

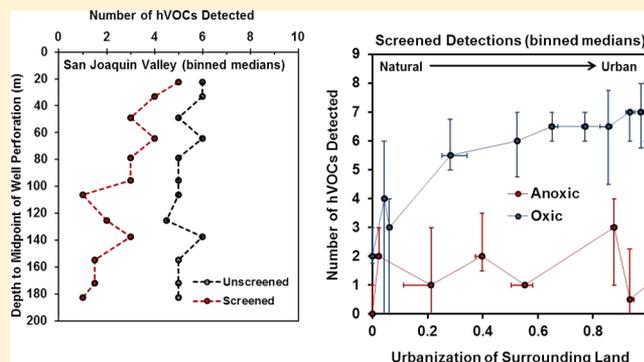
# Assessing California Groundwater Susceptibility Using Trace Concentrations of Halogenated Volatile Organic Compounds

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**S** Supporting Information

**ABSTRACT:** Twenty-four halogenated volatile organic compounds (hVOCs) and SF<sub>6</sub> were measured in groundwater samples collected from 312 wells across California at concentrations as low as 10<sup>-12</sup> grams per kilogram groundwater. The hVOCs detected are predominately anthropogenic (i.e., “ahVOCs”) and as such their distribution delineates where groundwaters are impacted and susceptible to human activity. ahVOC detections were broadly consistent with air-saturated water concentrations in equilibrium with a combination of industrial-era global and regional hVOC atmospheric abundances. However, detection of ahVOCs in nearly all of the samples collected, including ancient groundwaters, suggests the presence of a sampling or analytical artifact that confounds interpretation of the very-low concentration ahVOC data. To increase our confidence in ahVOC detections we establish screening levels based on ahVOC concentrations in deep wells drawing ancient groundwater in Owens Valley. Concentrations of ahVOCs below the Owens Valley screening levels account for a large number of the detections in pre-nuclear groundwater across California without significant loss of ahVOC detections in shallow, recently recharged groundwaters. Over 80% of the groundwaters in this study contain at least one ahVOC after screening, indicating that the footprint of human industry is nearly ubiquitous and that most California groundwaters are vulnerable to contamination from land-surface activities.



## INTRODUCTION

Groundwater supplies a significant amount of California’s water needs. Roughly one-quarter of the total water used in California is from groundwater sources,<sup>1</sup> and around 40% of Californians rely in-part on groundwater for domestic use.<sup>2</sup> Understanding the current and future quality of California groundwater are thus principal concerns for California policy makers and the public in general. The California State Water Resources Control Board’s Groundwater Ambient Monitoring and Assessment (GAMA) Priority Basin Project (PBP) was implemented in 2004 to assess groundwater quality and the natural and human factors that impact groundwater quality. The PBP covers key groundwater basins that account for over 90% of groundwater used in California. From May 2004 to March 2012, U.S. Geological Survey teams under the PBP have collected raw, untreated groundwater samples from nearly 2300 wells for the analysis of major and minor ions, trace elements and nutrients, radioactive constituents, microbial indicators, dissolved noble gases, naturally occurring isotopes and a large number of synthetic organic constituents, such as pesticides, pharmaceuticals, and volatile organic compounds (VOCs) including halogenated volatile organic compounds (hVOCs).

Halogenated VOCs are a subset of VOCs used as solvents, refrigerants, blowing agents, degreasers, extinguishers and as chemical feedstock.<sup>3</sup> The hVOCs, such as chloroform and tetrachloroethylene, have been found in groundwater since the

late-1970s, at concentrations of 10<sup>-5</sup> to 10<sup>-6</sup> g L<sup>-1</sup> H<sub>2</sub>O (e.g., refs 4 and 5). During the same time period, gas chromatography coupled with electron capture detection was being developed as a method to determine groundwater residence times using chlorofluorocarbon (CFC) concentrations, with detection limits on the order of 10<sup>-12</sup> g L<sup>-1</sup> H<sub>2</sub>O.<sup>6</sup> The utility of CFCs as groundwater-age tracers has diminished in recent years due to the slowing or reversal of their atmospheric growth rate<sup>7</sup> and their frequent detection in groundwater above air-saturated water concentrations.<sup>8</sup> The presence of trace concentrations of hVOCs in groundwater may still be used as an indicator of recently recharged water and thus the susceptibility of groundwater to other pollutants associated with human activity (e.g., refs 9–12).

To this purpose, the U.S. Geological Survey (USGS) CFC laboratory in Reston, Virginia has developed a purge-and-trap gas chromatography-electron capture detection (GC-ECD) methodology for the measurement of 25 hVOCs in groundwater at trace concentrations (~10<sup>-12</sup> g kg<sup>-1</sup> H<sub>2</sub>O).<sup>12</sup> During 2005–2006, groundwater samples were collected from 312 wells across California as a part of the GAMA PBP for analysis

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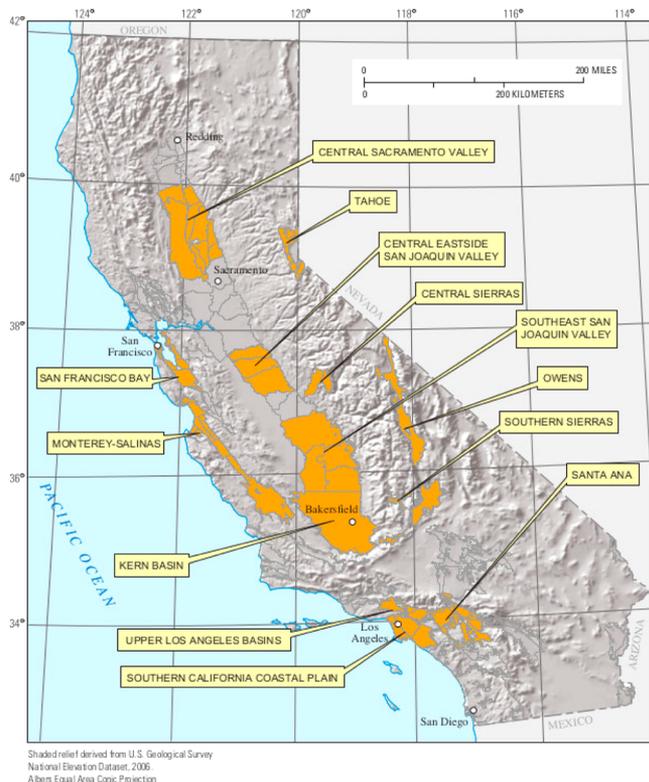
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by purge-and-trap GC-ECD, as well as by GC-MS techniques for comparison. We present the results from this sampling campaign and discuss their potential for identifying the human footprint in California groundwaters.

## MATERIALS AND METHODS

Groundwater wells were selected from 5 of the 10 Californian hydrogeologic provinces established as a part of the GAMA PBP framework.<sup>13</sup> Each hydrogeologic province is comprised of study units which in turn consist of multiple groundwater aquifers. Study units investigated here can be classified as predominantly urban (e.g., Upper Los Angeles Basins), natural (e.g., Central and Southern Sierras) and agricultural (e.g., Central-Eastside and Southeast San Joaquin Valley) (Figure 1).



**Figure 1.** Map of California with location of GAMA PBP study units containing wells sampled in this study. Corresponding GAMA PBP study unit IDs may be found in Supporting Information Table S1.

As such, hVOC measurements in this study provide an indicator of human activity in lightly- to heavily-impacted groundwaters, as well as in Californian aquifers in general. Full details on study units including climate, hydrogeology, well locations and construction, and hydrochemical data from the Priority Basin Project can be found online at <http://ca.water.usgs.gov/gama>.

Wells sampled in this study were predominately production wells used for municipal drinking-water supply, with a small number of domestic and irrigation wells also sampled. Wells were allowed to pump several well casing-volumes of water prior to sampling. All water samples were collected upstream of chlorination or disinfection units. Water samples in this study thus represent the state of groundwater in the aquifer and not water supplied to consumers post-treatment. For the purposes of hVOC analyses, up to three samples were collected at each

well into 125 mL amber glass bottles. Samples were classified as “primary”, “secondary”, and “tertiary” depending on their place in the order of sampling. Groundwater was drawn from the well through a length of refrigeration-grade copper tubing and discharged directly to the bottom of a sampling bottle, which had been placed within a larger-volume stainless-steel pail. Once the pail was filled to overflowing, the submerged sampling bottle was sealed with an aluminum foil-lined cap. Care was taken to ensure that no visible headspace was present in a sample bottle; if bubbles were present, the filling procedure was restarted. After sampling was complete the cap-bottle interface was sealed with tape, stored upside-down in the dark at room temperature until shipment to the USGS CFC laboratory for analysis. Samples are stable for months to years under anoxic conditions (ref 14, Supporting Information (SI) Figure S1).

Dissolved hVOCs were analyzed using purge-and-trap preconcentration followed by gas chromatographic separation coupled to electron capture detection. The full details of the technique may be found in Plummer and coauthors.<sup>12</sup> A roughly 30 mL aliquot of groundwater is extracted by syringe from a 125 mL sampling bottle and is injected into the purge-and-trap module. Ultrahigh purity nitrogen gas is bubbled through the extracted aliquot for 4 min, stripping hVOCs from the aqueous phase. Extracted gases are preconcentrated on a liquid nitrogen-cooled trap, followed by thermal desorption into the GC for separation prior to ECD detection. Blanks of the analytical system are performed daily and after high-concentration analyses to check for carry-over. Twenty-five refrigerants, propellants, solvents, extinguishers, and industrial feedstock chemicals have been identified by the retention time of commercial and/or prepared gas-phase standards (SI Table S1). While not technically an hVOC, sulfur hexafluoride is included in this study as it is often detected in groundwaters by GC-ECD (e.g., refs 11 and 15).

The ECD provides no structural information on detected analytes, and as such positive identification of hVOCs in an environmental sample can be complicated by coelution of multiple hVOCs with similar retention times. For example, the residence time of chloroform ( $\text{CHCl}_3$ ) is similar to that of trichloroethene (TCE) and detection of  $\text{CHCl}_3$  may not always be possible due to the co-occurrence of TCE.<sup>12</sup> Co-elution events are recorded as nondetects and thus detections of TCE or  $\text{CHCl}_3$  may be underestimated. The GC-ECD measures hVOC concentrations in the range of roughly  $1\text{--}10^7$   $\text{pg kg}^{-1}$   $\text{H}_2\text{O}$ , depending on the sensitivity of detection for specific compounds. The GC-ECD technique thus detects the human footprint in sampled groundwaters at concentrations that are 3–4 orders of magnitude lower than other contemporary techniques, such as purge-and-trap gas chromatography with mass spectrometric detection (GC-MS).<sup>16</sup>

At each location where samples were collected for GC-ECD analysis, triplicate groundwater samples were also collected into 40-mL borosilicate amber vials for GC-MS analysis. The full details of the GC-MS method can be found in Conner et al. (1998).<sup>16</sup> VOCs are stripped from a 25 mL aliquot of collected samples in a Tekmar model LSC 3000 concentrator equipped with a Tekmar Aquatek autosampler. VOCs are then thermally desorbed into a fused-silica Megabore, 75 m  $\times$  0.53 mm ID, 3.0  $\mu\text{m}$  film thickness column for chromatographic separation followed by analysis with a HP model 5972 MS detector. Field blanks, field spikes, analytical blanks, and calibrations are run on

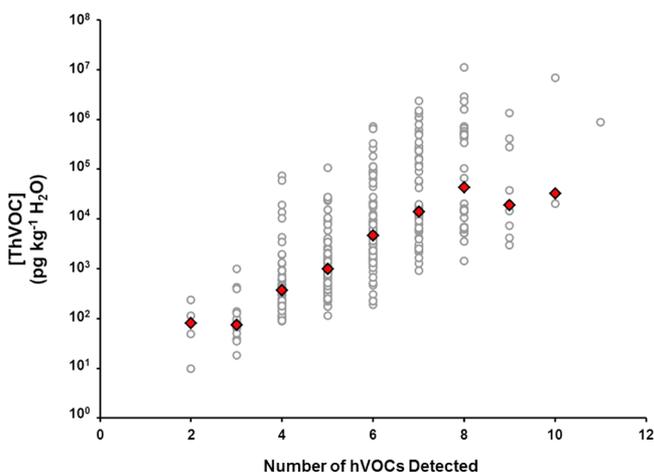
a routine basis for quality assurance purposes. The method is capable of detecting hVOCs to 10–100 ng kg<sup>-1</sup> H<sub>2</sub>O (SI Table S1).

Methyl chloride, methyl iodide, chloroform and sulfur hexafluoride all have significant natural sources (e.g., refs 15 and 17–20) which complicate their utility as indicators of human impact on groundwaters. Several other hVOCs, including PCE, TCE, and dichloromethane also have reported natural sources (e.g., refs 17, 18, and 21–23) but are predominately anthropogenic in origin.<sup>18,24,25</sup> We include general statistics for CH<sub>3</sub>I, CH<sub>3</sub>Cl, CHCl<sub>3</sub> and SF<sub>6</sub> in SI Table S1 but do not consider their individual detections as being anthropogenic in the discussion.

## RESULTS

State-wide statistics of hVOCs measured in California groundwaters are presented in SI Table S1. The full data set can be found in SI Table S2. In general, results presented are from primary samples only, unless comparison to secondary and tertiary samples clearly indicated entrainment of ambient air into the primary during or after sampling or if carry-over from a previous high-concentration sample occurred.

Given that we are concerned with the presence of hVOCs in groundwater samples, we focus on patterns of hVOC detection rather than hVOC concentrations. The quantity of hVOCs detected by the GC-ECD does correlate significantly with the total concentration of hVOCs measured by the technique ( $r = 0.70$ ,  $p < 0.1$ ,  $n = 312$ ) (Figure 2), and should provide a



**Figure 2.** Total hVOC concentration measured by GC-ECD (in pg kg<sup>-1</sup> H<sub>2</sub>O) increases exponentially with increasing number of hVOCs detected by the GC-ECD in groundwater samples. The significant correlation between number and log-concentration of hVOCs detected in California groundwaters ( $r = 0.70$ ,  $n = 312$ ,  $p < 0.1$ ) justifies the use of hVOC detection frequency as a measure of the impact of human activity in sampled groundwaters. Red diamonds represent median [ThVOC] binned by number of hVOCs detected.

measure of human impact on California groundwaters. The lack of data in the upper-left quadrant of Figure 2, which corresponds to high concentrations of a small number of a couple hVOCs,<sup>12</sup> suggests that point-source hVOC contamination is rare outside of heavily impacted aquifers.

At least two hVOCs were detected in every groundwater sample collected in this study (Figure 2). The median number of detections in California groundwaters by GC-ECD was six hVOCs, while more than half of GC-MS analyses detected

none. Tetrachloroethene (PCE, C<sub>2</sub>Cl<sub>4</sub>) and the chlorofluorocarbons CFC-11 (CCl<sub>3</sub>F) and CFC-12 (CCl<sub>2</sub>F<sub>2</sub>) were present in almost all groundwater samples analyzed in this study. TCE (C<sub>2</sub>HCl<sub>3</sub>) and CFC-113 (C<sub>2</sub>Cl<sub>3</sub>F<sub>3</sub>) are present in more than half of the groundwater samples. The high rate of detection for these compounds is likely a result of their historically widespread use (e.g., dry cleaning and refrigeration) and their relatively high atmospheric backgrounds (e.g., refs 7 and 26). In general, detection frequency is higher for compounds with a higher air-saturated water concentration (SI Table S1), consistent with hVOCs being sourced in recently recharged groundwater.

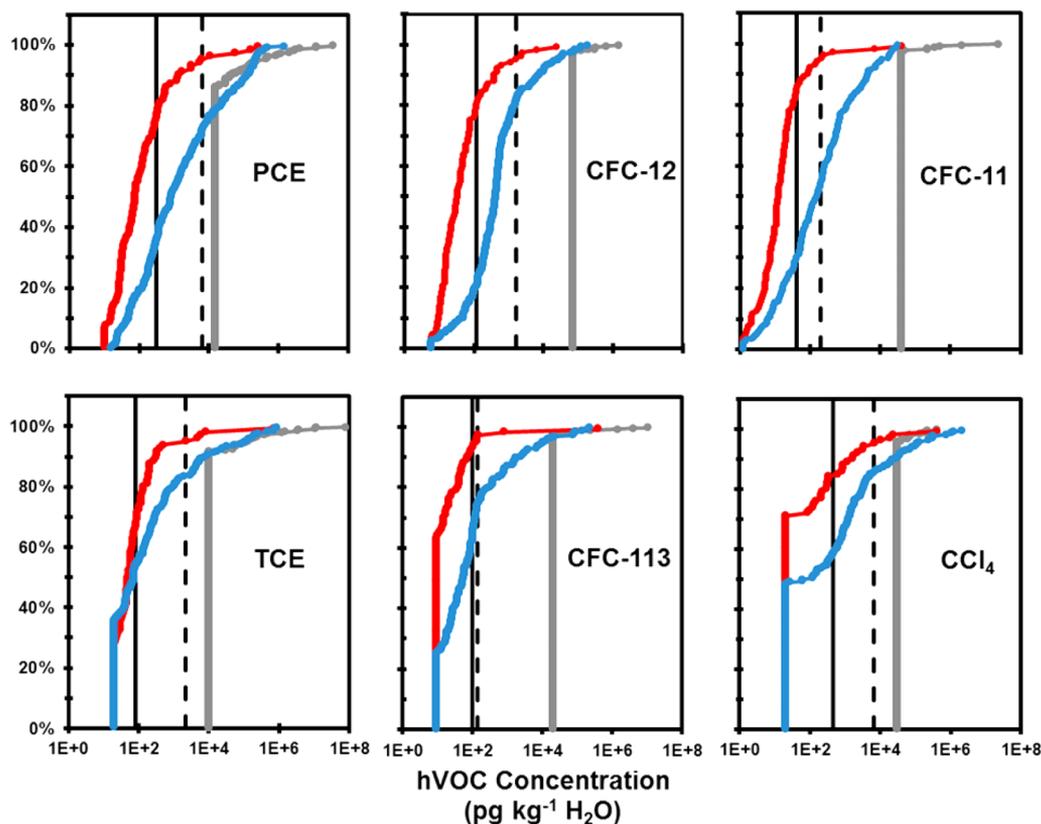
## DISCUSSION

Anthropogenic hVOCs (ahVOCs) will be associated predominantly with recently recharged groundwaters, as production of most ahVOCs began during the early- to mid-20th century (e.g., refs 7, 26, and 27). Preindustrial groundwater should contain no anthropogenic hVOCs. Industrial-era groundwater will contain ahVOC concentrations determined by equilibrium with the global atmosphere or a regional atmosphere influenced by nearby emissions. Direct point source contamination may also elevate groundwater ahVOC concentrations above expected values. By nature, ahVOCs will be mostly confined to shallow groundwaters, being sourced at the Earth's surface, entering a given aquifer through processes such as natural and artificial recharge, irrigation, leakage from landfills, underground tanks and septic systems and through direct spillage.<sup>8</sup> Thus we anticipate that ahVOCs will be associated with young, shallow groundwaters in regions with significant land modification, while older, deeper groundwaters in natural environments should contain low to undetectable concentrations of ahVOCs.

**Development of Explanatory Factors (Age and Land-use Classification).** The explanatory factors—groundwater age and land-use classification—were analyzed in relation to the ahVOC data in order to establish context for physical and chemical processes affecting groundwater. These explanatory factors provide a means to test the expected geochemistry of hVOCs, with the aim of increasing confidence that hVOCs in a sample are indeed present in a studied aquifer. We classify groundwater age based on measured tritium concentration. With a half-life of 12.3 years<sup>30</sup> and a peak production mid-20th century due to atmospheric bomb testing,<sup>31</sup> tritium is generally present only in groundwaters that have recharged since 1952, the same samples that have the potential to contain ahVOCs. We use the age classification of Belitz et al. (2011)<sup>43</sup> for California groundwaters,<sup>32</sup> with groundwaters containing <0.2 TU considered “prenuclear”, >2 TU considered “nuclear” and 0.2–2 TU considered a mixture of prenuclear- and nuclear-age groundwaters.

Land use categories are assigned to each well using an enhanced version of the satellite-derived USGS National Land Cover Data set<sup>33</sup> and based on the 500 m radius area surrounding a well. Wells with >50% of surrounding land-use identified as “natural”, “agricultural”, or “urban” are classified as such. Urban regions of California, such as the Greater Los Angeles Area, have a history of agricultural land-use prior to urban development,<sup>34</sup> and as such underlying groundwaters may have been exposed to a wide variety of human activity. Groundwater age and land-use classifications for each of the wells studied here can be found in SI Table S1.

**Establishing ahVOC Screening Levels.** The presence of detectable quantities of ahVOCs in groundwater implies



**Figure 3.** Empirical distribution functions (EDFs) for all ahVOC measurements by GC-MS (gray,  $n = 312$ ) and by GC-ECD in pre-nuclear-age (red,  $n = 84$ ) and nuclear/mixed-age (blue,  $n = 228$ ) groundwaters. Only compounds where the Owens SL differs from the MDL are shown. Black lines represent the Owens screening level (solid) and Prenuclear 95th-percentile screening level (PN SL) (dashed). The Owens SL screens most pre-nuclear age detections while retaining a large portion of detections in  $^3\text{H}$ -containing groundwaters. The PN SL tends to screen a larger portion of ahVOC detections in nuclear groundwaters, and in the case of PCE, TCE, and  $\text{CCl}_4$  resembles closely the MDL of the GC-MS technique.

recharge sometime in roughly the past 60 years, based on their atmospheric histories (e.g., refs 8 and 25–27). Groundwaters in this study that contain no detectable tritium have likely recharged prior to 1952, yet contain between 2 and 8 ahVOCs (SI Table S1). One possible explanation for the occurrence of ahVOCs in deep tritium-free groundwaters is vertical leakage from shallow aquifers that would impart low-level ahVOC concentrations (typically 10s of  $\text{pg kg}^{-1} \text{H}_2\text{O}$  or less) to deeper waters without adding detectable quantities of tritium. Alternatively, the GC-ECD technique employed in this study may be sufficiently sensitive that it detects small quantities of ahVOCs added during or after sampling that would be missed by an analytical technique with higher method detection limits. Potential nonrecharge sources of ahVOCs to groundwater samples are varied, and include leaching of ahVOCs from polymers and other materials in the sampling equipment or well materials,<sup>35–37</sup> or entrainment of ambient air during sampling, handling, storage, transport and/or analysis.

Some evidence for non-environmental addition of ahVOCs can be found in the median CFC-12/CFC-11 molar ratio in California groundwaters, 2.6 (interquartile range of 1.2–7.2,  $n = 296$ ), consistent with the mole ratio of  $\sim 2$  for the modern global atmospheric background<sup>38</sup> and greater than the mole ratio of  $\sim 0.5$  for air saturated water (SI Table S1). The CFC-12/CFC-11 molar ratio can be elevated above air-saturated water ratios by entrainment of excess air during recharge<sup>39</sup> or by anoxic degradation of CFC-11.<sup>40</sup> To minimize bias in the CFC-12/CFC-11 ratio due to excess air and anoxic degradation, we consider pre-nuclear oxigen groundwaters, which

have a median CFC-12/CFC-11 mol ratio of 2.4 (interquartile range of 0.9–4.0,  $n = 38$ ), consistent with the full data set. CFCs in the majority of collected groundwater samples may thus originate from the entrainment of small amounts of ambient air during or after sample collection. If ambient air is present in collected samples then the concentration of ahVOCs initially present at depth in the aquifer will be overestimated, although to what extent is uncertain given the semiquantitative nature of the hVOC analyses.<sup>12</sup> It is possible that air entrainment would add negligible quantities of other ahVOCs to samples given that their global atmospheric background tends to be much lower than that of CFC-12 and CFC-11.<sup>8,25–27</sup> However, local ambient hVOC mole fractions may be elevated by several orders of magnitude due to on-site degassing of greases, foams and other materials<sup>22</sup> or due to modern emissions to the regional atmosphere.<sup>8,28,29</sup>

It may not be feasible to differentiate between sources of low-level ahVOCs, given the possibility of multiple sources with unknown ahVOC signatures. We establish screening levels to help distinguish between ahVOC detections we have confidence are environmental and those that are potential artifacts. Screening levels for ahVOCs provide a concentration threshold above which detections represent environmental ahVOCs from groundwater and below which detections may be either low concentration environmental hVOCs or may represent addition during sampling or analysis. For the purpose of this study, hVOC concentrations below a screening level are treated as nondetects, while concentrations equal to or higher

than the screening level are considered environmental hVOC detections.

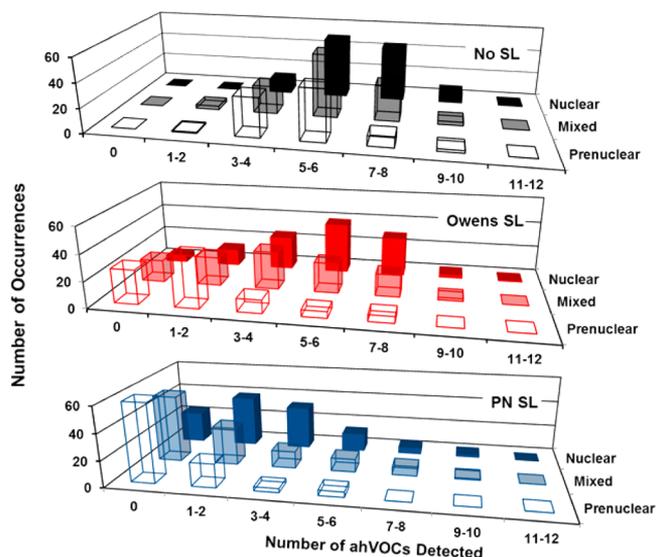
As a first step in establishing screening levels we consider all ahVOC detections in deep, pre-nuclear groundwaters in natural settings (>90% natural land-use) as being of indeterminate origin. To classify wells as deep, we used all GAMA tritium data available for a study unit to assign a depth below which only tritium-free waters had been collected. We then considered a well as “deep” if the entirety of its perforations lies below the assigned depth for the respective study unit. Of the 312 wells in this study, 14 could be characterized as “deep, old and natural”, with 12 from the Owens study unit and 2 from the Central Sacramento Valley study unit. CFC-12, CFC-11, and PCE were present in all 14 samples. CFC-113, CFC-114, TCE, and  $\text{CCl}_4$  were detected with varying frequency. The remaining compounds were undetected.

Empirical distribution functions (EDFs) for detected ahVOCs were constructed from measured concentrations for the “deep, old, natural” wells, ranking the data using the Blom formula for CFC-12, CFC-11, and PCE,<sup>41</sup> and using Regression on Order Statistics to account for nondetects of other compounds.<sup>42</sup> The EDF determines the cumulative probability of finding a given hVOC at, or lower than, a concentration in a sample, and is constructed from the empirical data. A screening level, hereafter called the “Owens SL”, was assigned for each detected ahVOC at the 95th percentile of its EDF. The Blom formula,  $(i - 0.375)/(n + 0.25)$ , where  $n$  is the total number of data and  $1 \leq i \leq n$ , was chosen as it is considered best for comparing data percentiles in a probability plot.<sup>42</sup> The Owens SL is sensitive to the ranking procedure employed: for example, if the data are ranked directly as  $i/n$ , Owens Valley screening levels would be on average 18% lower.

In Figure 3, Owens SL screening levels that differ from method detection limits are plotted as solid vertical lines, along with EDFs for all ECD measurements in tritium-free (red line) and tritium-containing (blue line) groundwaters and the full GC-MS measurements (gray line). ahVOC detections above the Owens SL indicate compounds present in the aquifer at depth, whereas detections below the Owens SL are either low concentrations environmental hVOCs or ahVOCs added as an artifact of sampling, storage and/or analysis. In essence, we use deep Owens Valley groundwaters as a “pristine” aquifer benchmark for comparison to other study units in California. The Owens SL is typically 2 orders of magnitude lower than the respective GC-MS method detection limit (MDL) and preserves the majority of ahVOC detections in  $^3\text{H}$ -containing groundwaters while screening out most ahVOC detects in pre-nuclear groundwaters (Figure 3). The majority of California groundwaters (84%) still contain at least one hVOC even after screening. Single detections tend to be TCE, 1,1-DCE (a degradation intermediate for TCE and PCE),<sup>34</sup> PCE, CFC-12, CFC-113, and CFC-11, in order of frequency of detection.

For comparison to the Owens SL, we also assign a screening level based on the 95th percentile of EDFs constructed from all pre-nuclear-age groundwaters (hereafter called the “PN SL”). This is a more stringent screening level than the Owens SL and likely precludes groundwaters containing environmental hVOC concentrations. The PN SLs for each ahVOC are dashed vertical lines in Figure 3. The PN SL screens out more ahVOC detections in  $^3\text{H}$ -containing groundwaters than the Owens SL, and in the case of PCE, TCE, and  $\text{CCl}_4$  is comparable in magnitude to the respective GC-MS MDL.

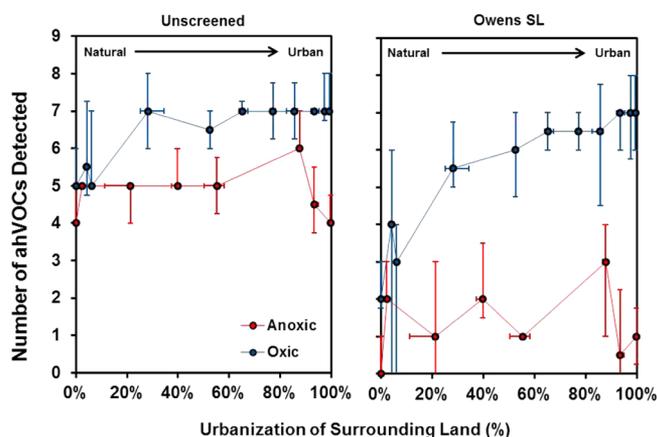
The distribution of ahVOC detections by age class for unscreened, and Owens SL and PN SL screened data are presented in Figure 4. In the case of the unscreened GC-ECD



**Figure 4.** ahVOC detection histograms for unscreened (black), Owens SL-screened (red), and Prenuclear 95th percentile screened (PN SL) (blue) GC-ECD results. Shading designates pre-nuclear (transparent), mixed (translucent) and nuclear (opaque) age classes. The distribution of ahVOC detections in the unscreened data appears to be independent of the groundwater age class. The application of the Owens SL to the unscreened data separates the main modes of the pre-nuclear- and nuclear-age distributions, consistent with the anticipated relation between ahVOC detection frequency and groundwater tritium-age, with little apparent loss of information. The PN SL appears to overscreen the data, as its application results in less distinguishable ahVOC distributions for the three age classes, centered at 0–2 ahVOCs detected per sample.

data, the distribution of ahVOC detections for pre-nuclear-, mixed-, and nuclear-age groundwaters appears to be very similar, with a main mode for each age class at 5–6 hVOCs detected. Use of the Owens SL moves the main mode of the pre-nuclear ahVOC detection distribution to 1–2 hVOCs detected while leaving the nuclear-age distribution centered at 5–6 hVOCs detected. The more stringent PN SL moves all three age-class distributions to 0–2 ahVOC detections, and the distinction between pre-nuclear and nuclear age distributions is lost. We conclude that applying the Owens SL to the unscreened GC-ECD data is more appropriate as it retains the anticipated ahVOC-tritium age relationship.

**ahVOCs, Redox Conditions and Land Use.** ahVOC detection frequency is expected to be higher in oxic groundwaters than in anoxic groundwaters as many ahVOCs are degraded under anoxic conditions.<sup>34</sup> Anoxic groundwaters also tend to be deeper and older than oxic groundwaters and should thus be spatially and temporally isolated from anthropogenic sources. The median number of ahVOC detections in oxic groundwater samples is higher than anoxic groundwaters in both unscreened and screened cases (Figure 5). The larger distinction between Owens SL-screened hVOC detections in anoxic and oxic groundwaters suggests that anoxic degradation of ahVOCs may be more significant than the unscreened data implies.

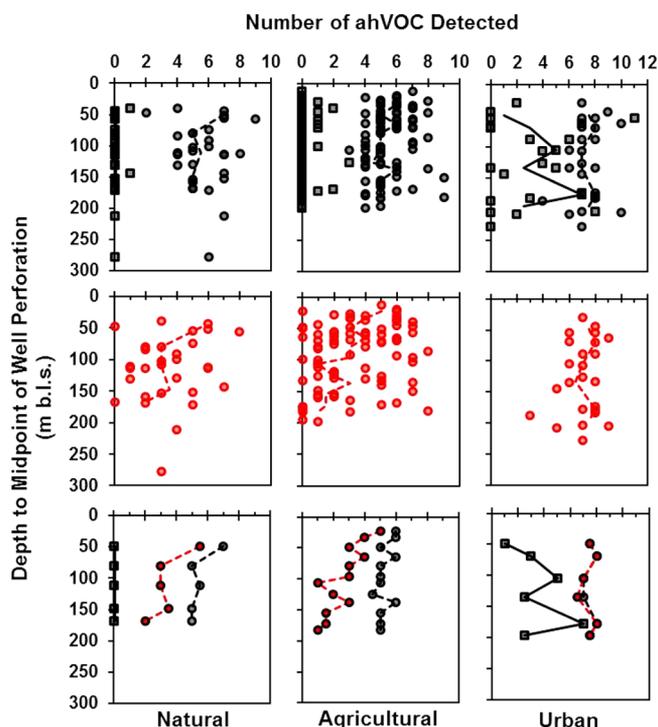


**Figure 5.** The median number of ahVOCs detected in groundwater samples as a function of the surrounding urbanization. Wells are classified as oxic (blue) and anoxic (red) redox states, as determined using the model of McMahon and Chapelle (2008).<sup>50</sup> Points plotted are medians binned for equal representation of the data. Whiskers represent the 1st and 3rd quartiles, or the inner 50% of the data. The urban-hVOC signal and the separation in hVOC detections for oxic and anoxic waters are more apparent when the data is screened using the Owens SL.

The detection frequency of ahVOCs is also expected to be higher in urban areas based on denser industrial and commercial uses (SI Table S1). However, the median number of ahVOC detections in unscreened California groundwater samples generally does not change with an increase in urban land use surrounding the wells (Figure 5, left panel). When the Owens SL is applied a clear correlation between detection frequency and percent urban land use is observed (right panel) suggesting a connection between surface activities and groundwater quality. This increase is not observed in anoxic groundwaters, consistent with anoxic ahVOC degradation and isolation from the surface.

Figure 5 includes only wells with 0% agricultural land-use. An analogous comparison to Figure 5 for percent agricultural land-use (not shown) revealed no discernible trend in ahVOCs with increasing agricultural land use, even after applying the Owens SL. This suggests that increased pumping and irrigation associated with agricultural regions produces an ahVOC signal that is similar to recharge in natural environments (i.e., recently recharged water in equilibrium with the global atmosphere).

**ahVOC Depth Profiles.** Depth profiles of ahVOC detections in several study units are presented in Figure 6. We chose to plot ahVOC detections for collections of study units in recognition of the varying hydrogeology and land-use history of the different regions of California. Study units are collected into natural (Sierra Nevada Mountains), agricultural (San Joaquin Valley) and urban (Greater Los Angeles Area) study regions. The natural study region includes wells in the Tahoe and Central Sierras study units and several wells from the Southern Sierras study unit.<sup>43</sup> The agricultural study region includes wells in the Central Sacramento Valley, Central-Eastside San Joaquin Valley, the Kern Basin and the Southeast San Joaquin Valley study units.<sup>44–46</sup> The urban study region includes wells in the Upper Los Angeles Basins study unit, and in the Bunker Hill-Rialto-Colton (BHRC) and Riverside-Arlington-Temescal (RAT) aquifers of the Santa Ana study unit.<sup>47,48</sup> The BHRC and RAT aquifers were selected since their overlying land-use history resembles the Upper Los



**Figure 6.** Depth profiles of ahVOC detections by GC-MS (squares) and GC-ECD (circles) for wells in natural (Sierra Nevada Mountains), agricultural (San Joaquin Valley) and urban (Greater Los Angeles Area) areas. Unscreened data (black) and Owens SL- (red) screened data are presented. Dashed lines in the upper and middle plots, and points in the lower three plots, are median ahVOC detections for GC-MS (solid) and GC-ECD (dashed) binned every 30 m (100 ft) starting from the shallowest well for a study region, colored according to the scheme above. Groundwaters in the natural and agricultural regions show a decrease in number of ahVOCs detected with increasing depth, while the urban study region shows near-constant detection of ahVOCs with depth.

Angeles Basin study unit. Wells from the Southern California Coastal Plain were not included because these aquifer systems are often confined and groundwater flow is primarily radial.<sup>49</sup> Depths presented in Figure 6 are the depth from the land surface to the midpoint of the well perforation, to better represent the effective depth of wells with long-screened perforations beginning at shallow depths. Accompanying GC-MS results (gray squares) are plotted in the upper panels of Figure 6 for comparison to the respective unscreened GC-ECD data (gray circles).

Depth profiles presented in Figure 6 illustrate the higher sensitivity of the GC-ECD compared to GC-MS, as the GC-MS rarely detects ahVOCs outside of urban environments. In the Greater LA area, the GC-MS frequently detects ahVOCs, although the number detected is typically fewer than that detected by GC-ECD. The high number and frequency of ahVOC detections by both GC-ECD and GC-MS likely reflects the long historical anthropogenic perturbations to groundwater flow (pumping, irrigation and artificial recharge) and widespread industrial releases of ahVOCs in the Greater LA area.<sup>47</sup> The GC-ECD detects between 5 and 7 ahVOCs over a range of depths in all study regions. This illustrates the inability of the unscreened GC-ECD data to distinguish between environmental ahVOCs in the aquifer and the ahVOCs that are likely introduced during sampling or analysis. Application of the Owens SL in the natural (Sierra Nevada Mountains) and

agricultural (San Joaquin Valley) study regions results in a pattern of decreasing number of ahVOC detections with increasing well depth (middle panels, Figure 6). This pattern is consistent with the introduction of ahVOCs at the surface in recently recharged groundwaters overlying deeper, older groundwaters. The Owens SL does not change the vertical profile of ahVOC detections in urban (Greater Los Angeles) groundwaters, primarily because these ahVOCs are present in the groundwater at all depths, due to their historical use in urban areas. This provides confirmation that the Owens SL does not censor the anthropogenic signal in studied groundwaters.

The hVOC screening levels in this study are not universal and are not necessarily intended for application on other data sets. The use of other sampling/analytical techniques, in other aquifers, might require establishing other screening levels based on benchmark groundwaters and prior knowledge of hVOC geochemistry. Screening levels in this study illustrate the need to approach the interpretation of low-level hVOC data with caution, given uncertainties about the source of low-level hVOCs. Regardless, applying screening levels based on the assumption that deep wells in natural environments drawing tritium-free water should be ahVOC-free provides a data set that is consistent with hydrogeological and geochemical conditions, without undue loss of information.

The ahVOC depth profiles presented in Figure 6 illustrate that ahVOCs are observed to depths of more than 150 m below the land surface in California groundwaters. In this study, 84% of the 312 groundwater samples had at least one ahVOC detection above the Owens screening level. Although in almost all cases the ahVOC concentrations observed do not pose a health concern,<sup>43–48</sup> their detection confirms that these compounds have impacted the majority of California aquifers. Given the widespread spatial distribution of ahVOCs we conclude that California groundwaters are likely more susceptible to contamination, and the extent of contaminant transport may be greater than previously thought.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Summary statistics (Table S1) and full hVOC concentrations (Table S2), as well as hVOC screening levels (Table S3) can be found in the Supporting Information. Figure S1 highlights hVOC stability with storage time. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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