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Passive monitoring of soluble pesticides linked to cannabis cultivation: a multi-scale analysis

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ABSTRACT

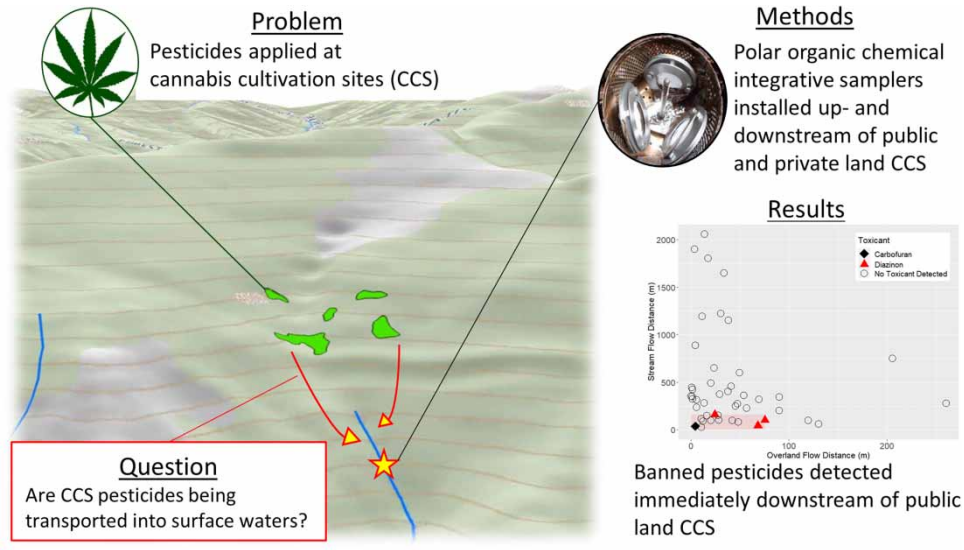
Several studies have documented the use of pesticides in cannabis cultivation. In northern California, one of the top cannabis production regions, several studies have identified cannabis-related impacts on multiple terrestrial wildlife species. To date, research has not focused on the potential for cannabis-related pesticides to contaminate downstream waterways and aquatic species. We conducted a two-part multi-scale study utilizing polar organic chemical integrative samplers (POCIS) to monitor pesticide contamination (1) immediately downstream and upstream of illegal public land cannabis cultivation complexes in low-order tributaries and (2) below a gradient of private land cannabis cultivation operations within higher-order streams. Diazinon and carbofuran were confirmed within sensitive headwater streams downstream of illegal public land cultivation sites in remote settings within four National Forests. Diazinon demonstrated higher downstream transport potential, with overland and in-stream flow distances totaling up to 186 m downstream of cultivation areas. While carbofuran displayed greater temporal longevity, being detected over 490 days after the last estimated pesticide application, no positive detections were identified within POCIS deployed within higher-order catchments. The utility of targeted POCIS deployed within low-order catchments is validated and confirms downstream cannabis-related water contamination on National Forest lands.

Key words: cannabis, pesticides, polar organic chemical integrative sampler, public lands, sensitive ecosystems, water quality

HIGHLIGHTS

- Foundational investigation of water quality impacts associated with cannabis cultivation.
- Carbofuran and diazinon water contamination confirmed downstream of public land cannabis cultivation complexes.
- Pesticides were detected at 11% of downstream sampling stations during the first wet season following site eradication.
- POCIS utility confirmed for low-order headwater streams.

GRAPHICAL ABSTRACT



INTRODUCTION

Pesticide use in regulated and unregulated settings poses environmental risks to natural resources and humans occupying habitats downstream of their use (Shankar Murthy *et al.* 2013; Sharma & Singhvi 2017; Souza *et al.* 2020). The use of highly toxic pesticides has been documented on both unpermitted and permitted private land cannabis farms (PLCF) (The Mendocino Voice 2018; Seltenrich 2019; Rich *et al.* 2020) and public land trespass cannabis (*Cannabis sativa* or *C. indica*) cultivation complexes (TCCC) (Thompson *et al.* 2017; Wengert *et al.* 2018) within California. Pesticides applied within PLCF and TCCC, referred to collectively as cannabis cultivation sites (CCS), protect crops from damaging vegetative pests and present an emerging concern as their mobilization into surface waters has the potential to deleteriously impact downstream water quality and aquatic populations.

CCS are often cryptic and scattered throughout remote areas (Butsic *et al.* 2017), requiring water quality survey strategies different from those typically implemented to monitor runoff from traditional agricultural production. Despite the potential for point source contamination to sensitive forested streams, an alarming paucity of research, data, and survey methods are currently available investigating water quality impacts from CCS. Until 2018 and the passage of California Proposition 64, legalizing both the medicinal and recreational use of cannabis, the pseudo-legal status of cannabis within California has presented obstacles to the intensive study of environmental impacts associated with cannabis cultivation (Short Gianotti *et al.* 2017). With the legalization of recreational cannabis production, the need for proper environmental evaluation is more urgent than ever. Pioneering research has identified environmental impacts linked to CCS from wildlife poaching (Wengert *et al.* 2018), intensive water consumption (Bauer *et al.* 2015; Zipper *et al.* 2019), landscape-scale habitat modifications (Butsic & Brenner 2016; Wang Brenner & Butsic 2017), and pesticide contamination to mammals (Gabriel *et al.* 2012, 2013; Thompson *et al.* 2018) and birds (Franklin *et al.* 2018; Gabriel *et al.* 2018). However, studies investigating potential impacts on water quality from pesticide contamination are substantially lacking.

Within California, impacts on fish and amphibian species of conservation concern have been directly linked to cholinesterase-inhibiting agricultural chemicals, including organophosphate and carbamate pesticides (Sparling *et al.* 2001; Davidson 2004; Jarrard *et al.* 2004). Runoff from agricultural practices has been identified as a source of water pollution from pesticide use, including diazinon, chlorpyrifos, malathion, and carbofuran (Bailey *et al.* 2000; Anderson *et al.* 2011, 2018; Moran *et al.* 2020). These and other studies implicate negative causal relationships between pesticides and the health of fish and amphibian populations. While investigations have primarily focused on California's traditional agricultural areas, the concentration of cannabis cultivation operations within remote mountain areas and headwater catchments carries the troubling potential to contaminate low-order streams and high-quality habitats.

Historically, the highest density and proportion of California cannabis cultivation is located within a tri-county region, composed of Humboldt, Trinity, and Mendocino counties in northwestern CA, known as the 'Emerald Triangle' (Corva 2014). The Emerald Triangle encompasses large regions of high-quality forest and riparian habitat for multiple aquatic species of conservation concern, including steelhead trout (*Oncorhynchus mykiss*), coho salmon (*Oncorhynchus kisutch*), foothill yellow-legged frogs (*Rana boylii*), and California red-legged frogs (*Rana aurora draytonii*). Due to the clandestine history of cannabis cultivation in California, growers have settled into the state's most rural regions, making it challenging to estimate the quantity of PLCF (Carah *et al.* 2015; Short Gianotti *et al.* 2017). However, available information indicates that the issue is extensive and growing, with the area of cannabis cultivation doubling between 2012 and 2016 (Butsic *et al.* 2018) and over 67,500 unpermitted PLCF (99% of the total PLCF) estimated statewide (California Growers Association 2018). In Humboldt County alone, up to 15,000 PLCF may be present, with only 8–13% initially seeking permits (Ascent Environmental Inc. 2018). In an investigation of the spatial distribution of PLCF, Butsic & Brenner (2016) found that growth in Humboldt County displayed clustering tendencies, with a majority (67%) of identified growth occurring in rural areas at distances >500 m from developed roads. Additionally, the scale of TCCC on public lands has remained consistent since 2012, with approximately 916,000 plants eradicated (cut down by law enforcement) annually and above-average eradications observed in 2020 (1.11 million plants) (State of California Department of Justice 2020).

To begin assessing watershed and aquatic species impacts from pesticides used in cannabis cultivation, we used innovative polar organic chemical integrative samplers (POCIS) deployed in a multi-scale sampling approach to investigate the presence of pesticides downstream of both PLCF and TCCC within forested waterways on both a targeted microscale and non-targeted watershed scales. POCIS are an inexpensive passive water quality sampling technology that effectively monitors waterborne pesticides and other emerging aquatic pollutants. POCIS sampling also allows researchers to place sampling equipment for extended periods of up to 1 year or more (Alvarez 2010) that would be difficult or impossible for grab sampling within cannabis settings due to the clandestine nature of the activity.

Our study focused on (1) the presence and types of pesticides transported from CCS through surface water runoff, (2) the assessment of the downstream transport capacity and persistence of CCS-associated pesticides, and (3) the utility of POCIS sampling for water quality monitoring of cannabis cultivation at multiple scales and the broader environmental implications of the findings. This study constitutes the first investigation on water quality impacts attributed to cannabis cultivation-related pesticides and the use of POCIS in these settings and may serve as a foundational framework for future CSS-specific pesticide loading investigations.

METHODS

We examined the utility of POCIS and the presence of pesticides associated with CCS at two spatial scales. The microscale component comprised the targeted deployment of POCIS devices immediately downstream and upstream of TCCC, primarily within low-order headwater streams. In comparison, the watershed-scale component involved deploying non-targeted POCIS within higher-order catchments containing a gradient of known outdoor PLCF and potentially unknown TCCC.

Study areas

Microscale study

The microscale component of the study incorporated sampling stations associated with 44 independent TCCCs distributed across five northern California counties (Figure 1 and Supplementary Material, Appendix A). Sampling stations ranged in elevation from 308 to 2,046 m (median: 1,310 m; sd: 419 m), drainage area from 0.1 to 18.75 km^2 (median: 1.4 km^2; sd: 11.76 km^2), and were established on four National Forests (Eldorado, Plumas, Shasta-Trinity, and Six Rivers).

Watershed-scale study

The watershed-scale component comprised 26 sampling stations distributed over 214.6 stream kilometers in central-eastern Trinity County near Weaverville, Douglas City, and Junction City (Figure 1, Supplementary Material, Appendix B). Between one and nine sampling stations were established within eight Trinity River subwatersheds (Table 1). Sampling stations ranged in elevation from 487 to 1,129 m (median: 690 m; sd: 147.93 m), drainage area from 4.2 to 190.51 km^2 (median: 56.53 km^2; sd: 64.79 km^2), and were established on public lands (Shasta-Trinity National Forest and Bureau of Land Management Public Domain Land) and private lands with the prior permission of landowners.

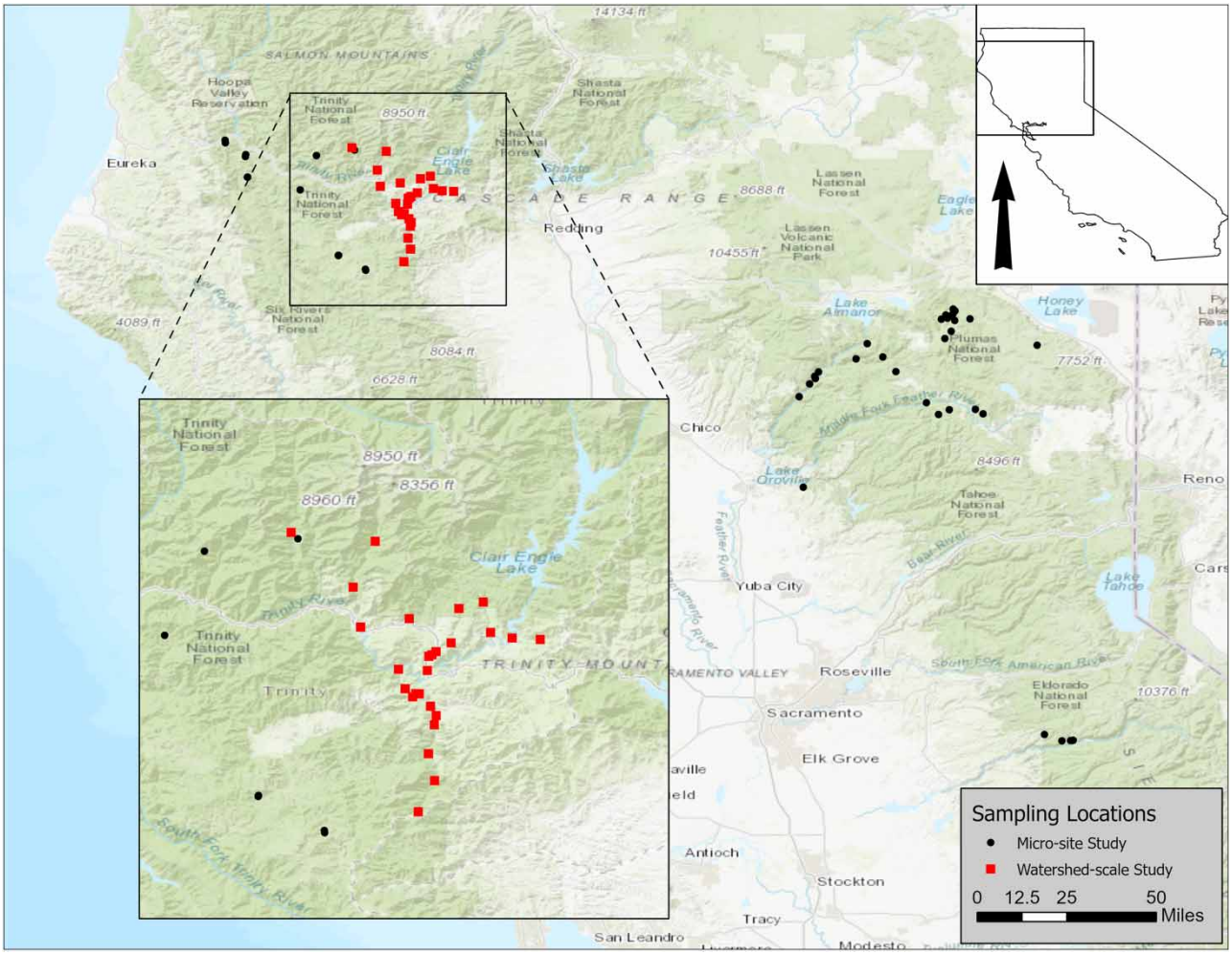


Figure 1 | Polar organic chemical integrative chemical (POCIS) sampling stations for the 44 trespass cannabis cultivation complexes monitored for the microscale study and 26 watershed-scale sampling sites distributed across five northern California counties on four National Forests.

Table 1 | Quantity of POCIS sampling stations within each Hydrologic Unit Code (HUC) 10 watershed and HUC12 subwatershed in Trinity County, California, USA. POCIS were placed to monitor selected pesticides

Watershed (HUC10)	Subwatershed (HUC12)	Sampling locations
Browns Creek	Lower Browns Creek	**8**
	Upper Browns Creek	**3**
Canyon Creek	Lower Canyon Creek	**2**
	Upper Canyon Creek	**1**
North Fork Trinity River	Lower North Fork Trinity River	**1**
Weaver Creek-Trinity River	Deadwood Creek-Trinity River	**2**
	Rush Creek	**2**
	Weaver Creek	**7**
		26

Private land cannabis farms. Data files identifying the location and permit status of PLCF within the study area were provided by the Trinity County Planning Department. Outdoor PLCF were identified and manually digitized using Google Earth imagery where *Cannabis* plants were clearly present (methods identical to Butsic & Brenner (2016)).

The cultivation area was calculated based on manually digitized polygons delineated by observable *Cannabis* spp. cultivation on satellite imagery. Due to the broad scale of the study area and the proclivity of private growers to conceal unpermitted, clandestine operations, we feel these numbers are a conservative minimum. Aggregate upstream PLCF and area were tabulated for each sampling station to identify thresholds and lag times for cumulative pesticide accumulations. Specific cannabis cultivation locations and their permit status are not presented due to the sensitive nature of the data.

Polar organic chemical integrative samplers

We deployed POCIS to passively collect polar or hydrophilic water-soluble organic chemicals from sampled water sources. For efficiency in allocating personnel and laboratory processing resources, a passive sampling approach was deemed most appropriate as most sampling sites were located across a large region within rugged and remote forest settings. Traditional grab sampling methods requiring multiple visits to capture temporal variability in aquatic pollution concentrations were deemed infeasible. Our study used POCIS as a screening technique to qualitatively determine the presence or absence of hydrophilic pesticides.

We installed a POCIS holder (i.e., cylindrical stainless steel perforated protective cage) accommodating three POCIS disks (Figure 2) at each sampling station. Each disk contained two microporous (0.1-μm pore size) polyethersulfone membranes with a 45.8 cm^2 surface area surrounding 220 mg of hydrophilic wettable OASIS-HLB sorbent polymer (Alvarez 2010; Harman Allan and Vermeirssen 2012) (660 total mg of sorbent per deployment). Water is permitted to pass through the membranes where the encased polymer material retains analytes. POCIS holders were anchored into the stream bed using a 1-m length steel rebar. A redundant rebar anchor was installed above anticipated bankfull water levels connected to the POCIS with an appropriate length of steel braided wire to reduce the risk of the POCIS devices being lost during high flows. POCIS anchoring was additionally reinforced with rocks positioned atop and surrounding the devices. Upon collection, disks were wrapped in aluminum foil and appropriately labeled and stored in a −40 °C freezer until submitted for laboratory analysis.

Deployments

The microscale study consisted of 145 POCIS deployed at 66 independent sampling stations associated with 44 TCCCs between 05 November 2014 and 05 March 2020. Detailed information associated with each POCIS deployment is available in Supplementary Material, Appendix A. POCIS were deployed successively for at least two deployment windows at 48 of the 66 sampling stations, while the other 18 were sampled just once. Sampling stations were established downstream of all sampled TCCC and upstream of 24 TCCCs. Eradication dates (date each TCCC was last active when raided by law enforcement officers) were used as the best available estimate of the last pesticide application date. Timing for installing POCIS

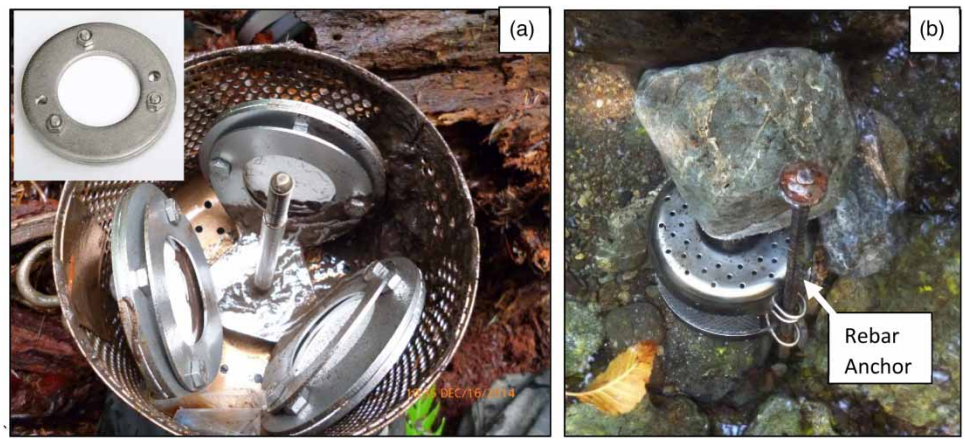


Figure 2 | (a) Photo of three POCIS disks installed within the outer protective cage with the lid removed. Close-up photo of disk provided in inset (image courtesy of Environmental Sampling Technologies). (b) Photo of POCIS deployed within a watercourse, including anchor rebar, and weighed down with large rocks to further prevent movement during high flows.

devices following the eradication date varied between 26 and 31,303 days (mean: 418; sd: 266). Approximately 29% of all POCIS ($n = 42$) were deployed during the first precipitation season (i.e., November – March) following eradication (Table 2), 49% during the second season, and 22% during the third or later precipitation season. POCIS membranes were deployed in the field for a mean window of 64 days (range: 17–252 days). Alvarez (2010) notes that POCIS may be deployed for any length of time, given that deployment time is known to account for variable sampling rates (volume of water sampled though POCIS per unit time). Thus, extended deployments are not a factor when determining chemical presence.

The watershed-scale study included 47 POCIS deployments at 26 sampling stations within 10 watercourses (Table 1, Figure 1) between 26 September 2017 and 08 November 2017 and removed between 21 November 2017 and 17 January 2018. POCIS membranes were deployed for a mean window of 35 days (range: 26–69 days) (Supplementary Material, Appendix B).

Flow velocity was recorded during 17 of the 47 POCIS deployments using a Global Water Instruments Flow Probe (Model FP111) accurate to 0.03 m/s, with a range of 0.1–6.1 m/s. Flow velocities were collected at six-tenths water depth, measured from the water surface, to capture the approximate mean vertical velocity within the water column for all project POCIS deployments (United States Bureau of Reclamation 2001).

Laboratory analysis

Laboratory confirmatory analysis of POCIS membrane material was conducted using gas chromatography with flame photometric detection (GC-FPD), gas chromatography–mass spectrometry (GC–MS), and liquid chromatography–mass spectrometry (LC–MS) techniques at the California Animal Health and Food Safety Laboratory (CAHFS) at the University of California, Davis. POCIS data were analyzed qualitatively for the presence or absence of 65 independent analytes (Table 3) from 3 chemical families: carbamates, organophosphates, and pyrethrins. Reporting limits for POCIS laboratory analyses are defined as the lowest quantifiable concentration of an analyte in a sample. If the analyte was detected at concentrations below the reporting limit, it was reported as 'Trace' and above reporting limits, it was reported as 'Positive'.

POCIS disks were stored in a −20 °C freezer and brought to room temperature immediately prior to extraction. All three disks associated with each POCIS were disassembled, and the OASIS-HLB sorbent was combined into a single 6-cc fritted syringe barrel placed on a solid-phase extraction manifold with a 50-cc tube underneath. The sorbent was spiked with 500 ng of $^{13}C_2$,^{15}N-methomyl as an internal standard, and the tube was eluted with 30 ml of methanol and 10 ml of acetonitrile. This extract was split into two 20-ml aliquots, both evaporated dry under nitrogen. One of the two dry extracts was reconstituted in 1 ml of 25% methanol in 10 mM ammonium acetate and analyzed for carbamate pesticides. The other was reconstituted in 1 ml of toluene and analyzed for organophosphate pesticides and pyrethrins. Batch quality control samples analyzed with each set of POCIS disks included blank OASIS-HLB sorbent and OASIS-HLB sorbent fortified with all of the listed carbamates and pyrethrins and a representative group of organophosphates at the reporting limit amounts.

Carbamates were analyzed by UHPLC-high-resolution mass spectrometry using a Thermo Exactive mass spectrometer interfaced with an Agilent 1260 liquid chromatograph. The column used was 100 × 2.1 mm, 1.7 μm Agilent Eclipse Plus C18. Electrospray ionization was used in positive ion mode. Thermo's ToxID program was used to detect any of the listed carbamates present in a sample.

Organophosphate pesticides were analyzed using an Agilent 6890 gas chromatograph interfaced with a flame photometric detector run in phosphorus mode. The column used was 30 M × 0.53 mm, 1.0 μm DB-17. Agilent's Chemstation GC software was used to detect any of the listed organophosphate pesticides present in a sample.

Pyrethrins were analyzed using an Agilent 6890/5975 GC–MS system. The column used was 30 M × 0.32 mm, 0.25 μm Agilent HP-5MS. The GC–MS was run in full scan mode. Pyrethrins were detected by displaying the selected ion chromatograms

Table 2 | Quantity of POCIS installed as part of the microscale study summarized by the in-stream deployment location in relation to each trespass cannabis cultivation complex and number of rain seasons following the eradication date

	Deployed POCIS	
Rain seasons following eradication date	**Downstream**	**Upstream**
1	36	6
2	42	29
3 +	23	9

Table 3 | Comprehensive list of 65 pesticide analytes grouped by chemical class assessed for qualitative presence/absence monitored by POCIS below known cannabis cultivation sites

Carbamate[a]	Pyrethrin[b]	Organophosphate[c]		
3-Hydroxycarbofuran	Allethrin	Diazinon	Methamidophos	Tetrachlorvinphos
Aldicarb	Cyfluthrin	Dicrotophos	Methidathion	Triazophos
Aldicarb sulfone	Cypermethrin	Dimethoate	Methyl parathion	Acephate
Bendiocarb	Fenvalerate	Dioxathion	Mevinphos	Azinphos-methyl
Carbaryl	Permethrin (trans)	Disulfoton	Monocrotophos	Carbophenothion
Carbofuran	Pyrethrins	EPN*	Naled	Chlorfenvinphos
Methiocarb	Phenothrin	Ethion	Parathion	Chlorpyrifos
Methomyl	Fenpropathrin	Ethoprop	Phorate	Coumaphos
Mexacarbate	Bifenthrin	Famphur	Phosalone	Crotoxyphos
Oxamyl	Deltamethrin	Fenamiphos	Phosmet	Crufomate
Propoxur	–	Fensulfothion	Phosphamidon	DDVP (Dichlorovos)
–	–	Fenthion	Profenophos	DEF**
–	–	Fonofos	Propetamphos	Demeton-O
–	–	Isofenphos	Ronnel	Demeton-S
–	–	Malathion	Terbufos	–
11 Analytes	***10 Analytes***		***44 Analytes***	

Reporting limits are the lowest quantified concentration of an analyte detected in a sample, and limits vary for each chemical class. Analytes detected at reporting limits are recorded as 'Trace' and above reporting limits as 'Positive'.
[a]Reporting limit = 0.5 μg per POCIS.
[b]Reporting limit = 0.1–1.0 μg per POCIS.
[c]Reporting limit = 5.0–25.0 μg per POCIS.
* Ethyl phenylphosphonothioate
** S,S,S-tributyl phosphorotrithioate

for each of the listed analytes and by comparison of spectra from analytes detected in samples with those from the analysis of analytical standards.

Sampling station catchments

Watershed boundary delineations and names were derived from the Watershed Boundary Dataset developed by the United States Geological Survey (USGS). Drainage areas for each sampling station were delineated using the USGS National Hydrography Dataset (NHD) in ArcGIS® Pro 2.6.0 and are used as a proxy for relative volumetric discharge.

Overland and in-stream flow distances were calculated for each sampling station installed downstream of TCCC as part of the targeted microscale study. Downslope distances were calculated from the closest cultivation plot edge to the sampling station representing the minimum possible flow distance. Overland flow distances were calculated using an eight-direction flow model approach described by Jenson & Domingue 1988 using a 30-m Digital Elevation Model derived from the USGS NHDPlus v.2 framework. In-stream flow distances were calculated along flow route polylines extracted from the NHD.

Data analysis

Boxplots were created for the areas draining to each POCIS sampling station, within the microscale study, grouped by up- and downstream deployments overlaid with the areas of positive detections. A scatterplot was produced comparing the overland and in-stream flow distances from the closest cultivation plot edge for all downstream POCIS sampling stations included in the microscale study. Positive detections by toxicant were highlighted. Data analysis was conducted using Rstudio v1.2.5033.

RESULTS

Microscale study

Laboratory analyses confirmed soluble pesticides within POCIS membranes at 5 of the 66 independent microscale sampling stations (Table 3). Diazinon, an organophosphate pesticide, was detected at three sampling stations located downstream of

TCCC during the first deployment window with pesticides not detected in subsequent deployments. Carbofuran, a carbamate pesticide, was detected at one downstream sampling station (Station ID: 008d) during the second of three deployment windows and one upstream sampling station (i.e., Station ID: 036u). All confirmed detections were reported as 'Positive,' indicating that the concentration was above the reporting limit (Table 3), equal to or greater than 0.025 μg per POCIS for diazinon and greater than 0.5 μg per POCIS for carbofuran. These positive detections were recorded within five subwatersheds spread across four northern California National Forests (Table 3).

The longest total flow distance for mobilized pesticides between the closest cultivation plot edge and the POCIS sampling station was 187 m for diazinon (Station ID: 020d) and 42 m for carbofuran (Station ID:008d) (Table 4). The positive sampling stations with the longest flow distances between the cultivation plot and the sampling station also correspond with larger drainage areas than other detections with 0.43 km^2 (Station ID: 020d) and 2.03 km^2 (Station ID: 008d) for diazinon and carbofuran, respectively. All downstream diazinon-positive sampling stations occurred where upstream drainage areas fell within the lower quartile compared to all downstream sampling stations (Figure 3). The area draining to the downstream sampling station where carbofuran was detected was approximately equal to the median of all downstream sampling stations.

Table 4 | POCIS summary for deployments and sampling stations where laboratory analysis confirmed soluble pesticides

Station ID	National forest	Overland flow distance (m)	In-stream flow distance (m)	Deployment duration (days)	Time since eradication (days)	Drainage area (km^2)	Result
007d	Six Rivers	68.36	44.66	44	102	0.27	Diazinon
008d	Plumas	4.37	37.54	181	92	2.03	Carbofuran
020d	Shasta-Trinity	24.29	162.36	38	91	0.43	Diazinon
026d	Six Rivers	75.52	101.18	36	104	0.13	Diazinon
036u	Eldorado	n.a.	n.a.	56	496	0.28	Carbofuran

Overland and in-stream flow distances represent the minimum downslope flow distance between the nearest cultivation plot edge and the sampling station. All positive detections were recorded during only one sampling deployment and tested negative during subsequent deployments.

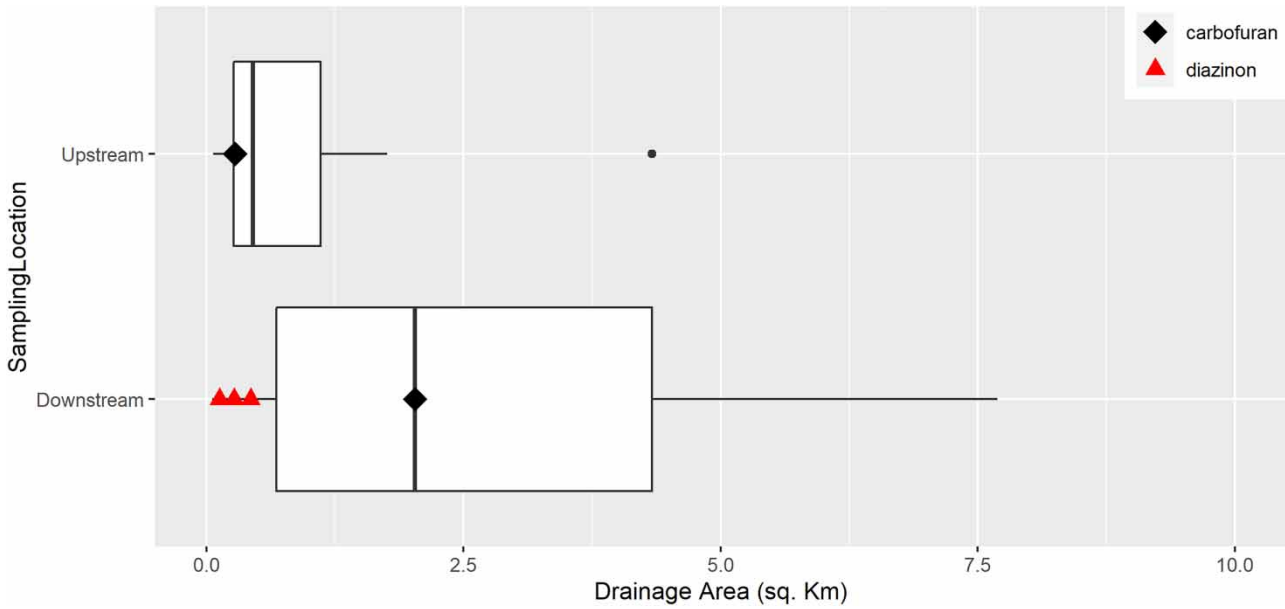


Figure 3 | Box plot of the area draining to all polar organic chemical integrative sampling stations deployed both up- and downstream of trespass cannabis cultivation complexes as part of the microscale study. Sampling stations where diazinon was detected are indicated by red triangles and carbofuran-positive sampling stations by black diamonds. Please refer to the online version of this paper to see this figure in colour: http://dx.doi.org/10.2166/wqrj.2022.101.

All downstream POCIS with positive detections were deployed less than 4 months after the eradication date and captured the first significant precipitation event of the wet season. Of the 36 downstream POCIS deployed during the first rain season (Table 2), 11% were positive for one analyte. All positive detections were recorded during only one sampling deployment and tested negative during subsequent deployments. The carbofuran-positive POCIS deployed upstream of the TCCC was installed during the second wet season nearly 1.5 years after the last known site activity (i.e., 496 days).

Dissolved diazinon demonstrated longer overland and in-stream transport distances from cultivation plots to the sampling stations than carbofuran. When the maximum transport distances are used to create a bounding box representing the maximum detection zone, we find that 23.9% of downstream TCCC sampling stations were deployed within this zone (Figure 4). The downstream sampling station where carbofuran was detected (Station ID: 008d) represented the second shortest stream flow distance and total transport distance measured from the closest plot edge of all downstream TCCC sampling stations.

Watershed-scale study

Laboratory analyses did not detect pesticide analytes within POCIS membranes from any sampling station deployed in the watershed-scale study. We removed POCIS at 6 of the 28 (21%) sampling locations after a single sampling window due to the logistical complications that included weather conditions, accessibility, and safety concerns (Supplementary Material, Appendix B). However, two independent samples across different time frames were collected from each of the remaining 22 POCIS installations. The mean water flow velocity recorded during POCIS deployments equaled 0.26 m/s, ranging from 0.1 to 0.4 m/s. The quantity of PLCF upstream of sampling stations ranged from 0 to 165, with a total upstream cultivation area between 0 and 61,814 m^2 (Supplementary Material, Appendix B).

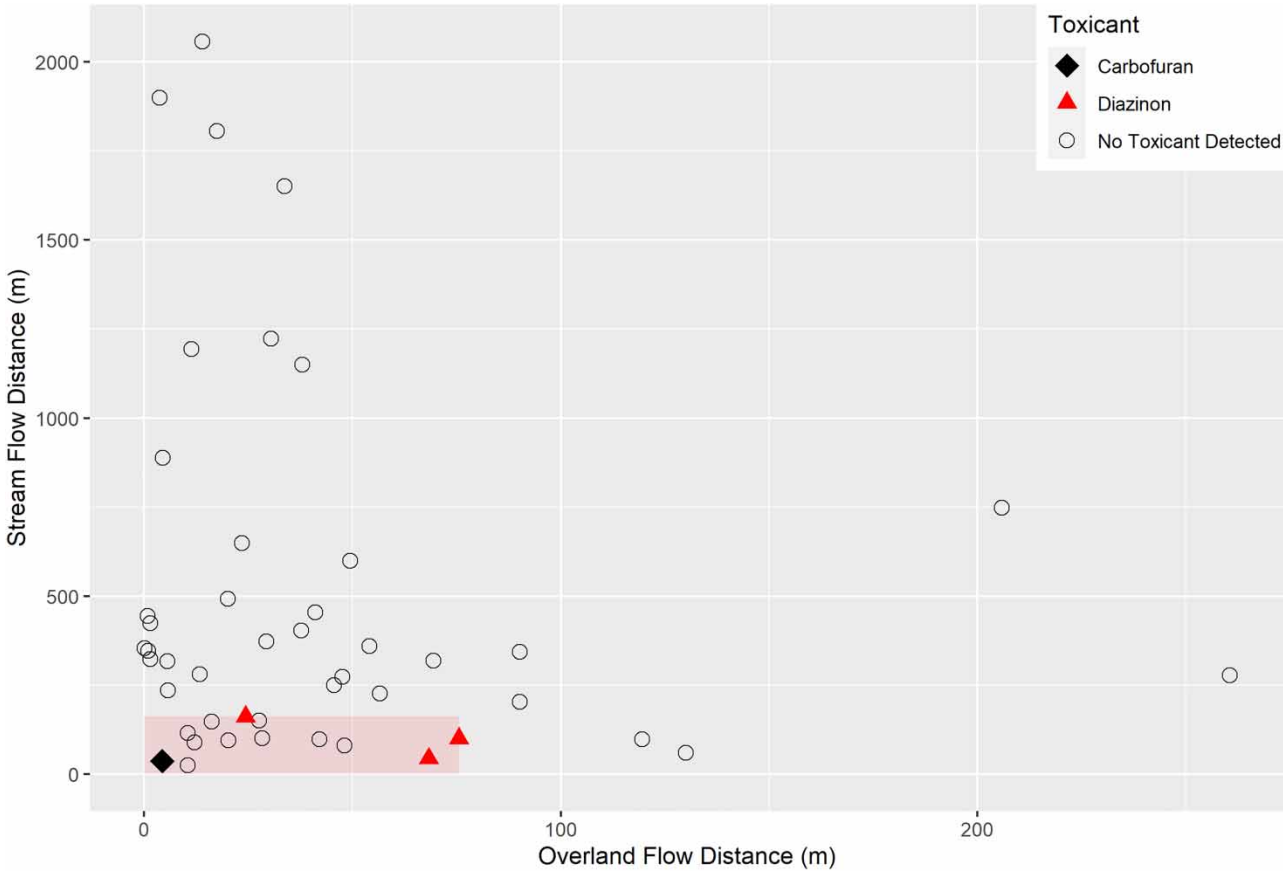


Figure 4 | Scatterplot of overland and in-stream flow distances of all downstream TCCC sampling stations, including locations with positive detections of diazinon and carbofuran. The red box outlines the maximum overland and in-stream flow distances, resulting in a positive detection and representing the maximum detection area. Please refer to the online version of this paper to see this figure in colour: http://dx.doi.org/10.2166/wqrj.2022.101.

DISCUSSION

Using a novel approach deploying POCIS in streams at a microscale near CCS, we confirmed that trespass cannabis cultivation complexes are water pollution point sources for both organophosphate and carbamate pesticides. Pesticides applied within remote TCCC are being mobilized and transported into sensitive headwaters through overland and in-stream surface flows. Positive detections suggest that diazinon demonstrates higher transport distances (at least 186 m, Table 4) than carbofuran (at least 41 m) and is capable of contaminating downstream reaches across a broader spatial scale. However, the downstream carbofuran detection occurred at a sampling station with the largest drainage area and, presumably, the highest flow volumes.

Variability in downstream persistence may be partially explained by differences in sensitivity to degradation processes within forested headwater settings and variable pesticide properties. Once in transport, degradation processes for both chemicals are dominated by abiotic hydrolysis, microbial metabolism, and, to a lesser extent, photolysis (Song 2005; Cohen 2006). Based on laboratory studies, diazinon is more resilient to hydrolysis at neutral pH values and may degrade more slowly in aquatic transport, with a hydrolysis half-life of 138 versus 57 days for carbofuran (World Health Organization 2004; U.S. EPA 2008). Additionally, although carbofuran is eight times more soluble than diazinon in water at 25°C (Wishart *et al.* 2022), diazinon demonstrates an order of magnitude higher adsorption rates (National Center for Biotechnology Information 2022), which may allow greater transport distances as pesticides are more strongly bound to suspended sediments.

The application of carbofuran was confirmed at the TCCC with a positive downstream detection through both visual determination (i.e., a labeled bottle was found) and toxicological sampling of cultivation plots and TCCC infrastructure (Gabriel *et al.* unpublished data). Diazinon was not confirmed during on-site assessments at any TCCC where it was detected in the downstream POCIS. Despite rigorous assessment efforts, the scale and complexity of TCCC often present difficulties in determining every applied chemical as bottles can be easily hidden, and applications may vary within the site. That said, diazinon has been detected at dozens of other TCCCs throughout California, so the positive downstream detections in this study are not surprising.

While the study only detected hydrologic pesticide transport at localized spatial scales, the downstream transport of these toxic pesticides is of immediate conservation concern as aquatic communities within the affected headwater streams are among the most sensitive freshwater ecosystems (Richardson 2019). Headwater ecosystems are subject to hydrologic independence and ecological autonomy and are intimately connected and dependent on the conditions of their catchments (Rodden 2005). As both diazinon and carbofuran are categorized as 'highly toxic' to fish species (Trotter *et al.* 1991; U.S. EPA 2008), their presence may jeopardize the ecological integrity of these important aquatic ecosystems. Additionally, sampled headwaters provide critical habitat during the life stages of several amphibian species of conservation concern, including Sierra Nevada yellow-legged frogs (*Rana sierrae*) and California red-legged frogs (*Rana. aurora draytonii*).

Lacking quantification, it is unclear if TCCC POCIS detections are at or above ecological or human health concern limits. However, many aquatic species with special conservation status are sensitive to these agricultural pesticides, with adverse sub-lethal effects being demonstrated in water concentrations as low as 0.1 mg/L of diazinon and 0.2 mg/L of carbofuran for coho salmon (*O. kisutch*), rainbow trout (*O. mykiss*) (Johnson & Finley 1980; Alam & Maughan 1992; Banaee *et al.* 2011), and California red-legged frogs (*R. aurora draytonii*). Thus, our study demonstrates an urgent need for additional, high-intensity water quality studies measuring the concentration of pesticide contamination downstream of TCCC.

For all downstream sampling stations with positive detections, the detections were recorded during the first wet season following eradication. Combined with the localized scale of measured downstream pollution, it is recommended that future studies deploy downstream POCIS devices as close to point sources as is feasible, timed specifically to capture first flush events. However, the positive carbofuran detection at site 008d during the second deployment window suggests that a lag time exists for pesticide transport immediately following eradication, which should be accounted for when determining the timing of deployments. A higher-resolution longitudinal array of POCIS should be deployed to capture downstream degradation rates over varying stream lengths. Additionally, in conjunction with water quality, future complementary aquatic invertebrate assessments would provide valuable insights regarding potential pesticide effects on invertebrate assemblages.

The reason for the upstream positive carbofuran detection point is currently unknown. During the assessment, all carbofuran containers and contaminated infrastructure were mitigated in hazmat-certified waterproof buckets. The mitigation buckets were observed to be present and intact during subsequent visits, indicating that the positive detection was not related to a post-eradication spill or cultivator transportation to another TCCC. Furthermore, comprehensive on-the-ground grid pattern searches

and aerial reconnaissance confirmed that no additional TCCC or related infrastructure was present upstream of the POCIS deployment station. The absence of an upstream TCCC and the lack of possibility of recontamination from mitigated materials suggest that the downstream TCCC is the only possible pesticide contamination source through wildlife transport following interaction with contaminated environmental media (e.g., soil or vegetation), possible groundwater connectivity in the short distance between the lower and upper sampling stations in the granite boulder field, or residual persistence related to an unknown pre-eradication spill by the original cultivators. Regardless of the contamination mechanism, the upstream detection constitutes the longest temporal persistence, with carbofuran being detected over 1 year following the eradication date.

Pesticides were not captured within any POCIS deployed in the non-targeted watershed-scale study. The higher flow volumes within larger catchments may dilute pesticide concentrations below detectable limits, combined with higher flow velocities decreasing adsorption rates to the OASIS-HLB sorbent polymer. Studies investigating the application of POCIS under various environmental conditions found that increased flow velocities resulted in only minor pesticide concentration increases when POCIS were exposed to flow rates between 2.6 and 37 cm/s (Li *et al.* 2010), while flow rates greater than 4.0 cm/s were found to significantly increase pollution molecules' desorption rates from the POCIS sorbent (Lissalde *et al.* 2014). Therefore, small concentration increases obtained through higher flow velocities would have been negated by increased desorption rates as mean flow velocities measured within the non-targeted watershed-level watercourses (i.e., 26 cm/s) were significantly higher than the flow rates within the Lissalde study. Accordingly, the lack of pesticide detections within higher-order streams may not indicate an absence of pesticides, rather flow velocities may not have been optimal for POCIS capture and retention of dissolved pesticides.

Single POCIS deployment has been proven as an effective pesticide survey method when deployed within headwaters, low-discharge waterways, or immediately downstream of potential source points. However, to account for higher flow rates, a broader longitudinal and latitudinal array of POCIS devices may be warranted to increase the detection potential when surveying larger watercourses. The deployment of additional POCIS increases the volume of water sampled and will improve capture potential within water bodies where dissolved chemicals are not uniformly distributed. Multiple samplers may also be composited into a single sample when surveying areas with very low pesticide concentrations (Alvarez 2010).

CONCLUSION

Investigations quantifying the impacts of CCS on water quality remain limited and underdeveloped; however, this study establishes that TCCC-applied pesticides are being mobilized into sensitive headwater streams on protected public land forests. Additionally, this study has confirmed the general utility of POCIS to detect CCS-related pesticide runoff when deployed immediately downstream of target point sources within smaller drainages. While watershed-level non-targeted POCIS did not return any positive detection during this study, additional investigations into the utility of POCIS for pesticide surveying within large watercourses may be warranted. Any future studies should employ a POCIS array stratified within the water column and across the latitudinal cross-section.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

CONFLICT OF INTEREST

The authors declare there is no conflict.

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