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# Targeted analysis and Total Oxidizable Precursor assay of several insecticides for PFAS

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ABSTRACT

Targeted analysis for 24 Per- and Polyfluoroalkyl Substances (PFAS) was conducted on 10 insecticide formulations used on a United States Department of Agriculture crop research field. Perfluorooctane sulfonic acid (PFOS) was found in 6 of the 10 formulations with concentrations ranging from 3.92 to 19.2 mg/kg. Further analysis of soil and plant samples collected at the site found several additional PFAS, with PFOS being the most prominent. Suspect screening was then conducted on the formulations and provided several suspected PFAS in addition to the 24 targeted analyzed PFAS in 7 of the 10 samples, one of which showed no PFAS during targeted analysis. PFAS-precursor oxidation was then conducted on the two insecticide formulations with the greatest lists of suspected PFAS as validation of potential unknown PFAS in the formulations. This study revealed a previously unknown potential PFAS contamination source for rural and agricultural environments.

## 1. Introduction

The chemical class per- and poly-fluoroalkyl substances (PFAS) have drawn regulatory focus due to their potential toxicity (Bach et al., 2016; Barry et al., 2013; Gallo et al., 2012; Halldorsson et al., 2012; Jantzen et al., 2016; Johansson et al., 2009; Melzer et al., 2010; Midgett et al., 2015; Savitz et al., 2012; Steenland et al., 2013; Wielsøe et al., 2015), tendency to trophic transport (Awad et al., 2011; Giesy and Kannan, 2001; Hagenaars et al., 2008; Kwadijk et al., 2010; Vestergren et al., 2013), and their environmental mobility and persistence (United States Environmental Protection Agency, 2019). Within the PFAS chemical group, perfluoroalkyl acids (PFAAs) have been the primary focus of research and legislation due to a strong display of the previously mentioned traits and relatively high environmental occurrence.

In February 2019, the United States' Environmental Protection Agency (EPA) published an action plan concerning PFAS exposure and contamination in the United States (United States Environmental Protection Agency, 2019). One of the research areas identified by the action plan as needing additional input was "What are the sources, fate and transport pathways, and exposures to humans and ecosystems?" (United States Environmental Protection Agency, 2019). The most common characterized sources of environmental PFAS contamination are associated with wastewater and biosolids, aqueous firefighting foam (AFFF), and products containing PFAS and PFAS precursor manufacturing and use (Key et al., 1997; Prevedouros et al., 2006). This list is not comprehensive, especially for agricultural or rural communities. To promote advancement in this area, the United States' EPA allocated $5 million on August 20th, 2020 for new research on managing PFAS in agricultural and rural communities.

In a trial run of a prior study on plant uptake of PFAS (Lasee et al., 2019, 2020), it was discovered that there was detectable PFAS contamination in control plant samples grown in a United States Department of Agriculture (USDA) cropping systems research laboratory greenhouse. Targeted Liquid Chromatography-Mass Spectrometry (LC-MS/MS) analysis was performed to find the source of the PFAS contamination; identified PFAS in the soil on site, other research plants grown on site, and various insecticides used on the site, while site water, potting soil, and fertilizers were all non-detect for PFAS. The objective of this study was to characterize the PFAS found in the tested insecticide formulations and to attempt to connect that PFAS to PFAS found in the soil. Suspect screening was conducted on the insecticide products in an effort to identify possible "unknown" PFAS in the products. Then we

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conducted the Total Oxidizable Precursor assay to quantify how much "unknown" PFAS were observed in two of the insecticide samples.

## 2. Materials and methods

### 2.1. Materials

All calibration (4:2 FTS, 6:2 FTS, 8:2 FTS, N-MEFOSAA, N-EtFOSAA, PFBA, PFPeA, PFBS, PFHxA, PFPeS, PFHpA, PFHxS, PFOA, PFOS, PFHpS, PFNA, PFOSA, PFDA, PFNS, PFUdA, PFDS, PFDoA, PFTrDA, and PFTeDA) and stable isotope ($^{13}$C4-PFBA, $^{13}$C5-PFPeA, $^{13}$C3-PFBS, $^{13}$C5-PFHxA, $^{13}$C2–4:2FTS, $^{13}$C4-PFHpA, $^{13}$C3-PFHxS, $^{13}$C8-PFOA, $^{13}$C2–6:2FTS, $^{13}$C9-PFNA, $^{13}$C8-PFOSA, $^{13}$C8-PFOS, $^{13}$C6-PFDA, $^{13}$C2–8:2FTS, $^{13}$C7-PFUdA, d3-MeFOSAA, d5-EtFOSAA, $^{13}$C2-PFDoA, $^{13}$C2-PFTeDA) standards were obtained from Wellington Laboratories (Guelph, Ontario). The 24 PFAS selected were those included in the EPA SW-846 Test Method 8327. Tested insecticides formulations were collected from the test site (a USDA crop research laboratory).

It is important to note that we have observed some 50- and 15-mL test tubes and analysis grade solvents have shown trace PFAS residuals that can lead to contamination of a sample. We recommend the careful use of solvent blanks and prior analysis of materials and products to remove the risk of sample contamination from these sources. LC-MS/MS-grade methanol, water, and acetonitrile used in this study were purchased from Honeywell (Charlotte, North Carolina). 50- and 15-mL test tubes used in this study were VWR® High-Performance Conical-Bottom Centrifuge Tubes with Flat Cap, Polypropylene (Radnor, Pennsylvania). Prior analysis of these solvents and test tubes did not show concentrations of the 24 PFAS targeted in this study. Scoopulas used in this study were disposable polypropylene scoopulas from VWR® (Radnor, Pennsylvania).

### 2.2. Insecticide collection and analysis

Ten different insecticide formulations were collected from the crop research site after the analysis of soil from the site found concentrations of a variety of PFAS species. The selected insecticides were only those recorded as used on the site in 2017. In 2020, the insecticides were confirmed to still be in use at the site. Insecticide formulates sampled were collected from a cabinet designated for storage of all pesticides in use on site. All pesticides stored in the cabinet were kept, if possible, in their original resealable packaging. If the original packaging did not allow for sealing or the seal was damaged, the pesticide, still in its original packaging, was place inside a secondary sealable plastic container. None of this studies sampled insecticides were stored in secondary containers.

Formulations samples were collected with disposable scoopulas and were placed into 15 mL centrifuge tubes for storage. Samples were stored in a hood at 20 °C. Formulations were diluted as 10–100 mg in 10 mL LC-MS/MS-grade methanol and were allowed to dissolve over 24 h in 15 mL centrifuge tubes in triplicates. Formulations were then sonicated in a 20 °C water bath for one hour. Each formulation solution was then diluted to 10 μg formulation/1 mL (10 ppm) with LC-MS/MS-grade methanol in a new 15 mL centrifuge tube. No extraction or filtration steps were used due to concerns that these steps could remove fractions of non-targeted PFAS. To prepare for targeted analysis, 537 μL of formulation/methanol dilution, 3 μL of a 120 ng/mL internal standard (in methanol), and 1260 μL of LC-MS/MS-grade water were added to an auto injector vial (recovery of internal standards presented in S1). To prepare samples for suspect screening, 540 μL of each 10 μg/1 mL formulation/methanol dilution and 1260 μL of LC-MS/MS-grade water were added to an auto injector vial. Samples were stored at 5 °C until analysis. For both targeted and non-target analysis, results were calculated between triplicates.

PFAS suspect screening was conducted on all tested insecticides. The list produced by the suspect screening was only partially validated and is therefore incomplete. Accordingly, the current work and discussion is presented in the Supplemental information. Library matches did validate the existence of PFOS in samples. Further identification of suspected PFAS was outside the scope of the current study. Additional information on the suspect screening is presented in the Supplemental information, with the results of the suspect screening presented in Table S2.

### 2.3. Total Oxidizable Precursor assay

The Total Oxidizable Precursor (TOP) assay developed by Houtz and Sedlak (2012) was used to convert suspected PFAS to PFAAs for which standards were available (ie. PFBA, PFBS, PFPeA, PFPeS, PFHxA, PFHxS, PFHpA, PFOA, PFOS, PFNA, etc.). Insecticide 6 was chosen for this technique because suspect screening (Table S2) showed that insecticide 6 was the only insecticide with a targeted analysis hit (PFOS in insecticides 1–6) with a suspected PFAS with an area of the same order of magnitude as its known PFAS (109,500 vs. 324,100). All other PFAS with a targeted analysis hit did not have suspected PFAS with an area of the magnitude as their known PFAS indicating that they may not have a large "unknown" PFAS fraction. Additionally, insecticide 6′s is one of the most commonly used organophosphate. Insecticide 10 was selected for TOP analysis due to being the only tested insecticide that did not show PFAS concentrations during targeted analysis, but showed activity during suspect screening (Table S2). Many of insecticide 10′s suspected PFAS had large areas indicating that TOP analysis may reveal a large "unknown" PFAS fraction.

### 2.4. Soil and vegetation sample collection and preparation

The study site was a USDA crop research laboratory that uses the 5 fields on site to said crops. Soil and vegetation samples were collected from these fields. Soil and vegetation sample were collected by a nitrile gloved hand and placed in 50-mL test tubes. Prior to ownership by the USDA, the site was owned by Texas Tech University and was kept as native rangeland. Wastewater, biosolids, or municipal sludge (known PFAS contamination sources) have not been applied to the site. Nearby fields (within 2 miles) also had PFAS concentrations in the soil. Accordingly, none of them were used as controls. This is not surprising as most agricultural fields in the area grew cotton and likely used the same or similar pesticides.

At the time of sampling, Fields 1 and 4 were planted with cotton, Fields 2 and 3 were planted with sorghum, and Field 5 as planted with corn, cotton, sorghum, peanuts, and beans. Approximate sampling locations are presented in Fig. 1. Soil samples were collected as a composite of 5–6 surface grab samples taken from a single field. It rained 0.4 in. the morning before samples were collected. Corn, bean, and peanut grab samples were collected from Field 5; corn samples were collected as kernels only from immature cobs, bean samples were collected as both seed and pod, and peanut samples were collected as seed and pod from the soil. Each sample was washed in DI water to remove clinging soil. Samples were then dried at 70 °C for 24 h. Dried soil and plant samples were then homogenized. Approximately 2 g of dried soil and 0.5 g of dried vegetation sample were placed in 50-mL polypropylene centrifuge tubes and stored at room temp (20 °C) to await extraction.

### 2.5. Soil and vegetation extraction

Soil and vegetation samples were extracted as published in Zhao et al. (2013) with the exception of filtering the final extract with a nylon filter. Prior work conducted in the laboratory showed that nylon filters may remove significant fractions of some longer chained PFAS and PFAS precursors. Extractions were reconstituted in 30 % methanol/ 70 % water and stored in 2-mL auto-sampler vials at 5 °C until analysis. Average recoveries for the 19 internal standards (IS) are presented in Table S3 for plant tissue samples. Recoveries using this technique were

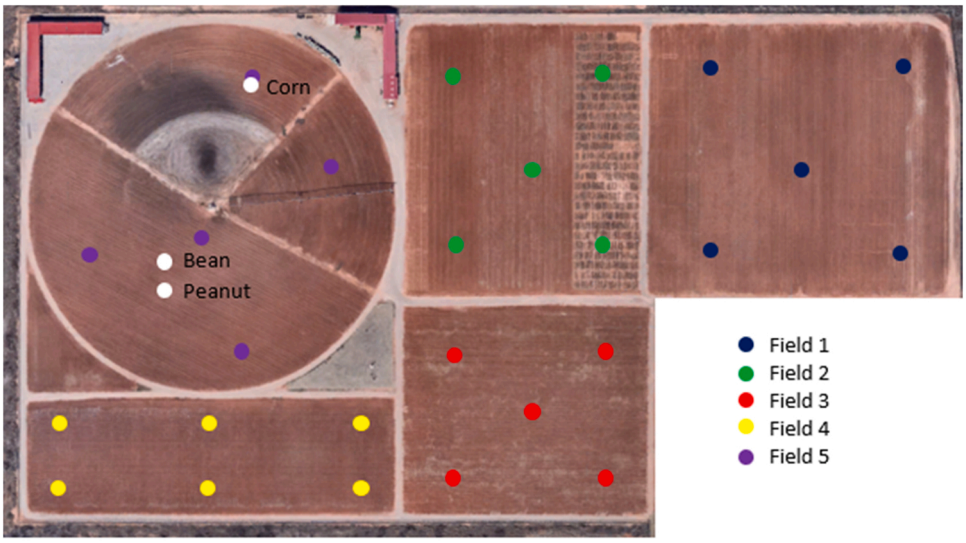


**Fig. 1.** Soil and plant sampling locations on the study site. All soil samples taken from the same field were combined as a composite sample for analysis.

low for several PFAS IS in soil samples, so soil samples were extracted again using a basic methanol extraction technique modified from Higgins et al. (2005) (IS recoveries presented in Table S4).

### 2.6. Quality assurance

All samples (insecticide formulations, soil, and plant tissue extractions) were injected in triplicate. Every 9 injections (3 samples) alternating 10 ng/L and 500 ng/L standards were injected for quality control. Extraction blanks were utilized for the plant tissue and soil extractions, and a solvent blank was used for the insecticide formulations as no extraction was done with these samples. Significant 6:2 FTS contamination was observed in the plant and soil extraction samples and as a result, 6:2 FTS concentrations in these samples were not reported due to concerns in their authenticity. SW-846 Test Method 8327 was used for acceptable recovery range (70–130 %). Limits of quantification (LOQs) were determined by injection of 1, 2, 5, and 10 ng/L standards and are presented in the Supplemental information.

### 2.7. Instrument conditions

Chromatographic separation was carried out using a SCIEX ExionLC™ equipped with a Phenomenex Gemini® C18 column (100 × 3 mm; 3 μm particle size) with a Phenomenex SecurityGuard™ Gemini® C18 (4 × 2 mm) guard column. The column oven temperature was set to 40 °C. The following conditions were used: elution solvents were 20 mM ammonium acetate in water (A), methanol (B) mobile phase composition (A:B; v/v) was 95:5 at 0 min, increasing to 35:65 at 1.6 min, increasing 0:100 at 8 min, and switching to 5:95 at 12.8 min which is maintained until 16 min. The flow rate was 700 μL/min and the injection volume was 500 μL. The LC was coupled to a X500R Quadrupole Time-of-Flight mass spectrometer (SCIEX). These settings were used for both the targeted analysis and suspect screening. Suspect screening was conducted using Electrospray Ionization in negative mode.

## 3. Results

### 3.1. Targeted analysis of formulations

The results of PFAS targeted analysis of the insecticide formulations are presented in Table 1. PFAS concentrations were above the LOQ for only one of the 24 species (PFOS) in the 10 analyzed formulations. PFOS was found in 6 of 10 formulations (3.92–19.17 mg/kg). Peaks for a variety of other PFAS were observed in the samples, primarily PFHxS and PFBS, although none of these peaks surpassed the instrument LOQ (1–10 pg/g in dilutions). This is not surprising as PFAS tend to exist as complex mixtures. Additionally, if the source of the PFOS found in the samples were PFAS precursors, PFAS precursors often degrade into several different PFAAs (Gebbink et al., 2015; Mejia Avendaño and Liu, 2015; Vestergren et al., 2008). The sample injection was a 1:100,000 dilution in methanol, therefore the < LOQ concentrations of PFHxS and PFBS could be detectable in a lower dilution and may still accumulate in soils overtime.

**Table 1**
Average concentration of PFOS in the analyzed insecticide formulations (mg PFAS/kg formulation or ppm, ± standard deviation). The concentrations reported were calculated from the dilution described previously in the "Insecticide Analysis section". PFAS with no concentrations above LOQ were not included in this table.

| Sample ID | Formulation type | Active ingredient | PFOS (mg/kg) |
|---|---|---|---|
| **1** | Liquid concentrate | Abamectin | 3.92 ± 0.51 |
| **2** | Emulsified suspension | Novaluron | 9.18 ± 0.34 |
| **3** | Liquid concentrate | Mineral Oil (Petroleum oil) | 8.64 ± 0.67 |
| **4** | Emulsified suspension | Imidacloprid | 13.3 ± 1.4 |
| **5** | Emulsified suspension | Spiromesifen | 19.2 ± 1.2 |
| **6** | Liquid concentrate | Malathion | 17.8 ± 0.7 |
| **7** | Wettable powder | *Beauveria Bassiana* | 0 |
| **8** | Wettable powder | Pyridalyl | 0 |
| **9** | Emulsified suspension | Spinosad | 0 |
| **10** | Wettable powder | Spinetoram, Sulfoxaflor | 0 |
| **BLANK** | | | 0 |

While the PFAS concentrations found in this study are a cause for concern, these insecticides are a highly concentrated product. The dilution and application directions for most of the collected insecticide formulations were approximately 4–8 fluid ounces diluted in 100 gallons of water. At 8 fluid ounces, that is a 1600-fold dilution by volume.

### 3.2. Targeted analysis of soils

Results of the targeted analysis of surface soil of the 5 tested fields are presented in Table 2. PFOS was the PFAS species with the highest

**Table 2**
Average soil concentrations (ng PFAS/kg dry soil, ± standard deviation) of PFAS from the targeted analysis of soil samples from five fields. All samples were aggregates of 5–6 surface soil grab samples that were homogenized. Standard deviations are presented in parentheses.

| | Field sampled | | | | | |
|---|---|---|---|---|---|---|
| PFAS | 1 | 2 | 3 | 4 | 5 | BLANK |
| **4:2 FTS** | 51 ± 7.0 | 36 ± 7.3 | 32 ± 5.3 | 23 ± 3.5 | 30 ± 5.0 | < LOQ |
| **PFOA** | 42 ± 9.2 | 72 ± 12 | 173 ± 38 | 46 ± 5.1 | 47 ± 6.5 | < LOQ |
| **PFNA** | 18 ± 2.5 | 33 ± 6.7 | 43 ± 7.5 | 12 ± 1.8 | 14 ± 1.5 | < LOQ |
| **PFOS** | 698 ± 120 | 1150 ± 165 | 1720 ± 299 | 156 ± 26 | 247 ± 14 | 0.0 |
| **8:2 FTS** | 31 ± 7.5 | 23 ± 4.6 | 19 ± 2.6 | 12 ± 0.8 | 11 ± 2.9 | 0.0 |
| **PFUdA** | 52 ± 13 | 58 ± 14 | 69 ± 8.8 | 30 ± 1.8 | 40 ± 8.9 | 0.0 |

concentration found in the soil followed by PFOA and 4:2 FTS, 8:2 FTS, PFNA, PFOA, and PFUdA (which all had similar concentrations). Many of the other 24 PFAS species in the targeted analysis were below the LOQ. The full results are reported in Table S5. The targeted analysis placed Field 3 as the field with the highest PFAS concentrations followed by Field 2, Field 1, Field 5, and Field 4. The goal of this sampling technique was to create a single sample that could be a qualitative representative of both known (targeted analysis) and unknown (non-target analysis) PFAS in a field. Additionally, PFAS are known to distribute heterogeneously in soils (Rankin et al., 2016). The soil sampling was only of the surface; different PFAS are known to have a variety of soil distribution patterns (Guelfo and Higgins, 2013). Given those three points, we would not consider concentrations presented in Table 2 to be accurate representatives of a quantitative distribution of PFAS in the tested fields.

The water used to irrigate the research center was also analyzed by mixing 1.4 mL of water with 0.6 mL methanol and directly injecting it. No quantifiable concentrations of target PFAS were found in the water, although, solid phase extraction of a greater volume of water could produce quantifiable concentrations of PFAS.

### 3.3. Targeted analysis of plant tissues

The results of PFAS targeted analysis of corn kernel, string bean, and peanut are presented in Table 3. In the analyzed insecticides, PFOS was the primary component observed, followed by PFHxS and PFBS (both were below the LOQ). The corn and bean samples, which were collected from the above ground portions of the plants, had PFAS concentrations an order of magnitude higher for PFBA, PFHxA, PFHxS, and PFOS than the peanut sample, which was collected as a below ground portion. For PFHpA, the concentration in the peanuts was an order of magnitude higher than those in the corn and bean tissues. These plant tissues were collected as single, opportunistic grab samples. Replicate sampling throughout the field was not done. Thus, concentrations found in these samples should not be considered representative of the harvested crop.

**Table 3**
Average tissue concentrations (ng PFAS/kg dry plant tissue or ppt) of PFAS from the targeted analysis of corn kernel, string bean pod, and peanuts. All samples are were collected from the commonly consumed tissue of these plants. Standard deviations are presented in parentheses.

| | PFBA | PFHpA | PFHxA | PFHxS | PFOA | PFOS |
|---|---|---|---|---|---|---|
| **CORN** | 1120 ± 143 | 38 ± 2.2 | 1020 ± 130 | 4900 ± 147 | 349 ± 138 | 3230 ± 316 |
| **BEAN** | 3300 ± 48 | 37 ± 0.8 | 138 ± 76 | 1150 ± 104 | 176 ± 72 | 4260 ± 154 |
| **PEANUT** | 580 ± 31 | 313 ± 39 | 0 | 200 ± 59 | 162 ± 35 | 407 ± 13 |
| **BLANK** | 0 | 0 | 0 | 0 | 0 | 0 |

### 3.4. Total Oxidizable Precursor assay

The TOP assay was done on insecticides 6 (active ingredient Malathion) and 10 (active ingredients Spinetoram and Sulfoxaflor). The results comparing the before assay to after assay concentrations are found in Fig. 2. The TOP assay technique converts PFAA precursors to PFAAs, although it is not a perfect or complete process. Both insecticides saw an increase in moles of PFAS after the TOP assay was conducted. Suggesting that both insecticides had significant "unknown" PFAS concentrations. Insecticide 6′s total PFAS moles nearly tripled (pre – 0.24 μmoles/L vs. post – 0.64 μmoles/L) and insecticide 10 was revealed to have nearly as much PFAS in it as insecticide 6 (0.61 μmoles/L vs. 0.64 μmoles/L) despite not showing any PFAS concentrations in targeted analysis.

## 4. Discussion

### 4.1. Targeted analysis

All insecticides tested in this study are still in production under the same brand names, though the formulations tested should not be assumed to be the same as the ones currently in production, as the sampled product was not new. However, PFAS are known to be incredibly environmentally stable, consequently, historic use of insecticides containing PFAS or PFAS precursors can translate into persistent soil contamination. Soil PFAS have been shown to be absorbed and translocated into plant tissues (Lasee et al., 2019; Bizkarguenaga et al., 2016; Blaine et al., 2014; Lechner and Knapp, 2011; Shobhna et al., 2020; Stahl et al., 2009; Wen et al., 2014). Manufacturing of PFAS began in 1949 (3M, 1999). Historical PFAS containing pesticide use could translate into high concentrations of several different PFAS in agricultural soils that can persist in the soil for many years.

Targeted analysis of PFAS concentrations in the tested insecticides (Table 1) showed PFOS to be the primary PFAS found in the formulations. This was reflected in the aggregate soil samples. Inspection of the chromatographs (Fig. 3, Figs. S1–S10) showed a split peak that is indicative of two isomers (a branched and linear) of PFOS being present. Although similar, the chromatographs are not identical in shape. Soil samples showed a smaller peak for the branched isomer than the formulations. An explanation for this phenomenon could be that the soil samples collected were of surface soil and branched PFOS isomers have shown greater environmental mobility than linear PFAS (Chen et al., 2015), leading to a disproportionately greater decrease of branched PFOS surface soil concentrations over time compared to its linear counterpart. In addition, these soil samples are environmental, so multiple PFAS input sources are likely. It is not uncommon to find a variety

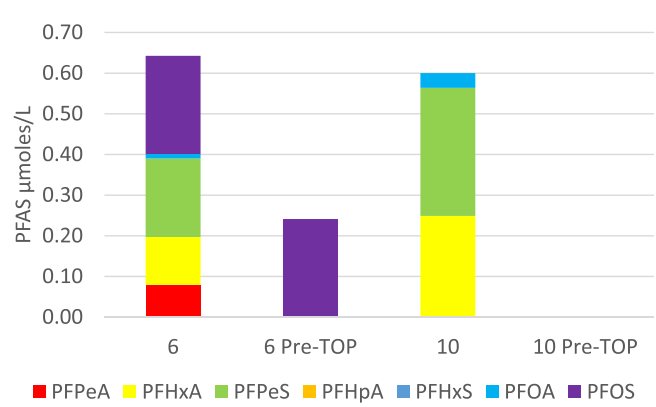


**Fig. 2.** Average pre- vs. post-TOP PFAS concentrations (μmoles/L) in insecticides 1 and 6.

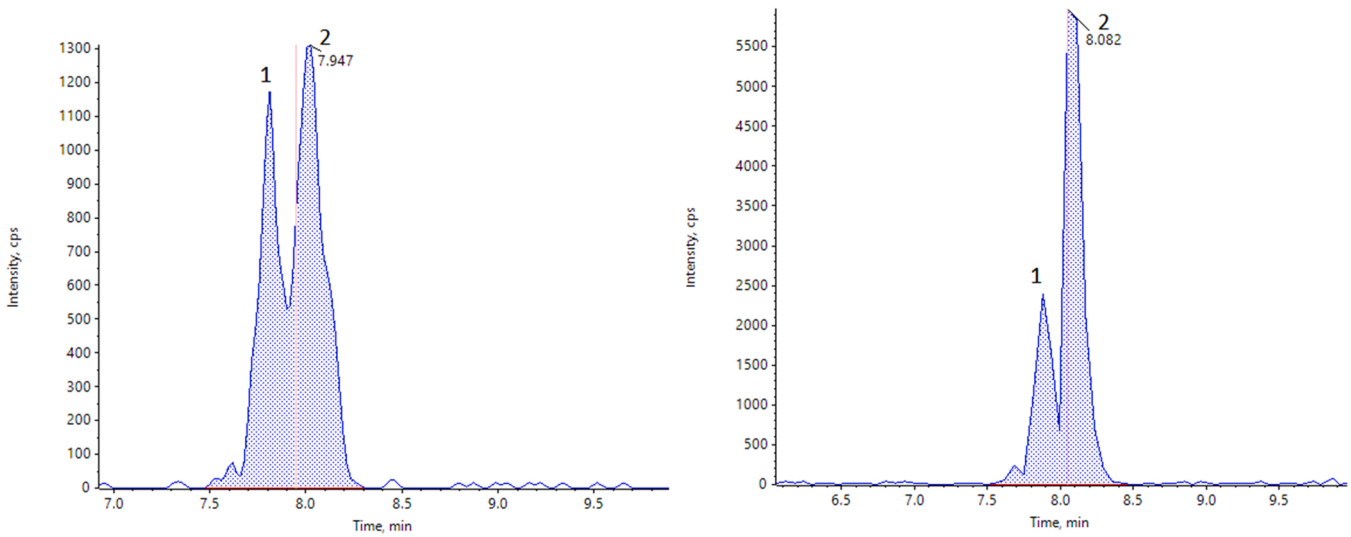


**Fig. 3.** Chromatographs of PFOS in insecticide 5 (right) and field 3 (left). The branched isomer of PFOS is labeled with 1 and the linear isomer of PFOS is labeled with 2.

of different PFAS in any soil grab sample. PFAS are solely made anthropogenically and many have been known to undergo long-range transport in the environment. Rankin et al. (2016) found dry weight concentrations ranging between 29 and 14,300 ng/kg for total perfluoroalkyl carboxylates and < LOQ-3270 ng/kg for total perfluoroalkyl sulfonates from surface soil samples collected from all continents, including areas judged to have no evident human impact.

Electrochemical fluorination (ECF) and telomerization are the two primary processes used in the production of PFAS and PFAS-related products. Production of PFAS by ECF was mostly phased out in the US in 2002. The existence of branched isomers of PFAS and homologs (like PFHxS for PFOS) are indicative of the ECF production process for PFAS (Benskin et al., 2010). The PFOS chromatograms of the sampled soil and insecticides (that contained PFOS) showed branched isomer peaks (Figs. S1–12). Another hallmark of PFOS produced by ECF is the significant presence of PFHxS also being found in the sample. In the present study's plant tissue grab samples, significant PFHxS concentrations were observed alongside significant PFOS concentrations.

### 4.2. Plant samples

Blaine et al. (2013) found that negligible amounts of soil PFAS were taken up and deposited in corn grains from corn plants grown in PFAS contaminated biosolid-amended soils. Scher et al. (2018) found negligible concentration of PFBA (the PFAS they found to have the highest bioconcentration potential) in corn kernels and low PFAS concentration in bean pods watered with PFAS-contaminated water. These two studies would suggest that if the corn and bean plants were collected were grown in PFAS-contaminated soil and water, little to no PFAS, other than small amounts of PFBA, would be found in their seeds. The PFAS concentrations found in the tested corn grain and bean pod samples (Table 3) would suggest that the source of these PFAS was not the soil or water they were grown in. Targeted analysis of the tested insecticide samples (Table 1) could account for the PFOS concentrations observed in the corn and bean samples, but not for the other 5 PFAS we observed (PFBA, PFHxA, PFHxS, PFHpA, and PFOA).

The tested formulations in Table 1 are only those found in the complete record of the pesticides applied to the fields in 2017. The tested insecticides likely do not encompass all the potential PFAS sources that could be applied to the site historically. The site is located near third party fields that could contribute pesticide and other product drift. Additionally, the site is located in a city that experiences dust storms several times a year. PFAS have been observed in a variety of dusts (Murakami and Takada, 2008; Wang et al., 2010; Fromme et al., 2009), and dust storms could result in environmental transport of top soil PFAS in dry environments.

The soil samples collected were surface samples. Surface level PFAS distribution often does not match distribution at lower levels (Sepulvado et al., 2011). The roots of the three plants species likely have access to soils whose PFAS concentrations and distribution may not match that of the surface samples collected for this study. This could explain why the peanut samples had concentrations of PFBA, PFHxS, and PFHpA, while none of the sampled surface soil had significant concentrations of those analytes.

### 4.3. Significance of PFAS in pesticides

Major PFAS contamination has mostly been associated with industrial production and use of PFAS, sites with the use of aqueous firefighting foams, and municipal and industrial waste. While the insecticides tested are commonly used on cotton, a non-consumptive agricultural product, PFAS are generally believed to not significantly degrade environmentally. Years of continuous use of PFAS and PFAS precursor-containing pesticides could lead to significant concentration of PFAS in the soil. Future use of soils treated with PFAS contaminated pesticides for other crops or pesticide drift could lead to PFAS concentrations being found in crops used for human or animal consumption. This potential was observed in three samples of foodstuff crops (corn, beans, and peanuts) that were grown on site, although the source of the PFAS in these crop samples does not appear to be the soil.

One PFAS, N-ethyl perfluorooctane sulfonamide or Sulfluramid (EtFOSA; $C_8F_{17}SO_2NHC_2H_5$), has been used in ant and roach insecticides. EtFOSA is known to degrade into PFOS and FOSA and contribute to environmental concentrations of these chemicals (Nascimento et al., 2018). EtFOSA was not detected in targeted analysis or suspect screening of this study's 10 test insecticides. Applied EtFOSA containing insecticides are currently known to be used in South America to deal with leaf cutter ant, an issue unlikely to occur at the test site.

Insecticide 6′s active ingredient is malathion. Malathion was, at one point, the most commonly used organophosphate insecticide in North America (Bonner et al., 2007). Only one specific formulation was tested. If many malathion formulations, for all of their many uses, contained PFOS concentrations similar to those found in insecticide formulation 6, many people around the world could be expose to PFOS through malathion use.

Suspect screening of all 10 insecticides and TOP assay on insecticides

6 and 10 showed potential for PFAS concentrations outside of the 24 targeted PFAS. Insecticide 10 showed no PFAS concentrations when run for target PFAS analysis, but both suspect screening and the TOP assay showed potential PFAS in the insecticide.

## 5. Conclusions

In the present work we have discovered PFOS in 6 out of 10 tested insecticides commonly used to treat cotton. In doing so, we identified a source of PFAS environmental contamination for rural and agricultural areas that potentially has been, and could continue to, impact PFAS concentrations in human and animal foodstuff crops grown in these areas. Suspect screening and PFAA-precursor oxidation tests showed evidence PFAS outside of the 24 PFAS included in the targeted analysis in 7 of 10 of the insecticides we tested. Our research also detected multiple PFAS species in soil and plant grab samples beyond what was observed in the insecticides we tested (PFOS). Results from our suspect screening and PFAA-precursor oxidation tests could offer a possible explanation for these concentrations. In this study, we only characterized PFAS concentrations in 10 different insecticides. Further investigation of a wider variety of pesticides as potential PFAS contamination sources should be done to better understand the PFAS exposure risk pesticides could present.

## Environmental Implications

(a) The studied material concerns the chemical group per- and polyfluorinated substances (PFAS) which are of utmost regulatory concern around the world.
(b) The work describes a previously unknown source, pesticides, for environmental PFAS contamination.

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This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

## Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: The corresponding author (Steven Lasee) currently is a research fellow for the Oak Ridge Institute for Science and Education that works with the United States Environmental Protection Agency. The Author also runs the consulting firm “Lasee Research and Consulting”.

## Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.hazl.2022.100067.

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