures to PFAS and pesticides.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.estlett.6c00132.

Description of QA/QC results, additional analytical method details, site photographs (Figures S1 and S2), methoxyfenozide site location map and application timing (Figures S3 and S4), Spearman correlation results (Figures S5−S9), pesticide and PFAS concentration results (Figure S10), pesticide concentrations by site and sampling time frame (Figure S11), tables describing pesticide formulations linked to PFAS (Table S1), 10 USGS sampling site details (Table S2), crop types adjacent to each sampling site (Table S7), rainfall data around sampling (Table S8), and description, figure, and table of additional PFAS sources in the watershed (Table S9 and Figure S12) (PDF)

Tables of site characteristics, PFAS results, and pesticide results (Tables S3 and S4) and pesticides applied and landcover within each watershed (Tables S5 and S6) (XLS)

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Notes

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