Factors affecting 1,2,3-trichloropropane contamination in groundwater in California

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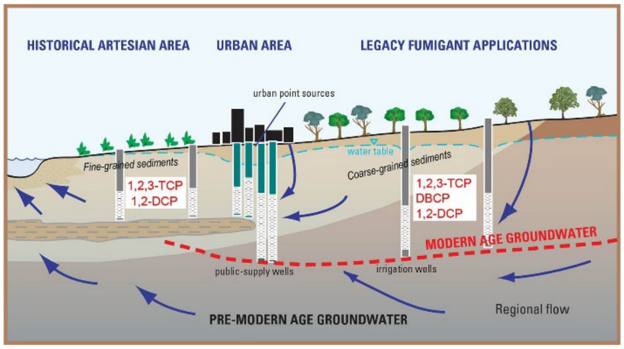
Abstract

1,2,3-Trichloropropane (1,2,3-TCP) is a volatile organic chemical of eminent concern due to its carcinogenic, mutagenic, and reproductive effects, and its frequent occurrence at concentrations of concern worldwide. In California, 1,2,3-TCP was detected in 6.5% of 1237 wells sampled by the U. S. Geological Survey (USGS). About 8% of domestic wells had a detection of 1,2,3-TCP, compared to 5% of public-supply wells. 1,2,3-TCP was detected in 5.5% of most recent samples from 7787 public-supply well sources of the California State Water Resources Control Board Division of Drinking Water (DDW). Concentrations ranged from <0.005 to 2.7 μg/L. The California maximum contaminant level (MCL) is 0.005 μg/L. Most of the detections occurred in the San Joaquin Valley, where 1,2,3-TCP was detected above the MCL in 16% of USGS sampled wells and 18% of DDW wells. 1,2,3-TCP occurrence and concentrations are related to legacy fumigant use and hydrogeologic factors. Understanding factors affecting 1,2,3-TCP will aid in determining vulnerability and long term persistence in the San Joaquin Valley, which can help focus efforts to manage drinking water resources on the most vulnerable areas and also inform efforts in other areas of the state and worldwide. Widespread occurrence of 1,2,3-TCP is related to nonpoint source agricultural contaminant inputs. High concentrations of 1,2,3-TCP are in young, shallow, oxic groundwater beneath primarily orchard/vineyard crops. These areas are in coarse-grained sediments that promote rapid recharge, related to proximal alluvial fan sediments deposited by large streams that drain glaciated watersheds of the Sierra Nevada. 1,2,3-TCP co-occurs with 1,2-dibromo-3-chloropropane (DBCP) and 1,2-dichloropropane (1,2-DCP) throughout modern age groundwater, indicating its long term persistence with little degradation. The highest concentrations of 1,2,3-TCP were observed at point source cleanup sites in urban areas; depending on the age and source of groundwater to nearby public-supply wells, these areas may see increasing concentrations of 1,2,3-TCP.



Introduction

1,2,3-Trichloropropane (1,2,3-TCP) is a chlorinated solvent used worldwide. 1,2,3-TCP is of concern because of its health effects, mobility in groundwater, and resistance to natural attenuation. The European Union Chemicals Agency (ECHA) has listed 1,2,3-TCP as a chemical of very high concern because of its carcinogenic, mutagenic, and reproductive effects (ECHA, 2012). Because of its mobility and improvements in analytical reporting methods, the number of detections of 1,2,3-TCP has increased. In the U.S., no federal maximum contaminant level (MCL) has been set (U.S. EPA, 2017); the California MCL of 0.005 μg/L was adopted by the California State Water Resources Control Board in 2017 based on cancer risk (California

State Water Resources Control Board, 2017); Hawaii established a state MCL of 0.6 μg/L in 2014. Other selected states in the U.S. have established health-based screening levels.

1,2,3-TCP is formed as a by-product during the synthesis of various chemicals; it is a persistent component of historically-used chlorinated fumigant formulations for agricultural use; it is also used as a solvent in cleaning or degreasing operations. 1,2,3-TCP-containing fumigant formulations used in California include products Telone and DD-mix. Telone is primarily cis- and trans-1,3-dichloropropene (1,3-DCP) and 1,2-dichloropropane (1,2-DCP), and DD-mix is also a 1,2-DCP/1,3-DCP mixture with 0.2 to 7% weight percent of 1,2,3-TCP (Oki and Giambelluca, 1987; Zebarth et al., 1998) and up to 25% 1,2-DCP (Leistra and Boesten, 1989). DD-mix was introduced in 1942; however, widespread use of fumigants began in the 1950s (Deeley et al., 1991; Loague et al., 1998). The oldest formulations of these fumigant mixtures had greater percentages of 1,2,3-TCP (Oki and Giambelluca, 1987; Zebarth et al., 1998). 1,2-Dibromo-3-chloropropane (DBCP) was often applied at the same time or alternate intervals to the use of 1,2-DCP/1,3-DCP containing products. DBCP use was banned in 1979 in California. Use of DCP-containing fumigants increased after DBCP was banned until they were banned in California in 1984 (Cardozo et al., 1988). The hydrolysis half-life of DBCP in groundwater has been documented to be on the order of 6 years (Burlinson et al., 1982; Burowet al., 2007; Deeley et al., 1991); 1,2,3-TCP is more persistent in groundwater than DBCP (Ellington et al., 1986; Milano et al., 1988; Pagan et al., 1998).

1,2,3-TCP is typically found at industrial sites and in areas with agricultural fumigant applications. Groundwater contamination by 1,2-DCP (up to 165 μg/L) and 1,2,3-TCP (up to 9 μg/L) was found in wells in the Netherlands (Leistra and Boesten, 1989). 1,2,3-TCPwas detected in 17% of groundwater samples at concentrations up to 0.61 μg/L in the 1,2-DCP-contaminated Abbotsford-Sumas aquifer in Canada and the U.S. (Grove et al., 1998; Tesoriero et al., 2001; Zebarth et al., 1998). Groundwater contamination by 1,2,3-TCP is widespread in Hawaii (Hunt Jr., 2004; Oki and Giambelluca, 1987) in wells also affected by DBCP and EDB in areas of pineapple cultivation. Concentrations of 1,2,3-TCP ranged up to 3 μg/L.

Groundwater contamination by 1,2-DCPwas documented in the San Joaquin Valley (Domagalski and Dubrovsky, 1992). They found that the alluvial deposits in the eastern San Joaquin Valley were most vulnerable to fumigant contamination due to the coarse-grained texture of the sediments and low organic content. Subsequent studies by the California Groundwater Ambient Monitoring and Assessment Program Priority Basin Project (GAMA-PBP) included systematic assessment of the occurrence of 1,2,3-TCP in groundwater resources used for public and domestic drinking water supplies. 1,2,3-TCPwas detected at concentrations above the MCL in 20% of the groundwater resource used for domestic drinking water in the southeastern San Joaquin Valley (Fram and Shelton, 2018; Shelton and Fram, 2017). Maximum concentrations detected in the GAMA-PBP studies were 1.2 μg/L in domestic wells and 0.88 μg/L in public-supply wells.

Physical and chemical properties of 1,2,3-TCP make it difficult to remediate. Removal with activated carbon is considered the best available technology. In situ reductive dechlorination using a lactic-acid-based reductant has been successful. Reductive dechlorination by zero-valent iron and zinc (Sarathy et al., 2010; Tesoriero et al., 2001) and selected biotransformation pathways have been studied (Samin and Janssen, 2012).

Water-quality data from wells sampled by the USGS and the California State Water Resources Control Board Division of Drinking Water (DDW) regulatory compliance dataset were used to establish overall 1,2,3-TCP occurrence in California. Assessment and understanding of 1,2,3-TCP occurrence and concentrations in California is timely due to the recent establishment of a state MCL. In this study, a statistical analysis of factors explaining 1,2,3-TCP occurrence was done using wells sampled by the USGS in the San Joaquin Valley. More complex time series analyses have been done to determine the sustainability of the San Joaquin Valley groundwater resource to agricultural impacts (e.g., Burow et al., 2008a, 2008b, 2012; Nolan et al., 2015; Ransom et al., 2017); however, these studies did not address 1,2,3-TCP contamination. Factors complicating the understanding of contaminant trends include variations in the duration and pathways of contaminant transport toward monitoring and production well locations, variations in application of contaminants at the land surface, and degradation of contaminants in the subsurface (Broers and van der Grift, 2004). Assessment of 1,2,3-TCP occurrence and determination of explanatory factors is required to evaluate long-term potential risk to drinking water supplies throughout the state and elsewhere. This study defines important factors that determine the vulnerability of groundwater to 1,2,3-TCP contamination in this dominantly agricultural landscape and shows the persistence of this chemical in modern age groundwater.

2. Materials and methods

2.1. Statewide and San Joaquin Valley datasets

Statewide, the USGS sampled 1190 wells for 1,2,3-TCP as part of the GAMA-PBP (https://ca.water.usgs.gov/projects/gama/water-quality-results/). Samples were collected using established collection methods (e.g., Koterba et al., 1995; U.S. Geological Survey, variously dated) and analyzed using documented methods depending on the date of sampling (e.g., U.S. EPA, 1992; Connor et al., 1998; California Department of Health Services, 2002; Rose et al., 2016); in general these methods use purge and trap capillary gas chromatography/mass spectrometry. For wells that were sampled more than once, the most recent value was used. The GAMA-PBP uses a stratified random design to create areally-distributed networks of wells that are statistically representative of study areas (Belitz et al., 2010). During 2004–17, the GAMA-PBP sampled wells in 87 networks representing 95% of the area used for public supply statewide (Belitz, 2015), and in 22 networks representing some of the areas of the state with large numbers of domestic wells. Of the wells sampled statewide for GAMA-PBP for 1,2,3-TCP at reporting levels of <0.006 μg/L, about half were public-supply wells and one-third were domestic wells. The regional analysis includes 352 GAMA-PBP wells in the San Joaquin Valley, about half are domestic wells and one-third public-supply wells.

In the San Joaquin Valley, GAMA-PBP results were combined with results from the USGS National Water-Quality Assessment (NAWQA) project (Arnold et al., 2016, Arnold et al., 2017, Arnold et al., 2018). NAWQA results include 46 domestic wells from areally-distributed networks, 20 monitoring wells from a local-scale (3 mi) transect of wells near Fresno (Burow et al., 1999, Burow et al., 2007, Burow et al., 2008a, Burow et al., 2008b), and 18 wells from a 28-mi regional extension westward from the local transect. The regional transect wells are monitoring and production wells sampled at multiple depths along a regional groundwater flow path. The NAWQA networks were sampled several times during 1993–2015; the most recent value was used. Nearly all of the wells sampled by the USGS for the GAMA-PBP or NAWQA in the San Joaquin Valley also had data for DBCP, 1,2-DCP, tetrachloroethene (PCE), dissolved oxygen (DO), iron (Fe) and manganese (Mn), nitrate (total, as N), and simazine.

To better characterize 1,2,3-TCP detections statewide, and to better determine concentrations in wells in urban areas in the San Joaquin Valley, the DDW regulatory compliance dataset was also used (https://www.waterboards.ca.gov/resources/data_databases/drinking_water.html; accessed July 9, 2018); 11,714 sources were available statewide with 1,2,3-TCP analyses; 7787 sources had 1,2,3-TCP data when censored at 0.005 μg/L; 1902 wells had 1,2,3-TCP, 1,2-DCP, DBCP, and PCE data for the San Joaquin Valley. 1,2,3-TCP analyses from monitoring wells at regulated cleanup sites in the Central Valley were also compiled (https://geotracker.waterboards.ca.gov/; accessed July 23, 2018) to evaluate the range of concentrations of 1,2,3-TCP from urban point sources.

1,2,3-TCP data were censored at the lowest common reporting limit for each dataset to maximize the amount of concentration information available. USGS data were censored at 0.006 μg/L; DDW data were censored at 0.005 μg/L. For the USGS dataset in the San Joaquin Valley, other constituents of interest were censored at the following detection limits: DBCP at 0.03 μg/L, 1,2-DCP at 0.029 μg/L, PCE at 0.04 μg/L, and simazine at 0.01 μg/L. In the DDW data in the San Joaquin Valley, DBCP was censored at 0.01 μg/L, 1,2-DCP at 0.5 μg/L, and PCE at 0.5 μg/L. The purpose of the censoring was to ensure that all wells had a common detection level for each organic constituent; results reported in the databases as detections at concentrations less than these censoring levels were considered non-detections for this study, and results reported as non-detections at concentrations higher than these censoring levels were excluded. No censoring was applied to nitrate, major ions, or trace element data.

A GIS-based program (Scott, 1990) was used to compute a spatially unbiased grid for the San Joaquin Valley DDW well data. The DDW well data are public drinking water wells that tend to be clustered in urban areas and were therefore gridded to remove spatial bias and oversampling of urban areas. An approximately 9 mi^2 grid was computed and wells in each grid cell were selected using a stratified random approach to represent nonbiased 1,2,3-TCP detection frequencies and reasonable estimates of minimum, maximum, and median concentrations.

2.2. Variables related to 1,2,3-TCP occurrence and concentrations

The USGS data in the San Joaquin Valley were used for analysis among 1,2,3-TCP and other explanatory variables. The reduction/oxidation (redox) conditions of groundwater at the time of well sampling were determined using field measurements of DO, nitrate, Mn, Fe, and sulfate using a defined redox classification (McMahon and Chapelle, 2008; Chapelle et al., 2009). A redox workbook (Jurgens et al., 2009) was used to classify samples into oxic, suboxic, anoxic, and mixed classification groups. These categories were further simplified into 3 redox categories: oxic samples ($O2 \geq 0.5$ mg/L) are classified as oxic, suboxic and anoxic samples are classified as reduced, and samples classified as mixed oxic and anoxic water are classified as mixed.

Groundwater age, referred to as the length of time groundwater resides in the aquifer system, was determined for the USGS San Joaquin Valley dataset using a classification scheme. For the age classification, 418 wells were classified as having modern, mixed, or pre-modern groundwater on the basis of tritium (^3H) and carbon-14 (^{14}C) concentrations, similar to Jurgens et al. (2016) (Table S1). ^3H activities were decay-corrected to 2016 and compared to the decay-corrected atmospheric ^3H input records from 1950 to 1955 for the latitude and longitude of the well site (Michel et al., 2018). Half of the samples with ^3H data also had ^{14}C data. Samples with decay-corrected $^3H > 1.1$ TU and uncorrected $^{14}C > 85$ pmC were defined as modern, primarily composed of water recharged after about 1955. Samples with $^3H < 0.19$ TU and uncorrected $^{14}C < 85$ pmC were defined as pre-modern, primarily composed of water recharged prior to 1955. Samples with substantial fractions of both modern and pre-modern components were designated as mixed. In reality, pre-modern groundwater could contain very small fractions of modern water, and modern groundwater could contain very small fractions of pre-modern water.

The percent land use around each well was calculated using an enhanced version of the satellite derived nationwide USGS National Land Cover Dataset (Price et al., 2003; Vogelmann et al., 2001) representing early 1990s land use. The imagery contains 25 land-cover classifications. Early 1990s land use was used because the land cover data has a separate classification for orchard/vineyard land use, and it is more likely to represent land cover at the time of recharge than more recent data. The orchard/vineyard land use includes almonds and other nuts, and fruit orchards, which are prevalent in the San Joaquin Valley. These were aggregated into three principal land uses: urban, agricultural, and natural. Based on the dominant land use (>50%) in 500-m (1,640 ft) buffers, each well was classified as urban, agricultural, natural, or mixed. Agricultural land use was further subdivided into orchard/vineyard and other agricultural land use for further explanatory analysis.

Groundwater model output from the Central Valley Hydrologic Model (CVHM) at 1 mi^2 resolution was assembled (Faunt, 2009). Areas of higher downward vertical water flux would be more vulnerable to contamination originating from the land surface. The model estimated physical aquifer property used in this analysis includes vertical flux in the upper active CVHM layer for variable months.

The normalized lateral position (proportional distance from valley axis) was calculated as part of CVHM. The normalized lateral position provides a measure of position of the well in the regional flow system. The lateral position of each well was calculated as the ratio of the distance from the valley trough to the well and the total distance from the valley trough to the edge of the valley. The edge of the valley was represented by the boundary of the valley fill deposits and was assigned a value of 1000. The valley trough was assigned a value of 0.

2.3. Hydrogeology of the San Joaquin Valley

The Central Valley of California covers an area of >20,000 mi^2 (50,000 km^2). This level-floored depression is about 30–60 mi wide and nearly 400 mi long, bounded by the Sierra Nevada on the east and the Coast Ranges on the west. The San Joaquin Valley occupies the southern two-thirds of the Central Valley (Fig. 1) and is made up of the San Joaquin basin in the north and the internally-drained Tulare basin in the south (Bertoldi et al., 1991). The San Joaquin Valley is an asymmetrical structural trough filled with marine and continental sediments up to 10 mi thick. The aquifer system is comprised of unconfined, semi-confined, and confined aquifers, which are primarily contained within the upper 1000 ft of alluvial sediments deposited by streams draining the surrounding Sierra Nevada and Coast Ranges (Faunt, 2009). The aquifer sediments are heterogeneous and typically range from 30 to 70% coarse-grained texture throughout the valley (Faunt et al., 2010). Significant work has been done to characterize the sedimentary structures of the alluvial fan sequences in the eastern San Joaquin Valley (e.g., Weissmann et al., 2002a) as they relate to overall recharge of groundwater and contaminant transport (Zhang et al., 2018), indicating preferential recharge and transport pathways in the high permeability sediments. In terms of the regional flow system, during pre-development conditions (prior to significant agricultural development), groundwater flowed from recharge areas in the proximal alluvial fans to discharge areas in the center of the basin (Faunt, 2009). Irrigation pumping and intensive agricultural recharge during agricultural production has caused modern-aged groundwater to move vertically downward and overprint the pre-development regional flow system.

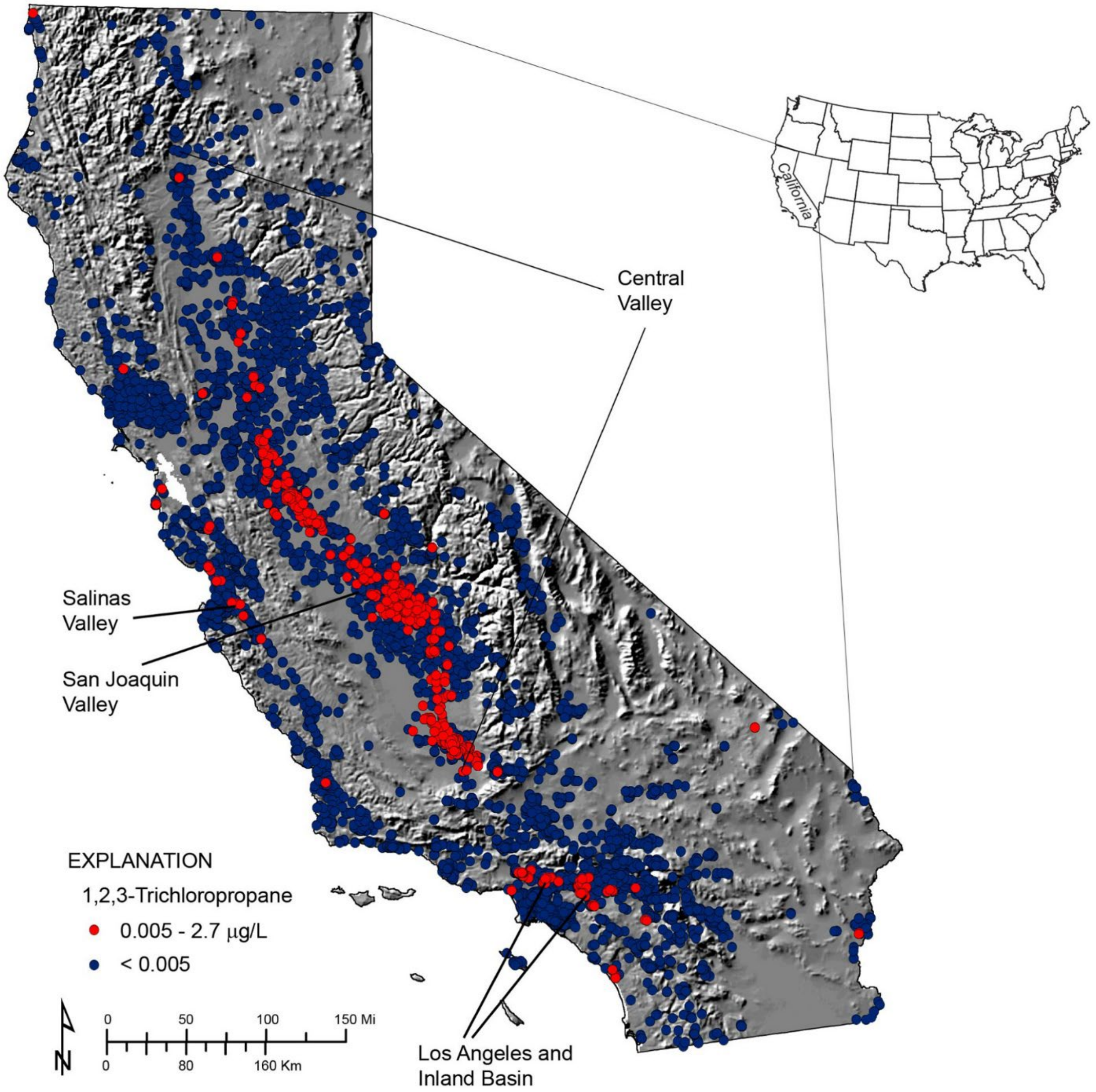


Fig. 1. Detections of 1,2,3-trichloropropane in wells sampled by the USGS and in data from the California Division of Drinking Water (DDW) sampled during 2004–2018. The most recent sample was used. Concentrations are censored to 0.006 μg/L in USGS wells and 0.005 μg/L in DDW wells.

3. Results and discussion

3.1. 1,2,3-TCP is detected in groundwater statewide

1,2,3-TCP was detected at concentrations of 0.006 μg/L or greater in 80 wells of 1237 USGS sampled wells statewide (6.5%). About 8% of domestic wells had a detection of 1,2,3-TCP, compared to 5% of public-supply wells. Similarly, 1,2,3-TCP was detected at concentrations of 0.005 μg/L or greater in 425 of 7787 samples (5.4%) from DDW well sources statewide (Fig. 1). Concentrations in USGS wells ranged from <0.006 to 1.2 μg/L; concentrations in DDW wells ranged from <0.005 to 2.7 μg/L. The CA-MCL is 0.005 μg/L. 1,2,3-TCP is detected throughout the state; however, the detections tend to cluster in developed areas in the Salinas Valley, Los Angeles and the Inland Basin, and the Central Valley.

Among wells sampled by the USGS, 72% of the detections of 1,2,3-TCP occur in the San Joaquin Valley; in the DDW data, more than half of the detections occur in the San Joaquin Valley. Because most of the detections are in the San Joaquin Valley, the rest of the analysis of occurrence and explanatory factors was done using a subset of wells in the San Joaquin Valley. Understanding factors affecting 1,2,3-TCP will aid in determining vulnerability and long term persistence in the San Joaquin Valley, which can also inform assessments of vulnerability in other areas of the state and worldwide.

3.2. 1,2,3-TCP is frequently detected in the San Joaquin Valley

In the San Joaquin Valley, 1,2,3-TCP was detected in 65 of 398 (16%) USGS wells in the areally-distributed network (Table 1). Concentrations ranged from <0.006 to 1.2 μg/L; detections generally occur in the eastern and southern San Joaquin Valley (Fig. S1). 1,2,3-TCP was detected in 18% of domestic wells and 12% of public-supply wells. 1,2,3-TCP was detected in 341 of 1902 (18%) DDW wells in the San Joaquin Valley. Because DDW wells cluster in urban areas, the DDW data were de-clustered by subsampling on an approximately 9 mi^2 grid of 1500 cells (Fig. S2). Wells in each grid cell were selected using a stratified random approach. Using the 1500 cell grid, 438 cells had a DDW well; the spatially weighted detection frequency for 1,2,3-TCP is 18%, which is similar to detection frequencies in USGS wells. Concentrations in the DDW data ranged from <0.005 to 0.82 μg/L, with detections again occurring in the eastern and southern San Joaquin Valley.

Table 1. Summary of 1,2,3-trichloropropane (1,2,3-TCP) in the San Joaquin Valley, California.

USGS sampled wells			
Censoring value			**0.006 μg/L**
Well type	**Number of wells**	**% of wells with 1,2,3-TCP**	**Maximum concentration (μg/L)**
All wells	398	16%	1.2
Domestic	204	18%	1.2
Public-supply	115	12%	0.88
Irrigation/other	41	7.3%	0.03
Monitoring	38	26%	0.43

California Division of Drinking Water (DDW) sources			
Censoring value			**0.005 μg/L**
	Number of cells	**Spatially weighted detection frequency**	**Maximum concentration (μg/L)**
Public drinking water sources	438	18%	0.82

3.3. 1,2,3-TCP occurrence and concentrations are related to legacy fumigant use and hydrogeologic factors

Concentrations of 1,2,3-TCP were correlated with concentrations of other agricultural constituents and variables representing land use, redox conditions, position of the well in the flow system, and recharge rates. Many of the variables used in this analysis were found to be important predictor variables in evaluating aquifer vulnerability to agriculturally-derived nitrate in Central Valley groundwater (Ransom et al., 2017).

3.3.1. 1,2,3-TCP is related to other nonpoint source agricultural contaminants

USGS sampled wells with 1,2,3-TCP detections also had detections of other soil fumigants, such as DBCP and 1,2-DCP (Table 2). 1,3-Dichloropropene was measured but not detected. Concentrations of 1,2,3-TCP were strongly correlated with DBCP and 1,2-DCP (Table 3). The positive correlation of 1,2,3-TCP with DBCP suggests that 1,2,3-TCP-containing fumigants may have been applied on the same fields at different times or possibly even co-applied with DBCP. The correlation of 1,2,3-TCP with 1,2-DCP is likely because they were components of the same fumigant formulations.

Table 2. Relation of 1,2,3-trichloropropane (1,2,3-TCP) to explanatory variables for USGS wells in the San Joaquin Valley, CA.

Co-occurrence with other constituents (% of 1,2,3-TCP detections)	
1,2-Dibromo-3-chloropropane (DBCP)	45%
1,2-Dichloropropane (1,2-DCP)	49%
Simazine	32%
Tetrachloroethylene (PCE)	7.7%
Nitrate above the MCL	42%
DBCP and 1,2-DCP	22%
DBCP and simazine	17%
1,2-DCP and simazine	14%
DBCP and PCE	4.6%
1,2-DCP and PCE	4.6%
DBCP and nitrate above the MCL	18%
1,2-DCP and nitrate above the MCL	17%
Land use (% of 1,2,3-TCP detections with >50% land use)	
Orchard or vineyard (111) [a]	58%
Other agricultural (183)	25%
Total Agricultural (294)	83%
Urban (52)	12%
Undeveloped (31)	1.5%
Mixed (20)	3.1%
Redox conditions (% of 1,2,3-TCP detections)	
Oxic (287)	97%
Mixed (10)	0
Reduced (77)	3.0%

Well type (% of 1,2,3-TCP detections)	
Domestic wells (204)	58%
Irrigation wells (27)	3.0%
Public-supply wells (115)	22%
Monitoring wells (38)	15%

Well depth (depth in ft of 1,2,3-TCP detections)	
Min	80
Max	1028
Median	262

Groundwater age (% of 1,2,3-TCP detections)	
Modern (241)	63%
Mixed (67)	31%
Pre-modern (74)	6%

Vertical water flux, in m^3/d (at wells with 1,2,3-TCP detections)	
Minimum downward flux	17
Maximum downward flux	62,410
Median of downward flux	3901
Maximum upward flux	12,809

[a] Indicates number of wells in specified category.

Table 3. Correlations among explanatory variables and constituent concentrations in USGS sampled wells in the San Joaquin Valley, California.

Kruskal-Wallis rank sum test		
Constituent concentration	**Grouping variable**	**p-Value**
1,2,3-TCP	Age category	0.004
DBCP	Age category	0.005
1,2-DCP	Age category	0.01
Simazine	Age category	<0.001
PCE	Age category	0.11
Nitrate	Age category	<0.001

Spearman's rank correlation			
Constituent concentration	**Variable**	**p-Value**	**rho**
1,2,3-TCP	DBCP	<0.001	0.45
1,2,3-TCP	1,2-DCP	<0.001	0.58
1,2,3-TCP	Simazine	0.003	0.15
1,2,3-TCP	PCE	0.06	0.09
1,2,3-TCP	Nitrate	<0.001	0.28
1,2,3-TCP	Orchard/Vineyard (%)	<0.001	0.26
DBCP	Orchard/Vineyard (%)	<0.001	0.34
1,2-DCP	Orchard/Vineyard (%)	<0.001	0.17
PCE	Orchard/Vineyard (%)	0.07	−0.09
Simazine	Orchard/Vineyard (%)	<0.001	0.20
Nitrate	Orchard/Vineyard (%)	<0.001	0.35
1,2,3-TCP	Other agricultural (%)	0.002	−0.16
DBCP	Other agricultural (%)	<0.001	−0.28
1,2-DCP	Other agricultural (%)	0.50	0.03
PCE	Other agricultural (%)	0.002	−0.16
Simazine	Other agricultural (%)	0.01	−0.13
Nitrate	Other agricultural (%)	0.07	−0.09
1,2,3-TCP	Total agricultural (%)	0.01	0.12
DBCP	Total agricultural (%)	0.12	0.08
1,2-DCP	Total agricultural (%)	0.001	0.16
PCE	Total agricultural (%)	<0.001	−0.18
Simazine	Total agricultural (%)	0.66	−0.02
Nitrate	Total agricultural (%)	<0.001	0.19
1,2,3-TCP	Dissolved oxygen	<0.001	0.25
DBCP	Dissolved oxygen	<0.001	0.27
1,2-DCP	Dissolved oxygen	0.08	0.09
Simazine	Dissolved oxygen	<0.001	0.21
PCE	Dissolved oxygen	0.06	0.09
Nitrate	Dissolved oxygen	<0.001	0.68
1,2,3-TCP	Well depth	0.33	−0.05
DBCP	Well depth	0.14	−0.07
1,2-DCP	Well depth	0.72	−0.02

Spearman's rank correlation

Constituent concentration	**Variable**	**p-Value**	**rho**
Simazine	Well depth	<0.001	−0.22
PCE	Well depth	0.82	0.01
Nitrate	Well depth	<0.001	−0.30
1,2,3-TCP	Proportional distance from valley axis	0.51	0.03
DBCP	Proportional distance from valley axis	0.06	0.09
1,2-DCP	Proportional distance from valley axis	0.33	−0.05
Simazine	Proportional distance from valley axis	0.001	0.16
PCE	Proportional distance from valley axis	0.52	0.03
Nitrate	Proportional distance from valley axis	<0.001	0.22
1,2,3-TCP	Vertical water flux, September 2000	<0.001	−0.17
DBCP	Vertical water flux, September 2000	0.002	−0.15
1,2-DCP	Vertical water flux, September 2000	0.01	−0.12
Simazine	Vertical water flux, September 2000	<0.001	−0.18
PCE	Vertical water flux, September 2000	0.75	0.02
Nitrate	Vertical water flux, September 2000	0.32	−0.05

1,2,3-TCP was also detected in wells with simazine, and in wells with nitrate at concentrations above the MCL. 1,2,3-TCP concentrations are positively correlated with simazine and nitrate concentrations. These constituents are commonly found in agricultural areas in the San Joaquin Valley (Burow et al., 2008a, Burow et al., 2008b). 1,2,3-TCP was detected in a few wells with PCE, which is a more common contaminant in urban areas. DBCP and 1,2-DCP co-occur with other constituents such as PCE, simazine, and nitrate concentrations above the MCL at similar rates, further corroborating their common use (Table 2). Widespread occurrence and correlation with other agricultural constituents indicates that most of the detections and the highest concentrations of 1,2,3-TCP are associated with nonpoint source agricultural use.

3.3.2. Nonpoint source input of 1,2,3-TCP is primarily beneath orchard or vineyard crops

Eighty-three % of the detections of 1,2,3-TCP occur in wells located in agricultural areas (Table 2); most of the detections were in orchard/vineyard areas. Fumigants containing 1,2,3-TCP or DBCP were commonly used on stationary crops (same location every year) such as orchards and vineyards, which tend to occur in the eastern parts of the San Joaquin Valley (Fig. S1). Twelve % of the detections of 1,2,3-TCP occur in urban areas.

1,2,3-TCP was detected in 18% of wells in the agricultural area and 15% of wells in the urban area. The similar detection frequency in urban and agricultural areas may be due to the proximity of urban areas to previous agricultural applications or due to urban-related sources. Concentrations in USGS wells located in agricultural areas were not significantly different from wells in urban areas ($p = 0.59$; Wilcoxon rank sum test). The USGS wells represent a spatially unbiased estimate of detection frequencies according to the proportion of total land area represented by each major category; however, concentrations in urban areas may be under-represented because only 8 wells in an urban area had detectable concentrations of 1,2,3-TCP. Therefore, gridded DDW data were also used to estimate concentrations. 1,2,3-TCP ranged from <0.005 to 0.46 µg/L in agricultural areas and <0.005 to 0.38 µg/L in urban areas, and concentrations were significantly higher in the urban areas than the agricultural areas in DDW wells ($p < 0.001$; Wilcoxon rank sum test) (Fig. 2). Potential urban source concentrations are discussed in greater detail in a later section. Because the explanatory variables were determined for USGS sampled wells and not the DDW wells, the remainder of the analysis is done using USGS sampled wells.

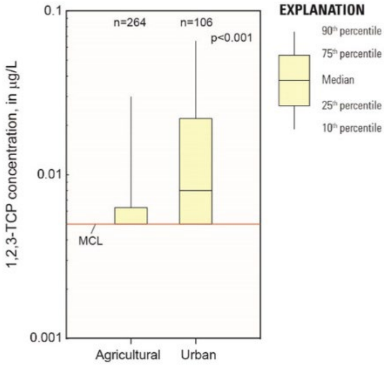


Fig. 2. Concentrations of 1,2,3-TCP in agricultural and urban areas in DDW wells in the San Joaquin Valley, California.

Concentrations of 1,2,3-TCP, DBCP, 1,2-DCP, simazine, and nitrate are significantly positively correlated with % orchard/vineyard land use within a 500-m radius of the well (Table 3). Concentrations are negatively correlated with other agricultural land use for 1,2,3-TCP, DBCP, simazine, and PCE. Orchard and vineyard crops are grown on the upper parts of the alluvial fans in coarse-grained sediments (Burow et al., 1998) (Fig. S1). The % orchard/vineyard is higher in wells with modern age groundwater than with mixed or pre-modern water (Fig. S3), indicating that groundwater beneath these crops is younger, predominantly irrigation recharge. In contrast, the % other agricultural land use, such as pasture, row crops, or small grains, is higher in wells with pre-modern age groundwater than mixed or modern water. Older groundwater from discharge of long regional flow paths mixes with the shallow, younger irrigation recharge in the distal parts of the alluvial fans where these other agricultural crops are grown. The % urban land use is higher in wells with mixed and pre-modern age groundwater than modern age groundwater. Urban wells in the USGS dataset are deeper than agricultural wells and thus urban wells represent older groundwater. The correlation between 1,2,3-TCP and younger-aged groundwater beneath orchard and vineyard crops indicates that these areas are the most vulnerable to 1,2,3-TCP, likely due to nonpoint source fumigant use and the coarse-grained sediments that promote rapid recharge.

3.3.3. 1,2,3-TCP occurs in oxic groundwater

In general, 1,2,3-TCP occurs upgradient from areas that were artesian about 100 years ago (Fig. S1), in the upper parts of the alluvial fans in coarse-grained sediments that were pre-development recharge areas. Artesian areas were swampy regional discharge areas prior to significant irrigation pumping (Mendenhall et al., 1916) and sediments are more fine-grained and likely contain more organic matter. Groundwater in these historically artesian areas tends to be geochemically reduced, although typically only Mn or Fe-reducing. Consistent with this concept, 97% of the 1,2,3-TCP detections were in oxic groundwater (Table 2). Oxic conditions preclude transformation of 1,2,3-TCP in most of the groundwater system (Samin and Janssen, 2012).

Similarly, 1,2,3-TCP is significantly positively correlated with DO concentrations (Table 3). DBCP, simazine, and nitrate concentrations were also positively correlated with DO. 1,2-DCP and PCE concentrations were not significantly correlated with DO. These results are consistent with greater 1,2,3-TCP occurrence and higher concentrations in oxic groundwater on the coarse-grained upper parts of the alluvial fans in predominantly orchard/vineyard land use.

3.3.4. 1,2,3-TCP occurs at higher concentrations in young, shallow groundwater

Fifty-eight percent of wells with 1,2,3-TCP detections were domestic wells and 22% were public-supply wells (Table 2). Only 3% of the wells were irrigation wells, but most of the analyses had high detection limits for 1,2,3-TCP and were thus excluded from the dataset. Groundwater from domestic wells in the San Joaquin Valley tends to be young (<30 years old; Spurlock et al., 2000), shallow groundwater because they are typically screened near the water table. The age of groundwater from public-supply wells tends to be older than domestic wells because they are screened in deeper, older groundwater. However, long-screened wells like public-supply wells can contain a significant fraction of young water if the top of screen is shallow (e.g. Burow et al., 2008a, Burow et al., 2008b; Eberts et al., 2012). The depth of USGS wells sampled in this study range from 80 to 1028 ft below land surface. 1,2,3-TCP occurs at all well depths, showing a slight decrease in concentrations with depth (Fig. 3). DBCP, simazine, and nitrate decrease in both detection frequency and concentration with depth, whereas 1,2-DCP and PCE increase in detection frequency with depth. Simazine and nitrate were the only constituents with concentrations that had a significant negative correlation to well depth (Table 3). Most of the deep wells (>400 ft) with 1,2,3-TCP are in parts of the eastern and southern San Joaquin Valley—areas where the water table is deep (Faunt, 2009).

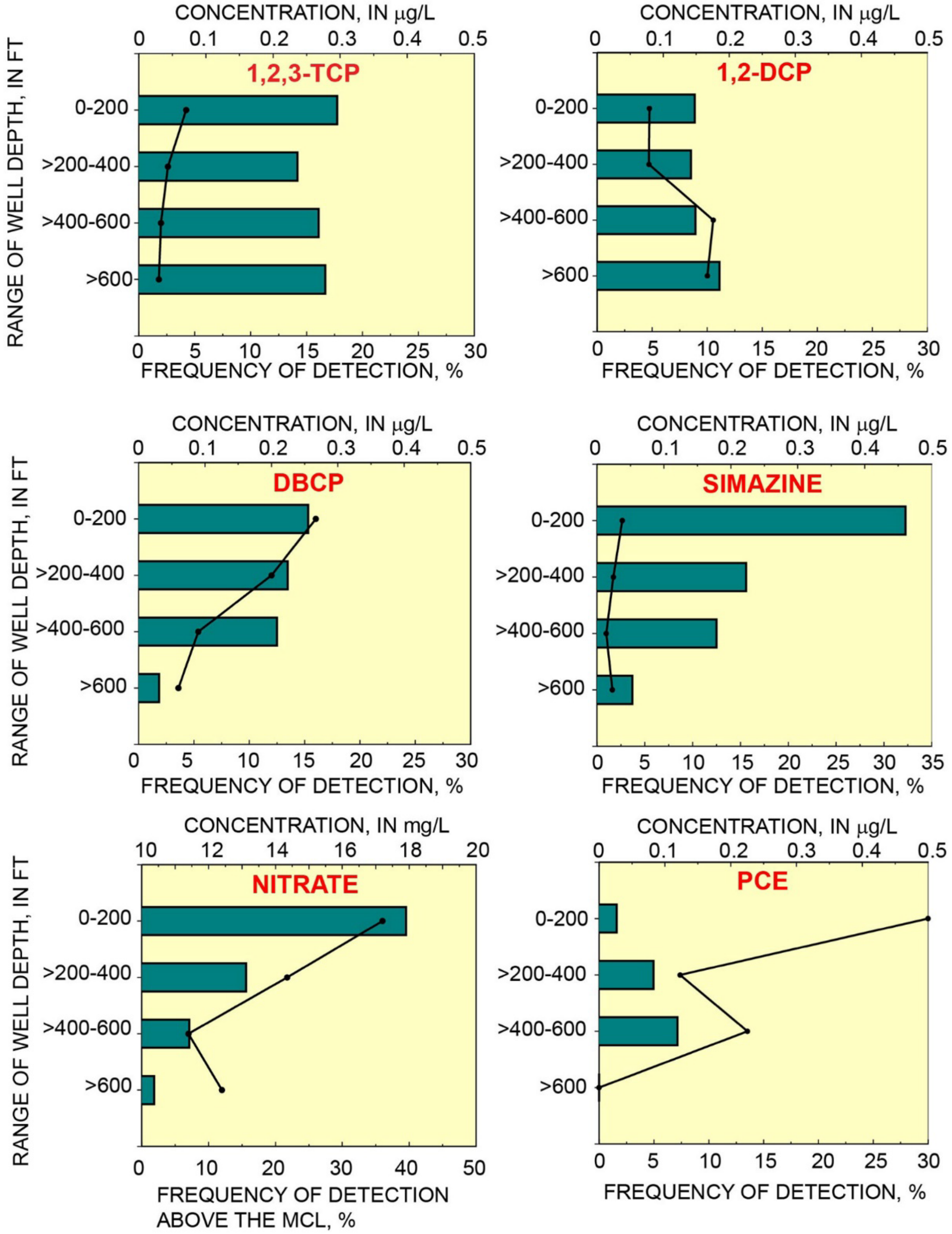


Fig. 3. Detection frequency and median concentration of 1,2,3-TCP and selected constituents with well depth.

Concentrations of selected constituents were higher in younger groundwater. Groundwater in 63% of wells with 1,2,3-TCP were classified as modern in age. Only 4 wells (6%) were pre-modern. Clearly, 1,2,3-TCP is not present in groundwater that is greater than about 75 years old; however, a well may contain 1,2,3-TCP and be classified as pre-modern if it has a small fraction of modern-aged groundwater that is too small to be detected with ^{3}H and C-14. Ninety-four % of wells with pre-modern groundwater did not have a detection of 1,2,3-TCP. 1,2,3-TCP concentrations were significantly higher in groundwater from wells classified as modern or mixed age than pre-modern (Table 3). Concentrations of DBCP and 1,2-DCP were also significantly higher in groundwater from wells classified as modern or mixed age than in pre-modern. Simazine and nitrate concentrations were significantly higher in modern groundwater than mixed and significantly higher in mixed than pre-modern groundwater. PCE was not significantly different among age classifications, but was detected only in mixed or modern groundwater.

Concentrations of fumigants tend to increase with distance from the valley axis (Fig. S4). However, the occurrence of 1,2,3-TCP, DBCP, and 1,2-DCP varies with proportional distance (Table 3). Elevated concentrations of 1,2,3-TCP co-occur with elevated DBCP (usually in the absence of 1,2-DCP) in oxic, modern- and mixed-age groundwater on the proximal parts of the alluvial fans—at the greatest distances (>75% of proportional distance) from the valley axis. Elevated DBCP concentrations occur without detectable 1,2,3-TCP or 1,2-DCP in modern water at proportional distances of about 500 to 750. Elevated 1,2,3-TCP co-occurs with both DBCP and 1,2-DCP from proportional distances of about 0 to 500 in oxic, modern- and mixed-age groundwater beneath agricultural (81%) and urban or mixed (19%) land use. 1,2-DCP occurs at elevated concentrations in the downgradient part of the regional groundwater flow system toward the axis of the valley. Concentrations of 1,2,3-TCP were positively correlated with concentrations of simazine and nitrate. Simazine and nitrate were positively correlated to proportional distance, indicating that concentrations were highest at the greatest distances from the valley axis. 1,2,3-TCP was detected in only 5 wells where PCE was also detected. These 5 wells tapped oxic, modern- and mixed-age groundwater beneath agricultural or urban land use. PCE was not significantly correlated with proportional distance.

These results indicate that 1,2,3-TCP occurs most frequently and at highest concentrations in young, shallow groundwater. As noted earlier, the co-occurrence of 1,2,3-TCP with 1,2-DCP, DBCP, and other agricultural contaminants such as simazine and nitrate indicates that the dominant source of 1,2,3-TCP is related to the agricultural use of fumigants. 1,2,3-TCP occurs at higher concentrations with DBCP, simazine, and nitrate in the proximal parts of the alluvial fans, whereas it occurs with 1,2-DCP in more distal parts of the fans toward the axis of the valley. 1,2,3-TCP can undergo reductive dehalogenation to 1,2-DCP (Peijnenburg et al., 1998); some of the 1,2-DCP in the distal parts of the alluvial fans could be from transformation of 1,2,3-TCP as it moves downgradient.

3.3.5. 1,2,3-TCP is highest in areas with high recharge rates

Wells with 1,2,3-TCP detections occur in areas of predominantly downward groundwater flow during irrigation season. Fifty-nine of 65 wells with a detection of 1,2,3-TCP (91%) had downward groundwater flow in the uppermost active layer of the CVHM (Faunt, 2009) during September 2000, which represents approximate maximum seasonal downward flow due to pumping (Fig. S5). Similarly, 1,2,3-TCP, DBCP, 1,2-DCP, and simazine concentrations were significantly correlated with increasing downward vertical water flux (Table 3), indicating that higher concentrations are associated with higher recharge rates. Downward flux was significantly higher in locations with domestic wells than either public-supply or monitoring wells ($p = 0.048$, Kruskal-Wallis test). Comparing CVHM vertical water flux to the early 1990s land cover data, the % orchard/vineyard land use in a 500-m radius of the well is significantly correlated to downward flux in August, 1992 ($p < 0.001$, $\text{rho} = -0.27$), during maximum seasonal downward flow, and significantly correlated to upward flux in January 1992, during the winter when water levels are recovering from pumping. Note that even during irrigation season, groundwater discharge to the Sacramento-San Joaquin River delta occurs in the northern San Joaquin Valley. Orchards and vineyards are grown primarily on the proximal parts of the alluvial fans in the coarse-grained sediments furthest from the valley axis, with increasing area in the southern San Joaquin Valley. The % other agricultural land use is not significantly correlated to flux in August 1992; however, other agricultural land use is significantly correlated to downward flux in January 1992 ($p < 0.001$; rho = −0.33). Agricultural crops other than orchard/vineyard are grown on the distal parts of the alluvial fans toward the center of the valley. Although seasonal trends in 1,2,3-TCP concentrations were not evaluated, the strong correlation between 1,2,3-TCP concentrations and downward flux during irrigation season, and the strong positive correlation between 1,2,3-TCP concentrations and % orchard/vineyard land use indicates that irrigation recharge of oxic groundwater beneath the orchard/vineyard land use on the proximal parts of the alluvial fans in the central and southern San Joaquin Valley is associated with the highest occurrence and concentrations of 1,2,3-TCP.

3.4. 1,2,3-TCP, DBCP, and 1,2-DCP occur throughout modern age groundwater

Fumigant concentrations along a regional and local-scale flow path transect in the eastern San Joaquin Valley near Fresno (location shown on Fig. S1) show the prevalence of these constituents in modern age groundwater (Fig. 4). 1,2,3-TCP co-occurs with DBCP and 1,2-DCP in shallow and moderately deep groundwater along the approximately 3 mi transect of monitoring wells (B-B′), indicating decades of fumigant use. In the San Joaquin Valley, pre-modern age groundwater (prior to significant agricultural development) flowed from recharge areas in the proximal alluvial fans to discharge areas in the center of the basin. Irrigation pumping and intensive agricultural recharge during agricultural production has caused the modern age groundwater to move vertically downward and overprint the pre-development regional flow system. This can be seen in the characteristics of the age classification in the wells along the regional (A-A′) and local (B-B′) transect. Groundwater >60 years old is at the leading edge of agriculturally-affected groundwater moving downward through the system. Mixed age groundwater is pre-modern groundwater and young, affected groundwater. Beneath this zone is old, unaffected groundwater from the pre-development groundwater flow system. The pre-modern-aged groundwater does not contain any detectable fumigants. 1,2,3-TCP occurs with both DBCP and 1,2-DCP in the upper part of the regional transect (northeast), and becomes less frequent downgradient (southwest) along the regional transect. 1,2,3-TCP and 1,2-DCP co-occur without DBCP in 2 wells in the lower part of the transect near the area mapped as the historical artesian area of regional discharge. The lack of DBCP in the lower part of the transect may be because DBCP was not applied on the crops grown in these areas or that DBCP is transformed more quickly than 1,2,3-TCP. These results are consistent with the findings reported earlier for the areally-distributed dataset that 1,2,3-TCP occurs throughout modern age groundwater.

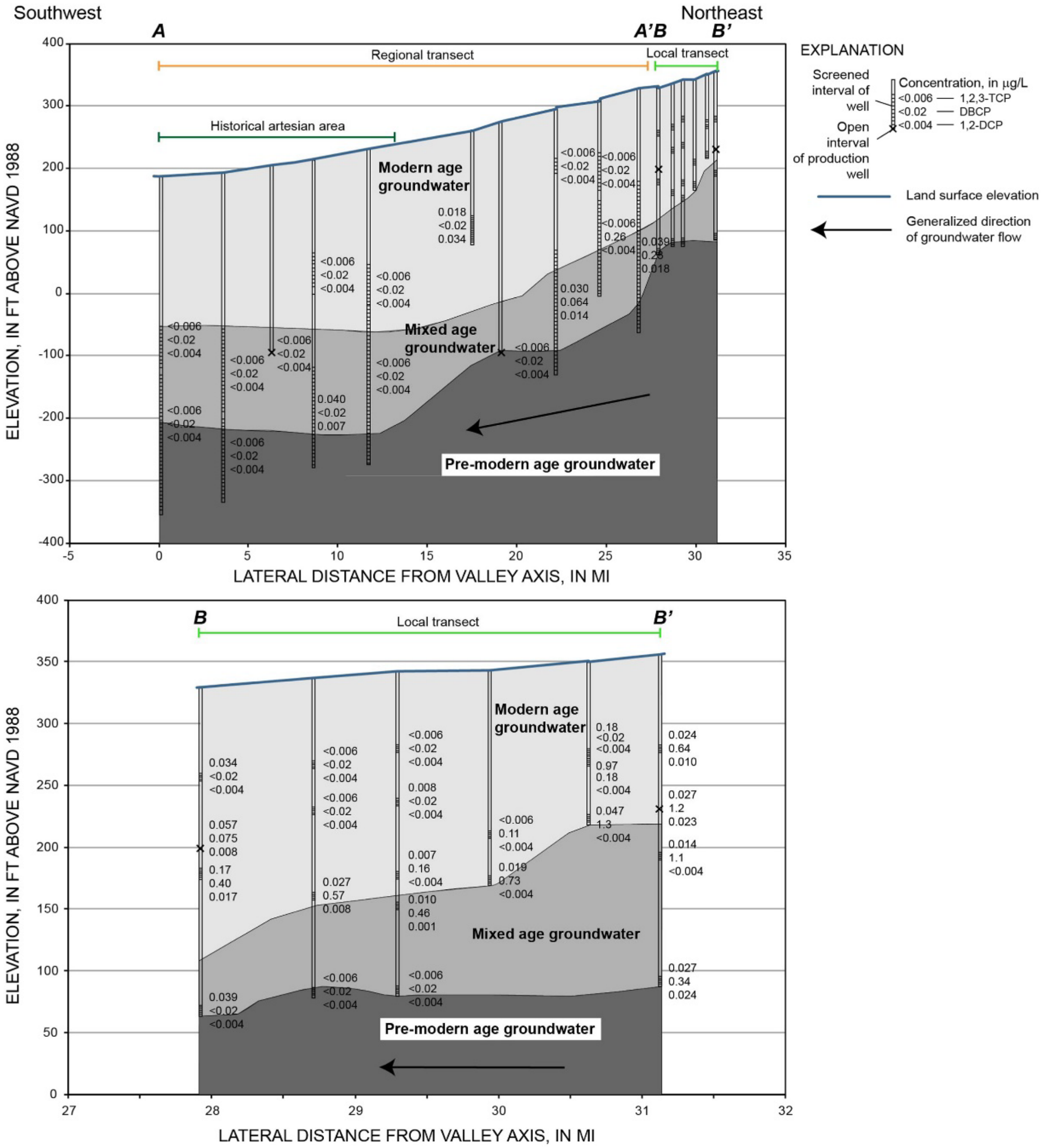


Fig. 4. Vertical transect of wells along approximate regional groundwater flow path (location shown on Fig. S1), showing fumigant-related concentrations and age of groundwater based on ^3H and ^{14}C. Transect B-B' is a 3-mi transect of monitoring wells (Burow et al., 2007); transect A-A' is a 38-mi westward regional extension of domestic, public-supply, and irrigation wells.

Determining the depth of modern age groundwater from long-screened production wells is more difficult than short-screened monitoring wells. Production wells typically pump at a high rate and integrate groundwater over a larger volume of aquifer than a monitoring well, which pumps at a low rate and primarily represents local-scale heterogeneities near the well screen. The monitoring wells along the local-scale transect contain groundwater spanning 10 s to 1000 s of years, although the depth associated with the fraction of young water is more discrete (Weissmann et al., 2002b; Zhang et al., 2018). Production wells represent both regional and local-scale heterogeneities as a wide distribution of ages, dominated by contributions from high hydraulic conductivity units (e.g., Visser et al., 2013). The distribution of ages in groundwater in the San Joaquin Valley aquifer system was well represented in both particle-tracking numerical models and in calibrated lumped-parameter models (LPM) (Eberts et al., 2012; Jurgens et al., 2016), indicating that well-calibrated LPM results are reasonable representations of the distribution of ages reaching production wells in this system. Regional scale "fast paths," such as incised valley fill deposits in the eastern San Joaquin Valley can have a significant influence on downward movement of contaminants in an aquifer (Weissmann et al., 2004; Zhang et al., 2018), although contaminant concentrations and LPM results from production wells may not readily distinguish the discrete depths of modern, agriculturally-affected groundwater in the subsurface.

3.5. High concentrations of 1,2,3-TCP and DBCP occur at cleanup sites in urban areas

1,2,3-TCP and DBCP were detected in monitoring wells at regulated cleanup sites in the Central Valley. The cleanup sites are those for which a responsible party has been identified and sufficient site characterization has been performed to identify 1,2,3-TCP as a chemical of concern. Most of the sites with 1,2,3-TCP data available were agricultural chemical supply sites in urban areas (Table S2), but 1,2,3-TCP was also detected at a grain silo, a landfill, and an oil recycling site. The agricultural chemical supply sites are located within urban areas or in suburban corridors. Concentrations of 1,2,3-TCP in monitoring wells at the cleanup sites ranged from <0.005 to 2300 μg/L, and DBCP concentrations ranged from <0.01 to 27 μg/L. These maximum concentrations are much higher than what has been observed in wells in this study. Because the use of 1,2,3-TCP-containing fumigant formulations were banned in 1984, the age of groundwater at these cleanup sites is likely decades old. Of 571 public-supply wells in the Central Valley that had a detection of 1,2,3-TCP above the MCL, only about 3% are currently associated with known releases at cleanup sites. It is possible that some of the 1,2,3-TCP and DBCP in urban wells are coming from fumigant applications in nearby agricultural areas (e.g., McMahon et al., 2008). During the last century in the San Joaquin Valley, urban areas have replaced agricultural areas, which may have had nonpoint source agricultural contamination. Additionally, urban areas have less recharge than agricultural areas but with similar pumping rates, resulting in wells pulling groundwater from adjacent agricultural areas. These complex interactions make it difficult to determine the urban versus agricultural contributions to public-supply wells, but quantifying the distribution of groundwater age reaching these wells is an important step (Eberts, 2011). More work needs to be done to predict long term impacts of 1,2,3-TCP on public-supply wells in the future.

4. Conclusions

This is the first known large-scale groundwater assessment of 1,2,3-TCP and primary factors controlling its occurrence and concentrations. This study demonstrates that 1,2,3-TCP is a contaminant of concern in groundwater because of its widespread occurrence at concentrations above the health-based threshold (MCL) in groundwater throughout California. Frequent occurrence in the San Joaquin Valley is primarily related to nonpoint-source input of 1,2,3-TCP-containing fumigant formulations in areas with coarse-grained sediment texture and the highest recharge rates. This study demonstrates that 1,2,3-TCP persists throughout oxic, modern age groundwater. 1,2,3-TCP contamination of groundwater is documented at point-source sites in urban areas; however, these sources only contribute locally to wells at this time. The factors that reflect the vulnerability of groundwater to persistent agricultural contaminants such as nitrate also predict 1,2,3-TCP occurrence and concentration. As with other legacy nonpoint source contaminants, remediation is difficult and often wellhead treatment is the only method of remediation. Avoiding placing new drinking-water wells in areas characterized by the primary factors described here could prevent the future spread of the problem.

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Appendix A. Supporting information.

This supporting information document contains supplementary tables and figures referenced in the text: table of age classifications for USGS wells sampled in the San Joaquin Valley; map of grid used to de-cluster the California DDW data; boxplots of percent land use in 500-m buffer for age classification; graph of the relation between fumigant-related concentrations and proportional distance from the valley axis; map of detections of 1,2,3-TCP and vertical water flux; a table of 1,2,3-TCP and DBCP concentrations at selected cleanup sites in the Central Valley, California.

Table S1. Age classification used for analysis of explanatory variables

USGS-ID	SAMPLE DATE	AGE	ASSIGNED AGE CLASS
B1-1	7/25/2013	Modern	Modern
B1-2	7/25/2013	ModernOrMixed	Mixed
B1-3	8/12/2013	Modern	Modern
B2.5-1	9/25/2013	Modern	Modern
B2.5-2	9/25/2013	Modern	Modern
B2-1	9/10/2013	Modern	Modern
B2-2	9/9/2013	Modern	Modern
B2-3	9/9/2013	Modern	Modern
B3-1	8/13/2013	Modern	Modern
B3-2	8/14/2013	Modern	Modern
B3-3	8/13/2013	Modern	Modern
B3-4	8/14/2013	ModernOrMixed	Mixed
B3-5	8/13/2013	PreModern	Pre-modern
B4-1	8/19/2013	Modern	Modern
B4-2	8/20/2013	Modern	Modern
B4-3	8/20/2013	Modern	Modern
B4-4	8/19/2013	PreModern	Pre-modern

B5-1	7/23/2013	Modern	Modern
B5-2	7/23/2013	Modern	Modern
B5-3	7/24/2013	ModernOrMixed	Mixed
CE-QPC-01	3/20/2006	Modern	Modern
DM-01	3/1/2010	Pre-modern	Pre-modern
DM-02	3/1/2010	Modern	Modern
DM-03	3/2/2010	Modern	Modern
DM-04	3/2/2010	Modern	Modern
DM-05	3/3/2010	Modern	Modern
DM-06	3/4/2010	Mixed	Mixed
DM-07	3/8/2010	Mixed	Mixed
DM-08	3/8/2010	Modern	Modern
DM-09	3/9/2010	Mixed	Mixed
DM-10	3/9/2010	Mixed	Mixed
DM-11	3/10/2010	Mixed	Mixed
DM-12	3/11/2010	Mixed	Mixed
DM-13	3/17/2010	Pre-modern	Pre-modern
DM-14	3/18/2010	Modern	Modern
DM-15	4/12/2010	Pre-modern	Pre-modern
DM-16	4/12/2010	Pre-modern	Pre-modern
DM-17	4/13/2010	Mixed	Mixed
DM-18	4/13/2010	Pre-modern	Pre-modern
DM-19	4/14/2010	Pre-modern	Pre-modern
DM-20	4/15/2010	Mixed	Mixed
DM-21	4/15/2010	Modern	Modern
DM-22	6/15/2010	Pre-modern	Pre-modern
DM-23	6/15/2010	Pre-modern	Pre-modern
DM-24	6/16/2010	Modern	Modern

DM-25	6/16/2010	Mixed	Mixed
DM-26	6/17/2010	Modern	Modern
DM-27	6/24/2010	Pre-modern	Pre-modern
DM-28	6/29/2010	ModernOrMixed	Mixed
DM-29	6/30/2010	Modern	Modern
DM-U-01	3/16/2010	Mixed	Mixed
DM-U-02	3/29/2010	Modern	Modern
DM-U-03	3/29/2010	Modern	Modern
DM-U-04	3/30/2010	Modern	Modern
DM-U-05	3/30/2010	Modern	Modern
DM-U-06	3/30/2010	Modern	Modern
DM-U-07	3/31/2010	Pre-modern	Pre-modern
DM-U-08	3/31/2010	Pre-modern	Pre-modern
DM-U-09	3/31/2010	Pre-modern	Pre-modern
DM-U-10	4/6/2010	Pre-modern	Pre-modern
DM-U-11	4/6/2010	Mixed	Mixed
DM-U-12	4/7/2010	Pre-modern	Pre-modern
DM-U-13	5/18/2010	Pre-modern	Pre-modern
DM-U-14	5/19/2010	Mixed	Mixed
DM-U-15	5/19/2010	Modern	Modern
DM-U-16	5/20/2010	Mixed	Mixed
DM-U-17	3/23/2011	Pre-modern	Pre-modern
ESJ-06	1/10/2005	ModernOrMixed	Mixed
ESJ-08	1/11/2005	ModernOrMixed	Mixed
ESJ-10	1/12/2005	ModernOrMixed	Mixed
ESJ-12	1/13/2005	Pre-modern	Pre-modern
ESJ-13	1/13/2005	PremodernOrMixed	Mixed
ESJ-14	1/13/2005	ModernOrMixed	Mixed

ESJ-15	1/25/2005	ModernOrMixed	Mixed
ESJ-16	2/8/2005	ModernOrMixed	Mixed
ESJ-17	2/14/2005	PremodernOrMixed	Mixed
ESJ-18	2/15/2005	PremodernOrMixed	Mixed
ESJ-19	2/18/2005	ModernOrMixed	Mixed
ESJDD-01	1/26/2005	ModernOrMixed	Mixed
ESJFP-07	1/10/2005	Pre-modern	Pre-modern
ESJFP-08	1/12/2005	ModernOrMixed	Mixed
ESJFP-09	1/12/2005	ModernOrMixed	Mixed
ESJMW-01	2/1/2005	Mixed	Mixed
ESJMW-02	2/2/2005	Mixed	Mixed
ESJMW-03	2/3/2005	Modern	Modern
FPC1-shallow	7/24/2013	Modern	Modern
FPC2-deep	8/28/2013	Modern	Modern
FPC2-shallow	7/22/2013	Modern	Modern
FPR1-deep	8/28/2013	Modern	Modern
FPR1-shallow	9/24/2013	PremodernOrMixed	Mixed
FPR2-deep	9/19/2013	PreModern	Pre-modern
FPR3-deep	9/18/2013	Modern	Modern
FPR4-deep	8/26/2013	PremodernOrMixed	Mixed
FPR5-deep	8/26/2013	ModernOrMixed	Mixed
FPR6-deep	8/21/2013	PremodernOrMixed	Mixed
HWY99T-01	10/25/2005	ModernOrMixed	Mixed
KERN-03	1/10/2006	ModernOrMixed	Mixed
KERN-12	1/24/2006	ModernOrMixed	Mixed
KERN-34	1/10/2006	Modern	Modern
KERN-35	1/25/2006	Modern	Modern
KERN-36	1/26/2006	Mixed	Mixed

KERN-37	2/15/2006	Modern	Modern
KERN-38	1/11/2006	Mixed	Mixed
KERN-39	2/14/2006	ModernOrMixed	Mixed
KERN-40	1/30/2006	PremodernOrMixed	Mixed
KERN-41	1/31/2006	Pre-modern	Pre-modern
KERN-42	2/1/2006	Pre-modern	Pre-modern
KERN-43	2/2/2006	PremodernOrMixed	Mixed
KERN-44	2/7/2006	Modern	Modern
KERN-45	2/8/2006	Mixed	Mixed
KERN-46	2/28/2006	PremodernOrMixed	Mixed
KERN-47	3/2/2006	ModernOrMixed	Mixed
KERNFP-01	1/26/2006	ModernOrMixed	Mixed
KERNFP-02	1/24/2006	Modern	Modern
KERNFP-03	1/25/2006	ModernOrMixed	Mixed
KING-04	10/17/2005	Mixed	Mixed
KING-09	10/19/2005	ModernOrMixed	Mixed
KING-10	10/19/2005	ModernOrMixed	Mixed
KING-11	10/20/2005	PremodernOrMixed	Mixed
KING-12	10/20/2005	ModernOrMixed	Mixed
KING-13	10/20/2005	PremodernOrMixed	Mixed
KING-15	10/25/2005	ModernOrMixed	Mixed
KING-16	10/25/2005	ModernOrMixed	Mixed
KING-17	10/26/2005	Pre-modern	Pre-modern
KING-20	10/27/2005	Modern	Modern
KING-25	11/2/2005	ModernOrMixed	Mixed
KING-30	11/3/2005	PremodernOrMixed	Mixed
KING-34	11/28/2005	ModernOrMixed	Mixed
KING-38	12/15/2005	PremodernOrMixed	Mixed

KINGFP-01	10/18/2005	Modern	Modern
KINGFP-02	10/19/2005	Pre-modern	Pre-modern
KINGFP-03	10/20/2005	Pre-modern	Pre-modern
KINGFP-04	10/25/2005	Modern	Modern
KINGFP-13	11/15/2005	Modern	Modern
KINGFP-14	11/16/2005	Modern	Modern
KINGFP-15	11/16/2005	Modern	Modern
KWH-03	10/31/2005	ModernOrMixed	Mixed
KWH-06	11/15/2005	ModernOrMixed	Mixed
KWH-11	11/17/2005	ModernOrMixed	Mixed
KWH-12	11/28/2005	Mixed	Mixed
KWH-14	11/30/2005	Modern	Modern
MADCHOW-01	4/14/2008	Modern	Modern
MADCHOW-02	4/15/2008	Pre-modern	Pre-modern
MADCHOW-03	4/15/2008	Mixed	Mixed
MADCHOW-04	4/16/2008	Modern	Modern
MADCHOW-05	4/16/2008	Mixed	Mixed
MADCHOW-07	4/21/2008	Mixed	Mixed
MADCHOW-08	4/22/2008	Mixed	Mixed
MADCHOW-09	4/22/2008	Modern	Modern
MADCHOW-10	4/24/2008	Pre-modern	Pre-modern
MADCHOW-11	4/24/2008	Pre-modern	Pre-modern
MADCHOW-12	4/28/2008	Mixed	Mixed
MADCHOW-13	4/29/2008	Mixed	Mixed
MADCHOW-14	4/30/2008	Mixed	Mixed
MADCHOW-15	4/30/2008	Pre-modern	Pre-modern
MADCHOW-16	5/1/2008	Pre-modern	Pre-modern
MADCHOW-18	5/6/2008	Modern	Modern

MADCHOW-19	5/6/2008	Mixed	Mixed
MADCHOW-20	5/7/2008	Modern	Modern
MADCHOW-21	5/7/2008	Pre-modern	Pre-modern
MADCHOW-22	5/8/2008	Pre-modern	Pre-modern
MADCHOW-23	5/12/2008	Pre-modern	Pre-modern
MADCHOW-24	5/13/2008	Mixed	Mixed
MADCHOW-25	5/13/2008	Modern	Modern
MADCHOW-26	5/14/2008	Modern	Modern
MADCHOW-27	5/14/2008	Modern	Modern
MADCHOW-28	5/19/2008	Modern	Modern
MADCHOW-29	5/20/2008	Modern	Modern
MADCHOW-30	5/21/2008	Mixed	Mixed
MADCHOWFP-01	4/23/2008	Modern	Modern
MADCHOWFP-02	5/5/2008	Mixed	Mixed
MADCHOWFP-03	5/15/2008	Modern	Modern
MADCHOWFP-04	5/21/2008	Modern	Modern
MER-02	3/29/2006	Mixed	Mixed
MER-03	3/30/2006	Mixed	Mixed
MER-09	4/10/2006	Modern	Modern
MER-10	4/11/2006	Modern	Modern
MER-11	4/12/2006	Modern	Modern
MERMW-02	3/27/2006	Modern	Modern
MOD-01	3/13/2006	Modern	Modern
MOD-02	3/14/2006	Modern	Modern
MOD-09	3/23/2006	Modern	Modern
NSJ-QPC-01	1/11/2005	Modern	Modern

NSJ-QPC-04	1/24/2005	ModernOrMixed	Mixed
NSJ-QPC-06	1/25/2005	PremodernOrMixed	Mixed
NSJ-QPC-09	2/10/2005	PremodernOrMixed	Mixed
NSJ-QPC-10	2/14/2005	ModernOrMixed	Mixed
S3-MACK-K01	1/7/2014	Modern	Modern
S3-MACK-K02	1/6/2014	Modern	Modern
S3-MACK-K03	1/28/2014	Mixed	Mixed
S3-MACK-K04	9/16/2013	Mixed	Mixed
S3-MACK-K05	1/30/2014	Pre-modern	Pre-modern
S3-MACK-K06	1/29/2014	Mixed	Mixed
S3-MACK-K07	4/8/2014	Mixed	Mixed
S3-MACK-K08	1/28/2014	Modern	Modern
S3-MACK-K09	2/23/2014	Pre-modern	Pre-modern
S3-MACK-K10	9/18/2013	Mixed	Mixed
S3-MACK-K11	9/12/2013	Pre-modern	Pre-modern
S3-MACK-K12	1/7/2014	Mixed	Mixed
S3-MACK-K13	1/27/2014	Modern	Modern
S3-MACK-K14	1/27/2014	Modern	Modern
S3-MACK-K15	2/3/2014	Modern	Modern
S3-MACK-K16	2/3/2014	Modern	Modern
S3-MACK-K17	2/4/2014	Modern	Modern
S3-MACK-K18	8/29/2013	Modern	Modern
S3-MACK-K19	2/5/2014	Modern	Modern
S3-MACK-K20	3/6/2014	Modern	Modern
S3-MACK-K21	2/5/2014	Modern	Modern
S3-MACK-K22	1/29/2014	Modern	Modern
S3-MACK-K23	1/9/2014	Modern	Modern
S3-MACK-K24	8/22/2013	Modern	Modern

S3-MACK-K25	2/26/2014	Modern	Modern
S3-MACK-K26	2/4/2014	Modern	Modern
S3-MACK-K27	3/4/2014	Modern	Modern
S3-MACK-K28	3/18/2014	Modern	Modern
S3-MACK-K29	3/17/2014	Modern	Modern
S3-MACK-K30	2/6/2014	Modern	Modern
S3-MACK-K31	2/27/2014	Pre-modern	Pre-modern
S3-MACK-K32	4/7/2014	Modern	Modern
S3-MACK-K33	9/17/2013	Modern	Modern
S3-MACK-K34	9/11/2013	Modern	Modern
S3-MACK-K35	1/8/2014	Modern	Modern
S3-MACK-K36	1/8/2014	Modern	Modern
S3-MACK-K37	1/9/2014	Modern	Modern
S3-MACK-K39	3/3/2014	Modern	Modern
S3-MACK-K40	2/25/2014	Modern	Modern
S3-MACK-K41	3/4/2014	Modern	Modern
S3-MACK-K42	3/17/2014	Modern	Modern
S3-MACK-K43	3/5/2014	Modern	Modern
S3-MACK-K44	3/5/2014	Modern	Modern
S3-MACK-K45	2/25/2014	Modern	Modern
S3-MACK-K46	2/24/2014	Modern	Modern
S3-MACK-K47	3/3/2014	Modern	Modern
S3-MACK-K48	2/24/2014	Modern	Modern
S3-MACK-K49	2/26/2014	Modern	Modern
S3-MACK-M01	3/19/2014	Modern	Modern
S3-MACK-M02	4/8/2014	Pre-modern	Pre-modern
S3-MACK-M03	4/10/2014	Modern	Modern
S3-MACK-M04	4/10/2014	Mixed	Mixed

S3-MACK-M05	11/20/2013	Modern	Modern
S3-MACK-M06	11/19/2013	Mixed	Mixed
S3-MACK-M07	12/12/2013	Modern	Modern
S3-MACK-M08	11/20/2013	Modern	Modern
S3-MACK-M09	11/21/2013	Modern	Modern
S3-MACK-M10	12/4/2013	Modern	Modern
S3-MACK-M11	12/3/2013	Modern	Modern
S3-MACK-M12	3/18/2014	Modern	Modern
S3-MACK-M13	12/2/2013	Modern	Modern
S3-MACK-M14	12/11/2013	Modern	Modern
S3-MACK-M15	12/5/2013	Modern	Modern
S3-MACK-M16	11/18/2013	Modern	Modern
S3-MACK-M17	3/20/2014	Modern	Modern
S3-MACK-M18	11/18/2013	Mixed	Mixed
S3-MACK-M19	12/11/2013	Mixed	Mixed
S3-MACK-M20	12/4/2013	Mixed	Mixed
S3-MACK-M21	12/3/2013	Mixed	Mixed
S3-MACK-M22	12/2/2013	Modern	Modern
S3-MACK-M23	12/9/2013	Modern	Modern
S3-MACK-M24	12/9/2013	Pre-modern	Pre-modern
S3-MACK-M25	3/19/2014	Pre-modern	Pre-modern
S3-MACK-M26	12/10/2013	Mixed	Mixed
S3-MACK-M27	12/10/2013	Modern	Modern
S3-MACK-M28	4/9/2014	Pre-modern	Pre-modern
S4-TUSK-KAW01	4/29/2015	Modern	Modern
S4-TUSK-KAW02	1/14/2015	Modern	Modern

S4-TUSK-KAW03	1/12/2015	Modern	Modern
S4-TUSK-KAW04	1/26/2015	Modern	Modern
S4-TUSK-KAW05	1/27/2015	Modern	Modern
S4-TUSK-KAW06	3/3/2015	Modern	Modern
S4-TUSK-KAW07	11/18/2014	Pre-modern	Pre-modern
S4-TUSK-KAW08	12/15/2014	Mixed	Mixed
S4-TUSK-KAW09	12/8/2014	Modern	Modern
S4-TUSK-KAW10	3/5/2015	Modern	Modern
S4-TUSK-KAW11	12/8/2014	Modern	Modern
S4-TUSK-KAW12	1/12/2015	Pre-modern	Pre-modern
S4-TUSK-KAW13	3/3/2015	Mixed	Mixed
S4-TUSK-KAW14	1/29/2015	Modern	Modern
S4-TUSK-KAW15	12/9/2014	Modern	Modern
S4-TUSK-KAW16	12/16/2014	Modern	Modern
S4-TUSK-KAW17	1/26/2015	Modern	Modern
S4-TUSK-KAW18	11/18/2014	Mixed	Mixed
S4-TUSK-KAW19	12/15/2014	Modern	Modern
S4-TUSK-KAW20	3/31/2015	Modern	Modern

S4-TUSK-KAW21	1/13/2015	Modern	Modern
S4-TUSK-KAW22	12/16/2014	Modern	Modern
S4-TUSK-KAW23	2/26/2015	Modern	Modern
S4-TUSK-KAW24	12/2/2014	Mixed	Mixed
S4-TUSK-KAW25	11/20/2014	Modern	Modern
S4-TUSK-KAW26	3/31/2015	Modern	Modern
S4-TUSK-KAW28	12/9/2014	Modern	Modern
S4-TUSK-KAW29	3/4/2015	Modern	Modern
S4-TUSK-TLA01	4/1/2015	Pre-modern	Pre-modern
S4-TUSK-TLA02	4/1/2015	Modern	Modern
S4-TUSK-TLA03	3/26/2015	Pre-modern	Pre-modern
S4-TUSK-TLA04	2/23/2015	Modern	Modern
S4-TUSK-TLA05	2/23/2015	Modern	Modern
S4-TUSK-TLA06	3/17/2015	Mixed	Mixed
S4-TUSK-TLA07	2/25/2015	Modern	Modern
S4-TUSK-TLA08	4/2/2015	Modern	Modern
S4-TUSK-TLA09	1/14/2015	Modern	Modern
S4-TUSK-TLA10	2/24/2015	Modern	Modern

S4-TUSK-TLA11	1/27/2015	Modern	Modern
S4-TUSK-TLA12	2/24/2015	Modern	Modern
S4-TUSK-TLA13	1/13/2015	Modern	Modern
S4-TUSK-TLA14	2/25/2015	Pre-modern	Pre-modern
S4-TUSK-TLA15	4/29/2015	Mixed	Mixed
S4-TUSK-TLE01	4/27/2015	Pre-modern	Pre-modern
S4-TUSK-TLE02	4/20/2015	Pre-modern	Pre-modern
S4-TUSK-TLE03	3/4/2015	Mixed	Mixed
S4-TUSK-TLE04	3/17/2015	Modern	Modern
S4-TUSK-TLE05	2/26/2015	Modern	Modern
S4-TUSK-TLE06	3/23/2015	Modern	Modern
S4-TUSK-TLE07	3/5/2015	Mixed	Mixed
S4-TUSK-TLE08	4/27/2015	Pre-modern	Pre-modern
S4-TUSK-TLE09	3/24/2015	Pre-modern	Pre-modern
S4-TUSK-TLE10	3/25/2015	Modern	Modern
S4-TUSK-TLE11	3/29/2015	Modern	Modern
S4-TUSK-TLE12	3/24/2015	Modern	Modern
S4-TUSK-TLE13	3/18/2015	Modern	Modern

S4-TUSK-TLE14	3/18/2015	Modern	Modern
S4-TUSK-TLE15	1/15/2015	Modern	Modern
S4-TUSK-TLE16	4/8/2015	Modern	Modern
S4-TUSK-TLE17	3/16/2015	Modern	Modern
S4-TUSK-TLE18	3/25/2015	Mixed	Mixed
S4-TUSK-TLE19	3/23/2015	Modern	Modern
S4-TUSK-TLE20	4/9/2015	Pre-modern	Pre-modern
S4-TUSK-TLE21	4/8/2015	Modern	Modern
S4-TUSK-TLE22	3/30/2015	Pre-modern	Pre-modern
S4-TUSK-TLE23	12/17/2014	Mixed	Mixed
S4-TUSK-TLE24	3/16/2015	Modern	Modern
S4-TUSK-TLE26	12/10/2014	Modern	Modern
S4-TUSK-TLE27	3/30/2015	Modern	Modern
S4-TUSK-TLE28	4/20/2015	Pre-modern	Pre-modern
S4-TUSK-TLE30	4/7/2015	Pre-modern	Pre-modern
sanjluscr1a-1	7/21/2015	Modern	Modern
sanjluscr1a-2	7/16/2015	Modern	Modern
sanjluscr1a-3	7/20/2015	Modern	Modern
sanjluscr1a-4	7/15/2015	Modern	Modern

sanjluscr1a-5	7/13/2015	Modern	Modern
sanjluscr1a-6	7/9/2015	Modern	Modern
sanjluscr1a-7	7/7/2015	Modern	Modern
sanjluscr1a-8	7/6/2015	Modern	Modern
sanjlusor1a-9	7/16/2013	Modern	Modern
sanjlusor1a-10	7/17/2013	Modern	Modern
sanjlusor1a-11	7/16/2013	Modern	Modern
sanjlusor1a-12	7/16/2013	Modern	Modern
sanjlusor1a-13	7/17/2013	Modern	Modern
sanjlusor1a-14	7/18/2013	Modern	Modern
sanjlusor1a-15	7/18/2013	Modern	Modern
sanjlusor1a-16	7/22/2013	Modern	Modern
sanjlusor1a-17	7/23/2013	Modern	Modern
sanjlusor1a-18	7/25/2013	Modern	Modern
sanjlusor1a-19	7/24/2013	Modern	Modern
sanjlusor1a-20	7/25/2013	Mixed	Mixed
sanjlusor1a-21	7/30/2013	Modern	Modern
sanjlusor1a-22	7/31/2013	Modern	Modern
sanjlusor1a-23	7/11/2013	Modern	Modern
sanjlusor1a-24	7/11/2013	Modern	Modern
sanjlusor1a-25	7/10/2013	Modern	Modern
sanjlusor1a-26	7/10/2013	Modern	Modern
sanjlusor1a-27	7/9/2013	Modern	Modern
sanjlusor1a-28	7/9/2013	Modern	Modern
sanjlusor1a-29	7/8/2013	Modern	Modern
sanjlusor2a-30	7/17/2014	Mixed	Mixed
sanjlusor2a-31	7/17/2014	Modern	Modern
sanjlusor2a-32	7/16/2014	Modern	Modern

sanjlusor2a-33	7/16/2014	Modern	Modern
sanjlusor2a-34	7/8/2014	Modern	Modern
sanjlusor2a-35	7/14/2014	Modern	Modern
sanjlusor2a-36	7/7/2014	Modern	Modern
sanjlusor2a-37	6/18/2014	Modern	Modern
sanjsus1-1	8/25/2015	Modern	Modern
sanjsus1-2	8/17/2015	Mixed	Mixed
sanjsus1-3	8/12/2015	Modern	Modern
sanjsus1-4	8/12/2015	Modern	Modern
sanjsus1-5	8/10/2015	Pre-modern	Pre-modern
sanjsus1-6	8/13/2015	Pre-modern	Pre-modern
sanjsus1-7	8/4/2015	Modern	Modern
TLR-02	11/29/2005	PremodernOrMixed	Mixed
TLR-04	12/1/2005	Pre-modern	Pre-modern
TLR-05	12/5/2005	Mixed	Mixed
TLR-06	12/6/2005	PremodernOrMixed	Mixed
TLR-08	12/12/2005	PremodernOrMixed	Mixed
TRCY-03	1/6/2005	Pre-modern	Pre-modern
TRCY-07	2/8/2005	Modern	Modern
TRCY-09	2/9/2005	ModernOrMixed	Mixed
TRCY-11	2/17/2005	PremodernOrMixed	Mixed
TRCYFP-01	1/3/2005	Pre-modern	Pre-modern
TRCYFP-02	1/4/2005	Mixed	Mixed
TRCYFP-03	1/5/2005	ModernOrMixed	Mixed
TRCYFP-04	1/5/2005	Mixed	Mixed
TRCYFP-05	1/5/2005	ModernOrMixed	Mixed
TRLK-01	3/15/2006	Pre-modern	Pre-modern
TRLK-02	3/16/2006	Mixed	Mixed

TRLK-03	3/21/2006	Pre-modern	Pre-modern
TRLK-05	3/22/2006	Mixed	Mixed
TRLK-10	3/27/2006	Modern	Modern
TRLK-11	3/28/2006	Mixed	Mixed
TRLKMW-04	3/16/2006	Modern	Modern
TULE-01	11/29/2005	Mixed	Mixed
TULE-03	11/30/2005	ModernOrMixed	Mixed
TULE-07	12/6/2005	ModernOrMixed	Mixed
TULE-08	12/7/2005	Pre-modern	Pre-modern
TULE-17	2/28/2006	ModernOrMixed	Mixed
WS-01	3/15/2010	Pre-modern	Pre-modern
WS-02	6/7/2010	Mixed	Mixed
WS-03	6/7/2010	Pre-modern	Pre-modern
WS-04	6/8/2010	Pre-modern	Pre-modern
WS-05	6/8/2010	Pre-modern	Pre-modern
WS-06	6/9/2010	Pre-modern	Pre-modern
WS-07	6/10/2010	Pre-modern	Pre-modern
WS-08	6/22/2010	Pre-modern	Pre-modern
WS-09	6/23/2010	Pre-modern	Pre-modern
WS-10	7/8/2010	Pre-modern	Pre-modern
WS-U-01	6/9/2010	Pre-modern	Pre-modern
WS-U-02	6/10/2010	Pre-modern	Pre-modern
WS-U-03	6/23/2010	Pre-modern	Pre-modern

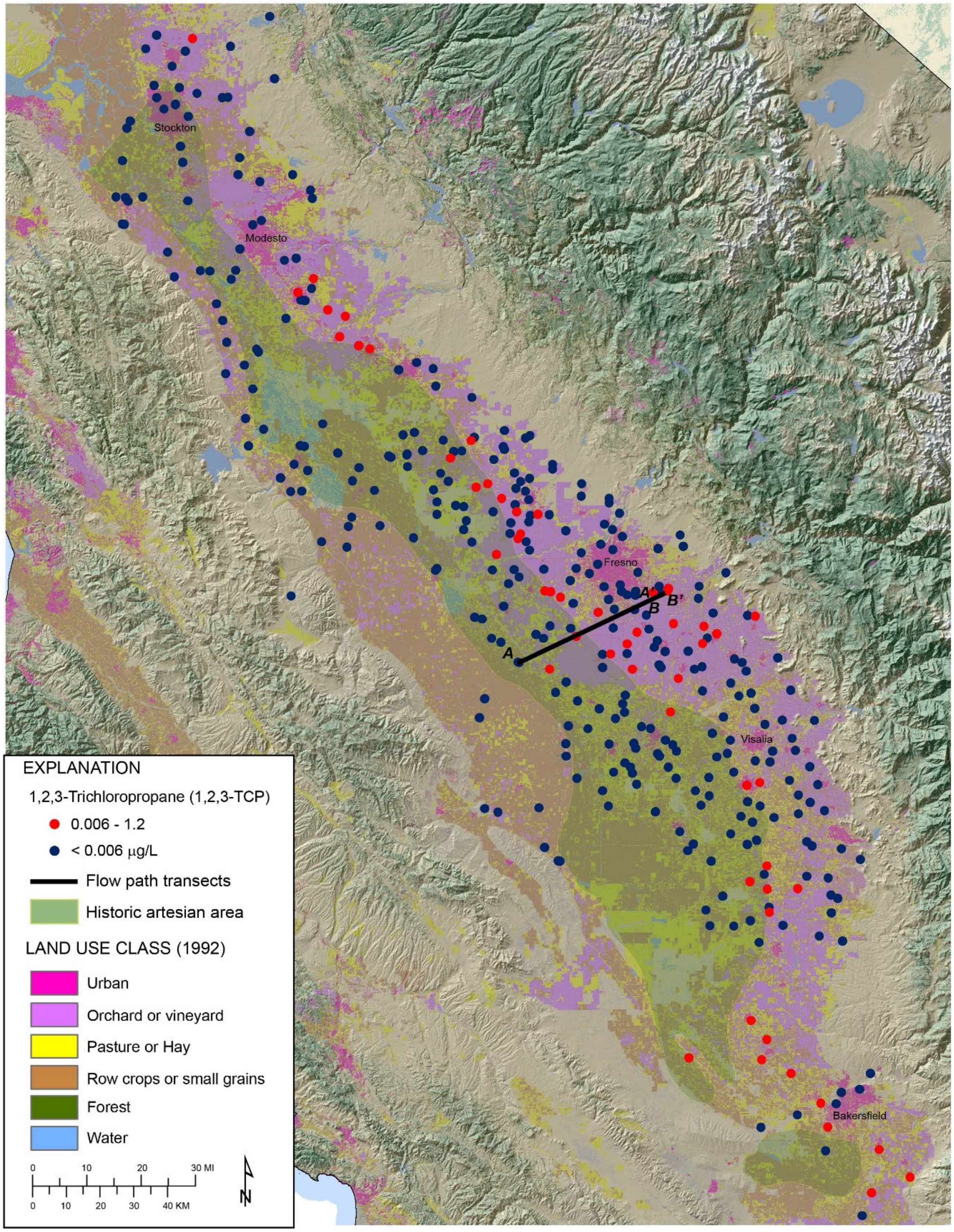
Stockton
Modesto
Fresno
Visalia
Bakersfield
A
A'
B
B'
EXPLANATION
1,2,3-Trichloropropane (1,2,3-TCP)
● 0.006 - 1.2
● < 0.006 μg/L
Flow path transects
Historic artesian area
LAND USE CLASS (1992)
Urban
Orchard or vineyard
Pasture or Hay
Row crops or small grains
Forest
Water
0 10 20 30 MI
0 10 20 30 40 KM
N

Figure S1. Detection of 1,2,3-TCP in wells above a common reporting limit of 0.006 µg/L in USGS wells sampled in the San Joaquin Valley, California. Location of flow path transects represented on Figure 4 are shown.

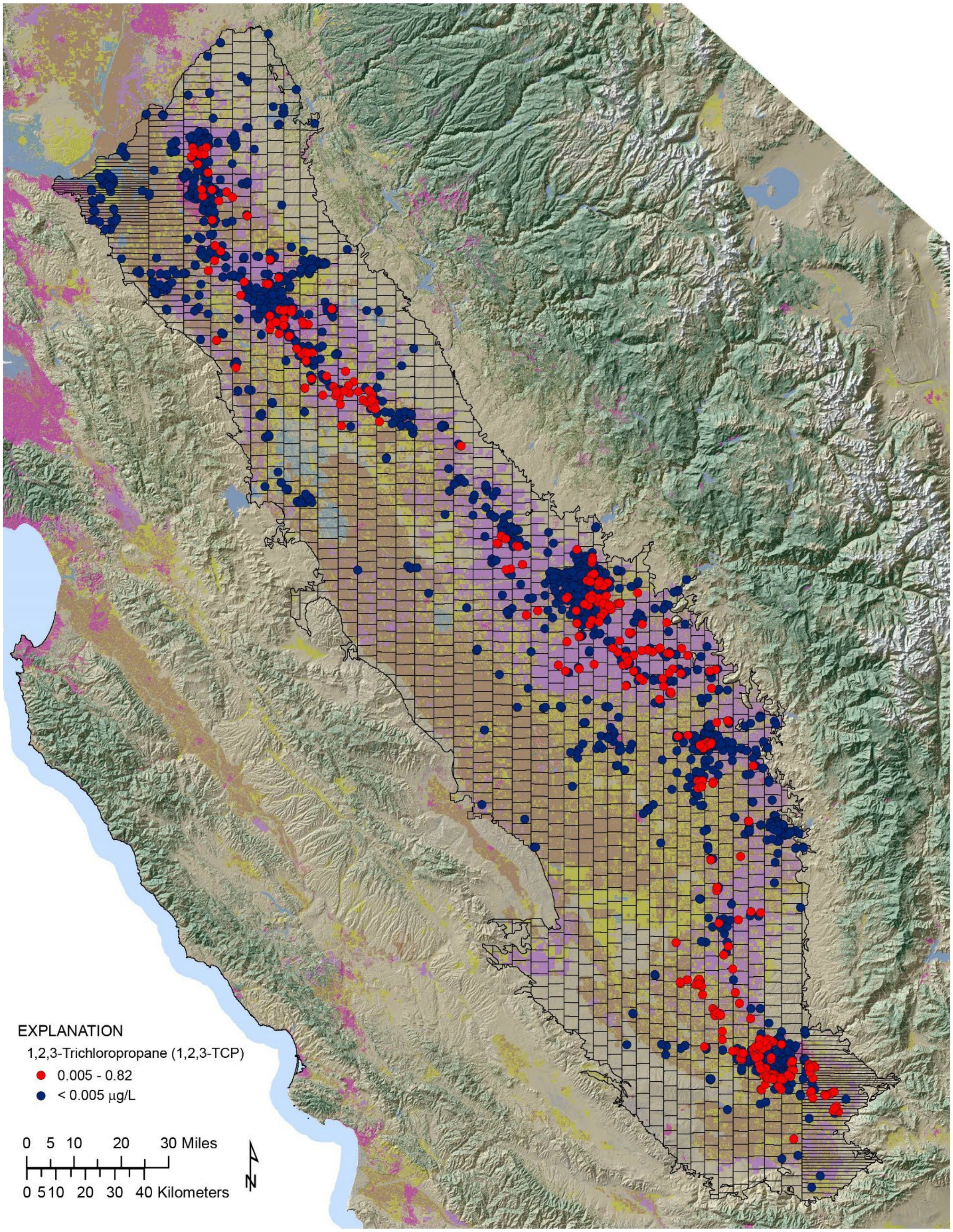

Figure S2. California DDW data and 9 mi^2 grid used to determine spatially-weighted detection frequency.

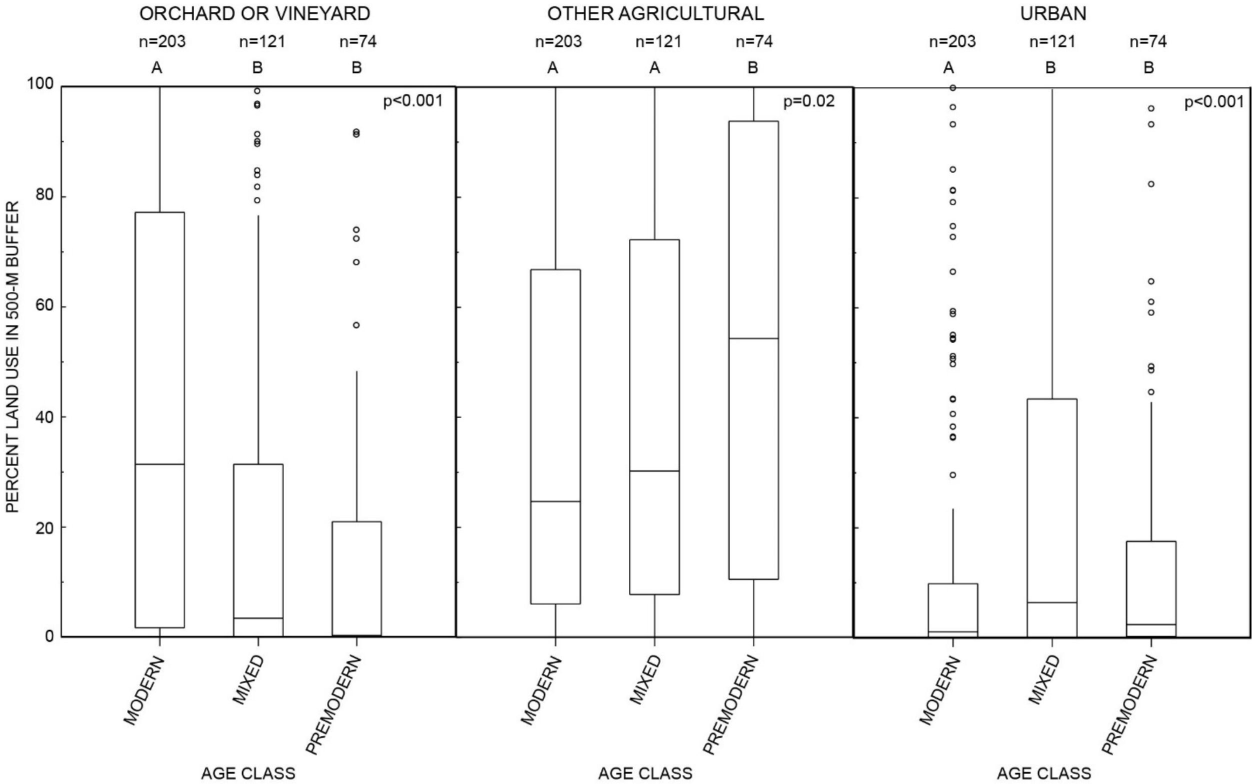

Figure S3. Percent land use in 500-m buffer and age classification. Boxplots labeled with different letters have medians that were significantly different at the 0.05 level.

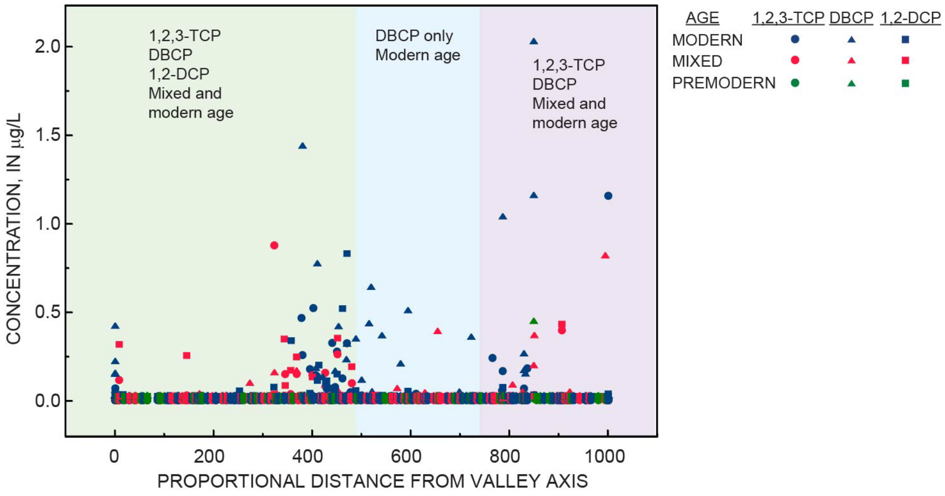

Figure S4. Concentrations of fumigant-related constituents and proportional distance from valley axis, San Joaquin Valley, California.

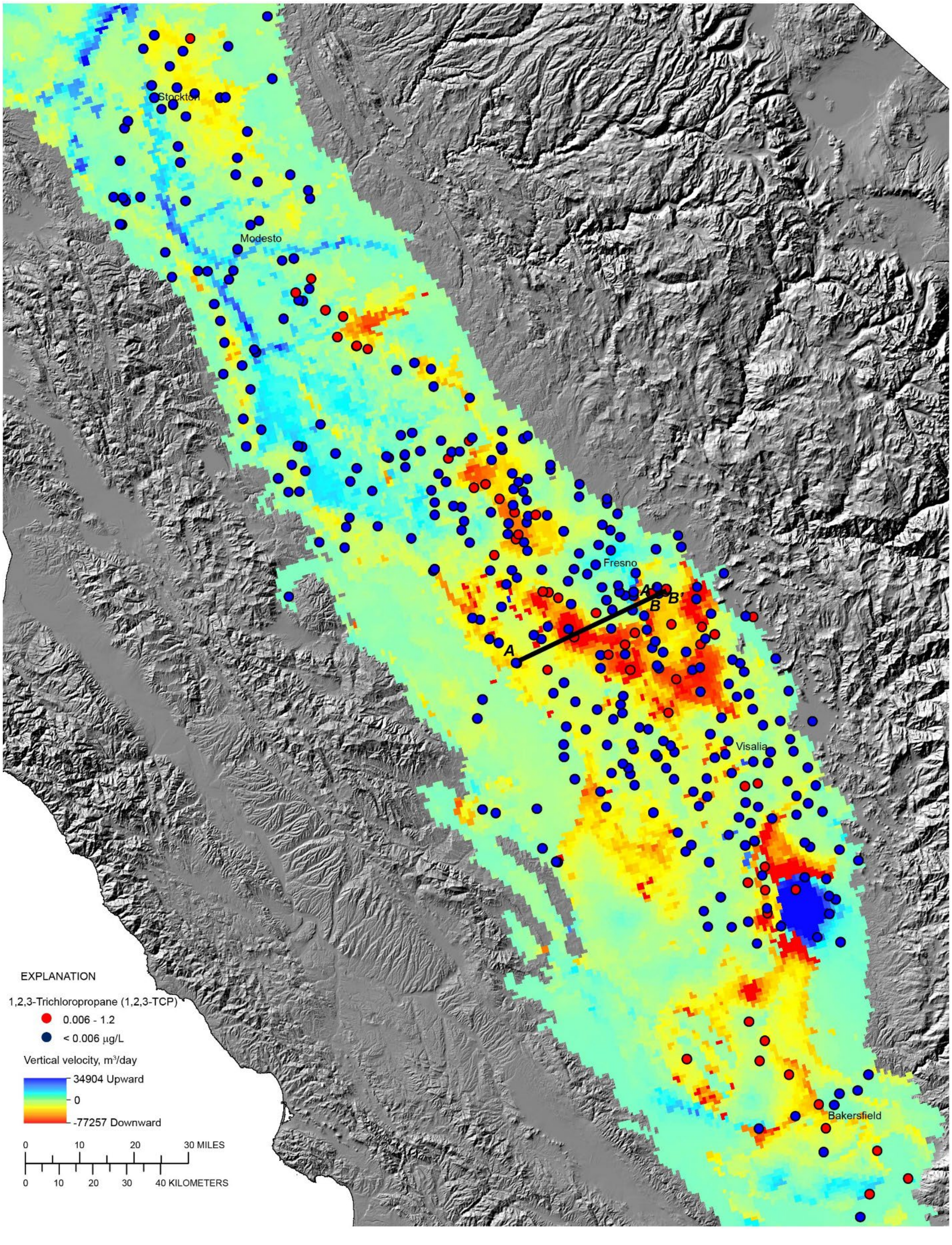

Figure S5. 1,2,3-TCP in USGS sampled wells and vertical velocity from CVHM (Faunt, 2009).

Table S2. Concentrations of 1,2,3-TCP and DBCP in monitoring wells at selected cleanup sites in the Central Valley, California*

Site type	1,2,3-TCP concentration, in μg/L			Number of monitoring wells with 1,2,3-TCP analyses	DBCP concentration, in μg/L		
	Minimum	Maximum	Median		Minimum	Maximum	Median
Agricultural chemical supply	<0.005	110	0.03	18	<0.01	0.26	<0.01
Agricultural chemical supply	<0.005	84	0.75	46	<0.01	1.4	0.014
Agricultural chemical supply	<0.005	14	0.023	8	<0.01	0.32	<0.010
Agricultural chemical supply	<0.005	66	0.13	19	<0.01	4.3	<0.01
Agricultural chemical supply	<0.005	390	0.094	17	<5	<5	<5
Agricultural chemical supply	<0.005	0.15	<0.005	9	<0.01	<5	<0.01
Agricultural chemical supply	<0.005	84	0.0065	22	<0.01	<0.01	<0.01
Agricultural chemical supply	<0.005	0.16	0.0035	6	<1	<5	<1
Agricultural chemical supply	<0.005	2,300	2.2	23	<2	<5	<2
Agricultural chemical supply	0.0037	380	0.66	45			
Agricultural chemical supply	<0.005	22	<0.005	7	<0.02	<0.02	<0.02
Agricultural chemical supply	<0.005	12	0.038	23	<0.01	11	<0.01
Agricultural chemical supply	<0.005	1.8	0.008	31	<0.01	5.6	<0.01

Agricultural chemical supply	<0.005	550	0.52	42	<0.01	3.2	0.034
Agricultural chemical supply	<0.005	17	<0.005	5			
Agricultural chemical supply	<0.005	0.64	<0.005	6	<0.01	3.9	<0.01
Agricultural chemical supply	0.061	9.6	0.19	5	<0.01	27	0.022
Agricultural chemical supply	<0.02	100	15	7	<0.02	25	1.1
Agricultural chemical supply	<0.50	19	6.7	7	<2	<2	<2
Agricultural chemical supply	<0.5	1.6	<0.5	6	<1	<1	<1
Grain Silo	<0.005	3.8	0.98	20	<0.5	<0.5	<0.5
Landfill	<0.005	9.6	0.016	116	<2	<2	<2
Oil Recycling	<0.3	1.8	0.6	29	<0.5	<0.5	<0.5

*Sample dates range from the early 2000s to 2018.