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Determining how almond (*Prunus dulcis*) harvest and processing contributes to low levels of glyphosate and glufosinate residues in almonds

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Abstract

California is the top producer of almonds [*Prunus dulcis* (Mill.) D.A. Webb] worldwide, generating more than \$6 billion in revenue in 2020; the European Union (EU) is the primary importer of California almonds. Weed control in almond orchards is an important part of the preharvest process, because weeds can interfere with harvest equipment and host diseases. Glyphosate and glufosinate are broad-spectrum herbicides commonly used for preharvest weed control. Global differences in maximum residue limits (MRLs) and regulated compounds can pose a challenge for growers who rely on broad-spectrum herbicides such as glyphosate and glufosinate for preharvest weed control. The EU MRL for glyphosate and total glufosinate is currently 0.1 mg kg^{-1}. The U.S. MRL for total glyphosate is 1 mg kg^{-1}, and total glufosinate is 0.5 mg kg^{-1}. An 8-wk field experiment, from spray to harvest, was conducted in an 8-ha commercial orchard to evaluate the potential contribution of the preharvest herbicide treatment to low levels of herbicide residue in almonds. Then, the same batch of almonds was followed through a commercial processing facility to evaluate the potential movement of herbicide residues from soil, debris, and hulls to almond kernels during processing. Glyphosate was not detected in any almond kernel samples at the end of processing. A glufosinate metabolite, 3-(methylphosphinico)propionic acid (MPP), was detected in kernels at the end of processing at about 0.1 mg kg^{-1}, which is above the EU MRL for total glufosinate. Almonds sampled directly from the tree, without any contact with soil, were found to have elevated MPP residues. This indicates glufosinate or MPP translocation may be a factor in low-level glufosinate residues detected in almonds in some EU exports.

Introduction

California produces 80% of the world's almonds [*Prunus dulcis* (Mill.) D.A. Webb], and this crop is the state's most valued export commodity, generating \$4.9 billion in revenue in 2019 (CDFA 2020). In 2020, there were more than 500,000 ha of bearing almond trees in California producing over 1.3 billion kg of almonds annually (USDA-NASS 2020). Depending on variety, almonds bloom beginning in February; the nuts grow to maturity through July and are harvested up until October; and the trees are dormant during November to January (UCANR 1996). Almonds are mechanically harvested by shaking the trees, sweeping them into windrows, and then picking them up from the orchard floor. Weeds on the orchard floor can reduce harvest efficiency by interfering with equipment, so many growers utilize relatively intensive herbicide programs to maintain bare ground in the months before harvest (Connell et al. 2001; UCANR 2002). Glyphosate and glufosinate are two commonly used herbicides for preharvest programs because of their broad-spectrum weed control and relatively short preharvest intervals: 3 and 14 d, respectively (Anonymous 2018, 2020). In 2018, more than 1 million kg of glyphosate and nearly 300,000 kg of glufosinate-ammonium were applied in California almond orchards (CDPR 2018). Because of the harvesting method, there is ample opportunity for whole almonds to come into contact with herbicide-treated soil.

After almonds are collected from the field, they are typically stockpiled under plastic covers before being transported to a processing facility for hulling and possibly shelling. At the huller/sheller facility, almonds are processed in large batches through rollers and gravity tables as well as pneumatic and sieve separatory equipment to remove dirt, debris, and hulls. These processes produce inshell almonds or include further steps to also remove shells (USEPA 2009). Contact with contaminated processing equipment, almonds, and debris is another avenue for pesticide residue contamination.

California exports nearly two-thirds of its almond production (CDFA 2020), mostly shipped as shelled almonds (ABC 2019). Historically, the European Union (EU) has been the largest importer of California almonds, with greater than 50% of the shelled product going there, whereas the largest importer of inshell almonds is Asia (ABC 2019). Exported shipments of almonds are subject to pesticide residue testing by the importing country's food safety authority, and residues must be at or below the maximum allowable concentration.

The maximum residue limit (MRL), commonly called "tolerances" in the United States, is defined by the Food and Agriculture Organization of the United Nations as the maximum allowable concentration of pesticide residue to be legally permitted in food commodities and animal feed (FAO 2022). In the United States, glyphosate and glufosinate MRLs are defined to include the parent compounds (i.e., the herbicides themselves) and their primary metabolites (Bryant Christie Inc. 2021). For clarity, these MRLs will be referred to as "total glyphosate" or "total glufosinate" if the concentrations of the metabolites are to be summed with the concentration of the parent compound. The U.S. MRL for total glyphosate is 25 mg kg^{-1} for almond hulls and 1 mg kg^{-1} for kernels. The U.S. MRL for total glufosinate in both almond hulls and kernels is 0.5 mg kg^{-1} (Bryant Christie Inc. 2021). There is no separate U.S. MRL for inshell almonds, because the residue for inshell almonds is determined by shelling and then measuring the residue in only the kernels.

In the EU, the MRL for glyphosate is 0.1 mg kg^{-1} in almond kernels (European Commission 2013) but there are no established MRLs for glyphosate metabolites. The EU MRL for glufosinate includes its metabolites, *N*-acetyl glufosinate and 3-(methylphosphinico)propionic acid (MPP); the MRL for total glufosinate is 0.1 mg kg^{-1} (European Commission 2016).

Glyphosate is registered in the EU until 2022 (European Commission 2017). A review completed by the European Food Safety Authority (EFSA 2019) recommended that the MRL for parent glyphosate be reduced to 0.05 mg kg^{-1} and an optional total glyphosate MRL for the summation of glyphosate and its primary metabolites, α-amino-3-hydroxy-5-methyl-4-isoxazolepropionic acid (AMPA) and *N*-acetyl-glyphosate, be set to 0.2 mg kg^{-1}. It is anticipated that in upcoming years, glyphosate MRLs will be reduced, and it is a possibility that the chemical may not be reregistered. If at any time the safety of a current MRL is reconsidered, the MRL can be reduced to the lowest limit of analytical detection, which currently is 0.01 mg kg^{-1}, according to European statute (European Parliament 2005).

An initial field study conducted in 2020 by Martin and Hanson (2022) revealed that very low levels of herbicide can transfer to almonds during harvest operations, and those residues appear to be primarily from herbicide bound to soil particles. The European markets are integral to the economic success of the California almond industry; however, glyphosate and glufosinate are also very important to preharvest operations in the almond production system. The work presented here is a continuation of the project aimed to identify possible causes of low herbicide residues in almonds. The objectives of this project were to determine whether low herbicide residues are still detectable in almonds throughout the process of commercial harvest operations and while the product moves through the huller/sheller processing facility.

Materials and Methods

Field Location

An 8-ha, mature, commercial almond orchard with alternating rows of 'Nonpareil' and 'Aldrich' (ABC 2019) almonds located in the northern San Joaquin Valley near Hughson, CA, USA (37.578°N, 120.857°W) was used to conduct this study. The orchard spacing was 6.7 m between rows and 5.5 m between trees within rows; the orchard was irrigated by furrow irrigation. Most of the orchard block is Tujunga loamy sand (mixed, thermic, Typic Xeropsamments; California Soil Resource Lab 2019) with some patches of Hanford sandy loam (coarse-loamy, mixed, superactive, nonacid, thermic Typic Xerothents; California Soil Resource Lab); the sand percentage of the orchard ranges from 70% to 80%.

Glyphosate and Glufosinate Treatments

The preharvest herbicide treatment was applied on July 30, 2021, as a tank mix of commercial glyphosate (Roundup WeatherMax®, Bayer Crop Science, 8400 Hawthorne Road, Kansas City, MO, USA) at 1,681 g ae ha^{-1}, commercial glufosinate (Rely® 280, BASF, 100 Park Avenue, Florham Park, NJ, USA) at 1,681 g ai ha^{-1}, nonionic surfactant at 0.25% v/v (Rainier-EA®, Wilbur-Ellis, 16300 Christensen Road no. 135, Tukwila, WA, USA), and ammonium sulfate at 1% v/v (Bronc® Max, Wilbur-Ellis). The herbicide was applied by the grower as part of regular commercial weed management using an unshielded boom sprayer. Applications were made 26 and 48 d before Nonpareil and Aldrich shakes, respectively. A table of all glyphosate and glufosinate applications made during the growing season is presented in Table 1.

Field Location Sampling

The field location was divided into three replicates (Figure 1) and three subsamples were taken within each replicate to form a composite sample from each variety. Leaves and almonds were sampled directly from both varieties of trees to help compare how much herbicide residue was present in the trees and on soil particles during and after harvest. Mature almond samples, including nuts with hulls, shells, and kernels, were taken from the windrow after undergoing the shaking and sweeping processes of harvest (Table 2). All nut, leaf, and soil samples were immediately dried in a drying room at 40 C after sampling and stored at room temperature until analysis. Both almond varieties were stockpiled at the huller sheller from the date of pick up until the date of processing (Table 3). Additionally, soil samples were taken at three important time points during the harvest process: before the preharvest herbicide treatment, before shaking, and from the windrow after sweeping (Table 3). These three time points allowed for a snapshot of herbicide movement with soil particles. Soil was collected at no more than a 2-mm depth by sweeping the area of a 0.25-m^2 quadrat. Soil samples were air-dried, sieved using a 2-mm sieve, and stored at room temperature until analysis.

Huller/Sheller Sampling

Sampling at the huller/sheller took place on October 28, 2021 (Tables 2 and 3). Almonds that were sampled during this time were from the same 8-ha field location but did not correspond with the field replicate sampling, because nuts from the 8-ha orchard were bulked together during harvest. Sampling within the facility began after the system was full, or after the first kernels from the truckload reached the shipping bin. Two truckloads, containing about 50,000 kg of whole almonds each, took about 1.5 h to go through the huller/sheller.

The experimental almonds were processed to ship as shelled almonds, with sampling occurring at the unloading, hulling, shelling, and shipment steps. First, composite samples were collected

Table 1. Glyphosate and glufosinate herbicide application throughout the 2021 growing season in the San Joaquin Valley near Hughson, CA, USA.[a]

Date	Active ingredient	Commercial product name	Supplier	Application rate
				L treated ha^{-1}
December 24, 2020	Glufosinate-ammonium	Reckon 280™ SL	Solera ATO, LLC, 12230 E Del Norte, Yuma, AZ, USA	4.6
June 9, 2021	Glufosinate-ammonium	Lifeline®	United Phosphorus Inc., 630 Freedom Business Center Ste 402, King of Prussia, PA, USA	4.6
June 9, 2021	Glyphosate	Honcho® K6	Bayer Crop Science, 8400 Hawthorne Road, Kansas City, MO, USA	3.2
July 30, 2021	Glufosinate-ammonium	Rely® 280	BASF, 100 Park Avenue, Florham Park, NJ, USA	6
July 30, 2021	Glyphosate	Roundup PowerMax®	Bayer Crop Science, 8400 Hawthorne Road, Kansas City, MO, USA	3

[a]Applications were made by AG Production Co., Turlock, CA 95380, USA.

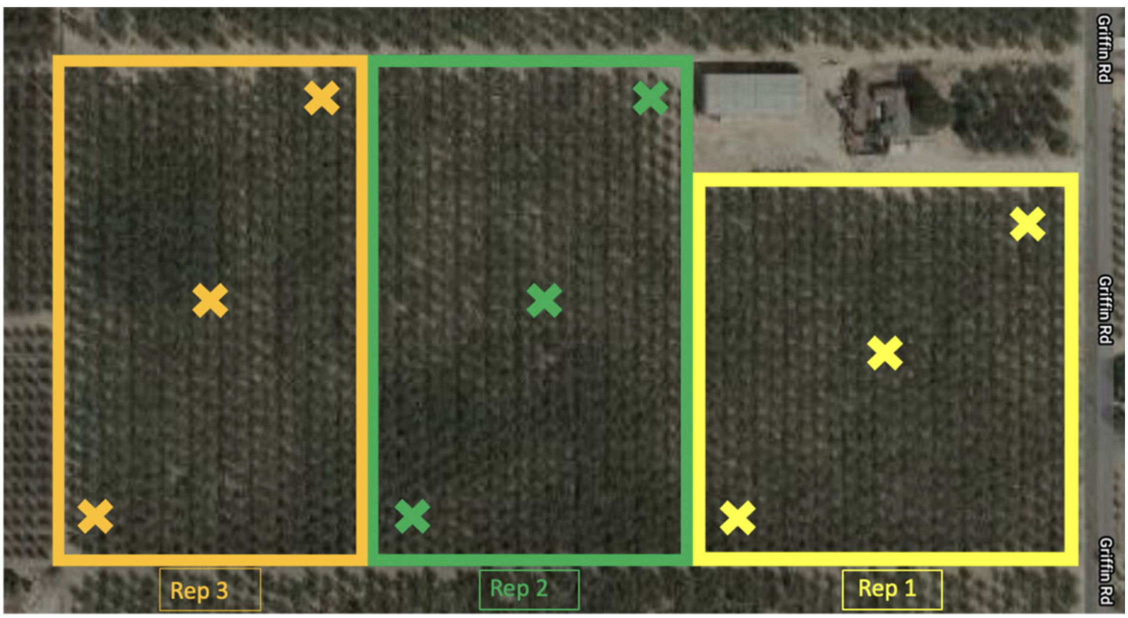

Figure 1. Field sampling layout. Each box represents a plot, with x marks indicating sampling locations.

from the material stream as it left the truck hopper into the receiving pit of the facility. Approximately 5 L of material was collected at the beginning, middle, and end of the truck unloading before the almonds entered the preprocess stage, where sticks, rocks, excess soil, and other debris were removed using air, sieves, and gravity tables. Meanwhile, a soil sample was collected from the outlet where the fine debris exits the preprocessor at the same time points of the truck unloading. Then, while the batch of almonds was going through the hulling and shelling processes, hulls, shells, and kernels were sampled three times over 1.5 h: at the beginning, middle, and end of the batch. Hulls were separated from the inshell almonds by gravity tables, while shells were separated from kernels by gentle cracking and gravity tables. This sampling process was carried out for Nonpareil and Aldrich varieties on the same day (Table 2). Throughout this processing day, three soil samples of approximately 1,000 g were collected in plastic ziplock bags from the baghouse, which collects the fine dust particles from multiple points in the hulling and shelling equipment, approximately 1.5 h apart. Additional soil samples were collected directly from the hulling equipment and floor. All samples were brought to the laboratory and stored at room temperature for approximately 2 wk until further hand processing and subsampling took place.

Sample Processing and Analysis

Almond samples were further processed by hand and dissected into their hull, shell, and kernel fractions; soil samples were sifted using a 2-mm sieve; and leaf samples were dried in a drying room at 40 C. From the processed samples, a representative 500-g sample was sent to a commercial laboratory (Safe Food Alliance, 2037 Morgan Drive, Kingsburg, CA, USA) for analysis. The laboratory used a proprietary method modified from QuPPe v. 10 (EURL-SRM 2019) and high-pressure ion chromatography (HPIC) (Dionex™ Integrion™ HPIC™ System, Dionex, Sunnyvale, CA, USA) coupled with a mass spectrometer (Orbitrap™ Exploris™ 120, Thermo Scientific, Waltham, MA, USA) to quantify glyphosate, *N*-acetyl-glyphosate, AMPA, *N*-acetyl-AMPA, glufosinate, *N*-acetyl-glufosinate, and MPP in all almond samples. The soil samples were analyzed using the same instrumentation and methods modified from Druart et al. (2011). The limit of detection for each compound was 0.010 mg kg^{-1} for almond samples and 0.040 mg kg^{-1} for soil samples.

Statistical Analysis

Data are presented as a worst-case scenario, meaning the nondetects were not included in the statistical analysis. Although this

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Table 2. Dates of significant farming practices for the 2021 growing season in the San Joaquin Valley near Hughson, CA, USA.

	Nonpareil	Aldrich
Final preharvest herbicide application	July 30, 2021	July 30, 2021
Leaf and almond samples taken directly from the tree	August 16, 2021	September 2, 2021
Tree shake	August 25, 2021	September 16, 2021
Almond sweep	August 30, 2021	September 18, 2021
Almond sampling from the field	September 6, 2021	September 22, 2021
Almonds picked up and stockpiled	September 6, 2021	September 24, 2021
Huller/sheller processing of almonds	October 28, 2021	October 28, 2021

Table 3. Dates and definitions of non-almond samples taken throughout the field and processing facility during the 2021 growing season in the San Joaquin Valley near Hughson, CA, USA.

Soil sample	Date
“Pre-Spray” soil sample: Sample was taken before the preharvest application of glyphosate and glufosinate.	July 21, 2021
“Pre-Sweep” soil sample: Sample was taken after the preharvest but before the almonds were swept into the windrow.	August 16, 2021
“Post-Sweep” soil sample: Sample was taken from the strips after the almonds had been swept into the windrow.	September 6, 2021
“Pre-Process” soil sample: Soil and debris were taken from the outlet leading to the debris pile.	October 28, 2021
“Baghouse” sample: Dust sample was taken from the baghouse outlet leading to the fine dust pile.	October 28, 2021
“Huller” sample: Sample was taken directly from the hulling equipment during processing.	October 28, 2021
“Floor” soil sample: Sample was taken from floor sweepings around the hulling equipment during processing.	October 28, 2021

Table 4. Summary of the concentration of glyphosate and its metabolites detected in soil during the different harvest and processing operations.[a]

Soil sample	Glyphosate	AMPA	*N*-acetyl-glyphosate	*N*-acetyl-AMPA	Total glyphosate
	mg kg^{-1} ± SE				
Pre-Spray	0.525 ± 0.111	0.192 ± 0.025	< LOD	< LOD	0.715 ± 0.134
Pre-Sweep[b]	0.408 ± 0.058	0.214 ± 0.070	< LOD	< LOD	0.622 ± 0.128
Post-Sweep[c]	0.261 ± 0.047	0.146 ± 0.020	< LOD	< LOD	0.407 ± 0.028
Aldrich Pre-Process	0.302 ± 0.102	< LOD	< LOD	< LOD	0.302 ± 0.102
Nonpareil Pre-Process	0.392 ± 0.108	< LOD	< LOD	< LOD	0.392 ± 0.108
Baghouse	0.864 ± 0.072	0.0483	< LOD	< LOD	0.892 ± 0.085
Floor[d]	0.973	0.062	< LOD	< LOD	1.035

[a]Values are presented as mean concentration ±SE ($n = 3$). AMPA, α-amino-3-hydroxy-5-methyl-4-isoxazolepropionic acid.
[b]Two replicate samples were below the limit of detection.
[c]One replicate sample was omitted from the data set due to an extremely high value that was an anomaly.
[d]The floor sample was taken as one composite sample from the huller/sheller.

is a biased way to present the data, it is relevant and informative when discussing regulatory issues, as a shipment can be rejected if even one sample is above the designated MRL. The data were subject to ANOVA using R statistical analysis software (R Core Team 2020) and multiple comparisons were performed with Tukey’s HSD with $\alpha = 0.05$.

Results and Discussion

When examining the data presented, it is worth noting that the field data (sample locations “Tree” and “Windrow”) are treated as a separate data set from the huller/sheller data (sample locations “Truck” and “Huller/Sheller”), because it was not possible to follow field replicates through the huller/sheller due to the harvest process resulting in the three replicates being stockpiled together; two truckloads from each stockpile (Aldrich and Nonpareil) were run through the processing facility.

Soil sampling revealed quantities of parent compound and metabolites at every stage of the experiment (Tables 4 and 5). Replicate 1 of the “Pre-Sweep” and “Post-Sweep” samples had very high concentrations of glyphosate and glufosinate parent compounds and metabolites. Replicate 1 is at the front of the field, so it is suspected that the first subsample may have been contaminated by high levels of herbicide from initial equipment testing before the remainder of the field was sprayed; therefore, replicate 1 was not included in the analysis of those samples.

There were no significant differences between or within any of the soil samples taken at the processing facility. The higher levels of herbicide from the baghouse and the floor indicate there is detectable herbicide reside in particulate matter in the processing facility, but the filtration system is effectively collecting those dust particulates in the baghouse. When comparing the soil data with the almond kernel data (compare Tables 4 and 5 with Tables 6 and 7) it is noteworthy that the major contributor to residues detected in almonds is not the parent compound but the metabolites, while the soil samples from the field and processing facility all contain detectable levels of parent compound, including the soil samples taken at the time of processing.

Glyphosate was detected in Aldrich leaf samples at an average concentration of 0.036 mg kg^{-1}; no glyphosate metabolites were detected. Nonpareil leaves were below the limit of detection of for glyphosate compounds. Glufosinate was detected in two Aldrich leaf samples at an average concentration of 0.192 mg kg^{-1}. MPP was detected in all Aldrich and Nonpareil leaf samples at an average concentration of 0.348 mg kg^{-1}.

Table 5. Summary of the concentration of glufosinate and its metabolites detected in soil and debris during the different harvest and processing operations.[a]

Soil sample	Glufosinate	*N*-acetyl-glufosinate	MPP	Total glufosinate
	mg kg^{-1} ± SE			
Pre-Spray[b]	0.441 ± 0.142	0.074 ± 0.011	0.807 ± 0.336	1.322 ± 0.484
Pre-Sweep[c]	0.224 ± 0.055	0.043 ± 0.002	0.478 ± 0.152	0.745 ± 0.209
Post-Sweep	0.182 ± 0.028	0.043[d]	0.235 ± 0.002	0.438 ± 0.008
Aldrich Pre-Process	0.142[3]	0.054[d]	0.126 ± 0.049	0.215 ± 0.101
Nonpareil Pre-Process	0.280 ± 0.112	0.047[d]	0.185 ± 0.041	0.494 ± 0.166
Baghouse	0.407 ± 0.058	0.046 ± 0.001	0.322 ± 0.042	0.772 ± 0.100
Floor[e]	0.477	< LOD	0.374	0.851

[a]Values are presented as mean concentration ±SE. MPP, 3-(methylphosphinico)propionic acid.
[b]Two replicate samples were below the limit of detection.
[c]One replicate sample was omitted from the data set due to an extremely high value that was an anomaly.
[d]Three replicate samples were below the limit of detection.
[e]The floor sample was taken as one composite sample from the huller/sheller.

Table 6. Summary of the concentration of glyphosate and its metabolites in almond hulls, shells, and kernels at different sampling locations.[a]

	Hulls				
Sampling location	Glyphosate	AMPA	*N*-acetyl-glyphosate	*N*-acetyl-AMPA	Total glyphosate
	mg kg^{-1} ± SE				
Tree[b]	0.033 ± 0.005	< LOD	< LOD	< LOD	0.033 ± 0.005
Windrow[c]	0.072 ± 0.031	< LOD	< LOD	< LOD	0.072 ± 0.031
Truck	0.044 ± 0.013	< LOD	< LOD	< LOD	0.044 ± 0.013
Huller/Sheller	0.057 ± 0.030	< LOD	< LOD	< LOD	0.057 ± 0.030
	Shells				
Sampling location	Glyphosate	AMPA	*N*-acetyl-glyphosate	*N*-acetyl-AMPA	Total glyphosate
	mg kg^{-1} ± SE				
Tree[d]	0.015	< LOD	< LOD	< LOD	0.0154
Windrow[c]	0.031 ± 0.013	< LOD	< LOD	< LOD	0.031 ± 0.013
Truck[b]	0.027 ± 0.008	< LOD	< LOD	< LOD	0.027 ± 0.008
Huller/Sheller	< LOD	< LOD	< LOD	< LOD	< LOD
	Kernels				
Sampling location	Glyphosate	AMPA	*N*-acetyl-glyphosate	*N*-acetyl-AMPA	Total glyphosate
	mg kg^{-1} ± SE				
Tree[d]	< LOD	< LOD	0.012	< LOD	0.018
Windrow	< LOD	< LOD	< LOD	< LOD	< LOD
Truck[d]	0.010	< LOD	< LOD	< LOD	0.010
Huller/Sheller	< LOD	< LOD	< LOD	< LOD	—

[a]Values are presented as mean concentration ±SE ($n = 6$). AMPA, AMPA, α-amino-3-hydroxy-5-methyl-4-isoxazolepropionic acid.
[b]Three replicate samples were below the limit of detection.
[c]Two replicate samples were below the limit of detection.
[d]Five replicate samples were below the limit of detection.

A summary of glyphosate residues detected in almond fractions is presented in Table 6. Total glyphosate is presented as the sum of glyphosate, AMPA, *N*-acetyl-glyphosate, and *N*-acetyl-AMPA. Almond variety was not a significant factor in analysis, so the Nonpareil and Aldrich data were combined for a total of six replicate samples per sample location. The sample location was also not a significant factor in this field or in huller/sheller data.

There were no differences between glyphosate concentrations in almond hulls and shells; the majority of kernel samples at all sampling stages were below the limit of detection. Glyphosate was not detected in any kernels from the final processing step of the huller/sheller (Table 6). AMPA and *N*-acetyl-AMPA were not detected in any almond samples. Therefore, all kernel samples tested would be below the residue limits for total glyphosate within the United States and for glyphosate within the EU.

There were two kernel replicates with glyphosate compounds detected (Table 6), one was sampled from the truck and contained 0.010 mg kg^{-1} of glyphosate, and the other was sampled directly from the tree and contained 0.012 mg kg^{-1} of *N*-acetyl-glyphosate. Both of these detections are at allowable concentrations as determined by the United States and EU; additionally, the detection of glyphosate in these individual samples was below the ESFA proposed glyphosate MRL of 0.05 mg kg^{-1}.

A summary of glufosinate residues detected in almond fractions is presented in Table 5. Total glufosinate is presented as the summation of glufosinate, *N*-acetyl-glufosinate, and MPP. The majority of glufosinate residues detected in almond samples were in the form of the metabolite MPP. Almond variety was a significant factor in the data collected from the field (sample locations "Tree" and "Windrow") but not in the data collected from the processing steps (sample locations "Truck" and "Huller/Sheller"). Variety being a

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Table 7. Summary of the concentration of glufosinate and its metabolites in almond hulls, shells, and kernels at different sampling locations.[a]

	Aldrich hulls					Nonpareil hulls			
Sampling location	Glufosinate	*N*-acetyl-glufosinate	MPP	Total glufosinate	Sampling location	Glufosinate	*N*-acetyl-glufosinate	MPP	Total glufosinate
	——— mg kg^{-1} ± SE ———					——— mg kg^{-1} ± SE ———			
Tree	< LOD	< LOD	0.366 ± 0.052	0.366 ± 0.052	Tree	< LOD	< LOD	0.271 ± 0.025	0.271 ± 0.025
Windrow	0.069 ± 0.029[b]	< LOD	0.498 ± 0.043[b]	0.567 ± 0.014[b]	Windrow	< LOD	< LOD	0.205 ± 0.008[b]	0.205 ± 0.008[b]
Truck	< LOD	< LOD	0.227 ± 0.030	0.227 ± 0.030	Truck	< LOD	< LOD	0.218 ± 0.020	0.218 ± 0.020
Huller/Sheller	0.1322	< LOD	0.240 ± 0.007	0.284 ± 0.040	Huller/Sheller	< LOD	< LOD	0.225 ± 0.007	0.225 ± 0.007
	Aldrich shells					**Nonpareil shells**			
Sampling location	Glufosinate	*N*-acetyl-glufosinate	MPP	Total glufosinate	Sampling location	Glufosinate	*N*-acetyl-glufosinate	MPP	Total glufosinate
	——— mg kg^{-1} ± SE ———					——— mg kg^{-1} ± SE ———			
Tree	< LOD	< LOD	0.251 ± 0.043	0.251 ± 0.043	Tree	< LOD	< LOD	0.197 ± 0.033	0.197 ± 0.033
Windrow	0.055[c]	< LOD	0.494 ± 0.153	0.512 ± 0.151	Windrow	0.0202	< LOD	0.232 ± 0.018[b]	0.242 ± 0.008[b]
Truck	< LOD	< LOD	0.291 ± 0.012	0.291 ± 0.012	Truck	< LOD	< LOD	0.214 ± 0.018	0.214 ± 0.018
Huller/Sheller	< LOD	< LOD	0.275 ± 0.009	0.275 ± 0.009	Huller/Sheller	< LOD	< LOD	0.273 ± 0.004	0.273 ± 0.004
	Aldrich kernels					**Nonpareil kernels**			
Sampling location	Glufosinate	*N*-acetyl-glufosinate	MPP	Total glufosinate	Sampling location	Glufosinate	*N*-acetyl-glufosinate	MPP	Total glufosinate
	——— mg kg^{-1} ± SE ———					——— mg kg^{-1} ± SE ———			
Tree	< LOD	< LOD	0.076 ± 0.008	0.076 ± 0.008	Tree	< LOD	< LOD	0.104 ± 0.004	0.104 ± 0.004
Windrow	< LOD	< LOD	0.111 ± 0.025	0.111 ± 0.025	Windrow	< LOD	< LOD	0.099 ± 0.004[b]	0.099 ± 0.004[b]
Truck	< LOD	< LOD	0.077 ± 0.001	0.077 ± 0.001	Truck	0.0162	< LOD	0.122 ± 0.010	0.127 ± 0.012
Huller/Sheller	< LOD	< LOD	0.089 ± 0.003	0.089 ± 0.003	Huller/Sheller	< LOD	< LOD	0.109 ± 0.003	0.109 ± 0.003

[a]Values are presented as mean concentration ±SE. Almond variety was a significant factor. MPP, 3-(methylphosphinico)propionic acid.
[b]One replicate sample was below the limit of detection.
[c]Two replicate samples were below the limit of detection.

significant factor in glufosinate analysis is likely due to tree physiological traits beyond the scope of this study. However, both cultivars were grafted to the same peach [*Prunus persica* (L.) Batsch] rootstock, so differences in glufosinate concentration are likely not related to rootstock. The potential interaction between herbicide residue and rootstock and scion cultivars could be explored in future research.

There were no significant differences between total glufosinate concentrations in hulls and shells at any sampling location or within the sampling locations. Sample location was also not a significant factor in total glufosinate concentrations in the Aldrich or Nonpareil kernels. Interestingly, total glufosinate concentrations in some Aldrich and Nonpareil kernel samples were above the EU MRL of 0.1 mg kg^{-1}, with the major contributor to the summation being MPP (Table 7).

The average concentration of MPP in Aldrich kernels coming from the huller/sheller, the last step of processing, was 0.89 mg kg^{-1}, and the average concentration of MPP in the Nonpareils from the same sampling location was 0.109 mg kg^{-1}, which is above the EU MRL for total glufosinate (Table 7). However, the more surprising data came from the almonds sampled directly from the tree. Aldrich kernels from almonds sampled directly from the tree, having had no contact with the orchard floor, had an average MPP concentration of 0.76 mg kg^{-1}, while the Nonpareil kernels had an average concentration of 0.104 mg kg^{-1} (Table 7).

A study of [^{14}C]glufosinate-ammonium metabolism and translocation of soil-applied chemical conducted in apples (*Malus pumila* Mill.) revealed that MPP did translocate into fruits, leaves, and shoots 14 d after application (EFSA 2005, 2015). The study reported concentrations of MPP in apple fruits at 0.104 mg kg^{-1}, similar to the concentrations observed in almonds in this study; no parent compound was detected in the apples. The study conducted by Martin and Hanson (2022) found MPP concentrations in almond kernels was roughly 0.05 mg kg^{-1}. These differences are suspected to be due to soil type differences between the 2020 site and the 2021 data in this paper and will be examined further in future studies.

Almond hull, shell, and kernel residues were all below the U.S. MRLs for glyphosate, glufosinate, and their metabolites. However, the EU MRLs for total glufosinate in almond kernels were exceeded in some Nonpareil kernel samples. Importantly, the concentration of MPP detected in almond kernels sampled directly from the tree indicates that movement of the metabolite from the soil to the fruit may be playing a role in elevated residues before the almond touches the orchard floor. Glufosinate was used consistently in the orchard throughout the growing season (Table 1), as is standard practice in many orchards. California growers will face challenges when choosing preharvest herbicide programs if the movement of glufosinate metabolites, specifically MPP, is proven to be a cause of herbicide residue in almonds, in addition to the pressures of potential MRL changes in the EU.

Future research in MPP residue levels in almonds before and after tree shake across California and across different soil types will help address domestic and export market concerns. Additionally, studies will continue to examine harvest operations for other sources of pesticide residues, such as insecticides, fungicides, and other herbicides.

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