ABSTRACT: The variables affecting the occurrence of hydrocarbons in aquifers used for public supply in California were assessed based on statistical evaluation of three large statewide datasets; gasoline oxygenates also were analyzed for comparison with hydrocarbons. Benzene is the most frequently detected (1.7%) compound among 17 hydrocarbons analyzed at generally low concentrations (median detected concentration 0.024 μg/l) in groundwater used for public supply in California; methyl tert-butyl ether (MTBE) is the most frequently detected (5.8%) compound among seven oxygenates analyzed (median detected concentration 0.1 μg/l). At aquifer depths used for public supply, hydrocarbons and MTBE rarely co-occur and are generally related to different variables; in shallower groundwater, co-occurrence is more frequent and there are similar relations to the density or proximity of potential sources. Benzene concentrations are most strongly correlated with reducing conditions, regardless of groundwater age and depth. Multiple lines of evidence indicate that benzene and other hydrocarbons detected in old, deep, and/or brackish groundwater result from geogenic sources of oil and gas. However, in recently recharged (since ~1950), generally shallower groundwater, higher concentrations and detection frequencies of benzene and hydrocarbons were associated with a greater proportion of commercial land use surrounding the well, likely reflecting effects of anthropogenic sources, particularly in combination with reducing conditions.

(KEY TERMS: organic chemicals; drinking water; environmental sampling; groundwater hydrology; geochemistry; hydrocarbons; gasoline oxygenates.)

INTRODUCTION

Biofuels, including ethanol, are expected to provide a greater contribution to the fuel supply in the United States (U.S.) in the future. Research in the past decade (Molson et al., 2000, 2002; Deeb et al., 2002; Ruiz-Aguilar et al., 2003; Mackay et al., 2006; Gomez and Alvarez, 2010; Corseuil et al., 2011) has shown that ethanol in gasoline may cause plumes of benzene in groundwater to be larger than they would otherwise be. Benzene mobility in the presence of ethanol or other fuel alcohols may result from several factors, including a decrease in benzene degradation rates due to consumption of dissolved oxygen by preferential microbial oxidation of ethanol (Molson et al., 2000, 2002; Corseuil et al., 2011). A key step in determining the vulnerability of public-supply wells to the increased use of biofuels is to identify public-supply wells in key settings of the U.S. that have had historical detections of fuel components and to evaluate what variables may explain those detections.
California provides an ideal location to evaluate the relation of environmental factors to the occurrence of fuel components in public-supply wells for several reasons. First, there are thousands of public-supply wells, providing the statistical mass necessary for comprehensive analysis. Second, there is an abundance of ancillary data available to facilitate statistical analysis; the U.S. Geological Survey (USGS) has assembled extensive ancillary data for the California State Water Resources Control Board's (CA SWRCB) Groundwater Ambient Monitoring and Assessment (GAMA) program Priority Basin Project (PBP) (CA SWRCB, GAMA. Accessed on July 29, 2011, at http://www.swrcb.ca.gov/gama/; USGS, GAMA PBP. Accessed on December 8, 2011 at: http://ca.water.usgs.gov/gama/). Third, California is an important setting in the national landscape, superimposing large urban populations dependent on groundwater supplies, with a high density of fuel sources, and large groundwater withdrawals.

The objective of this study was to identify relations of source, transport, and receptor variables to the occurrence of hydrocarbons in groundwater used for public supply in California. Relations of variables to hydrocarbon distributions are compared to relations for gasoline oxygenates.

Previous studies have discussed the occurrence of volatile organic compounds (VOCs) and relations of occurrence to selected explanatory variables in groundwater in parts of California (Shelton et al., 2001; Dawson et al., 2003; Belitz et al., 2004; Densmore et al., 2004; Wright et al., 2004; Hamlin et al., 2005; Johnson and Belitz, 2009) or the U.S. (Grady, 2003; Moran et al., 2005; Zogorski et al., 2006; Squillace and Moran, 2007). In comparison, this study focuses specifically on organic constituents derived from spilled fuel and explores relations of the occurrence of these constituents in aquifers primarily used for public supply in California to potential explanatory variables. This study also includes analysis of three disparate datasets, having varying analytical reporting limits and spatial distributions, to compare results between different depths, land uses, and concentration ranges of fuel constituents. In a previous study, Landon and Belitz (2012) described that benzene and other hydrocarbons detections in relatively deep groundwater used for public supply in California are more commonly attributable to geologic sources of petroleum (geogenic) than anthropogenic sources based on analysis of two datasets. In contrast, the focus of this study is to describe the results of statistical analysis of the relations of hydrocarbons and oxygenates to a broader range of explanatory variables, including relations in relatively shallower groundwater in more urban areas in California, and to compare results for hydrocarbons and oxygenates.

METHODS

Data Sources

This study, a partnership of the USGS PBP and U.S. Environmental Protection Agency (USEPA), includes data from three sources. First, the study includes data collected by the USGS as part of the California State Water Board's GAMA program PBP, hereafter referred to as GAMA data (USGS, GAMA PBP Publications, Data Series Reports. Accessed on December 8, 2011, http://ca.water.usgs.gov/gama/publications.html). Second, data assembled for drinking water regulatory monitoring purposes by the California Department of Public Health (CDPH) were included and are hereafter referred to as CDPH data (CDPH, Drinking Water Program. Accessed on September 7, 2011, http://www.cdph.ca.gov/programs/Pages/DWP.aspx). Third, the study analyzed data from the USGS National Water Information System (NWIS) hereafter referred to as NWIS data (USGS, NWIS. Accessed on December 8, 2010, http://waterdata.usgs.gov/ca/nwis/). The GAMA and NWIS data include age tracers and ancillary water chemistry data, and use of low laboratory reporting levels (LRLs) at a smaller number of wells (~1,000-2,000) compared to the CDPH data, which has less extensive ancillary data and LRLs that are typically one to two orders of magnitude higher, at a larger number of wells (~12,000).

GAMA and NWIS data were collected using protocols to ensure that representative samples are collected while minimizing the potential for sample contamination (Koterba et al., 1995; USGS, variously dated). Detailed descriptions of sample collection, analysis, and quality-assurance (QA) methods and results for GAMA data are available in previous publications (USGS, GAMA PBP Publications, Data Series Reports. Accessed on December 8, 2011, http://ca.water.usgs.gov/gama/publications.html). About 80% of the wells in the GAMA data were public-supply wells or other types of large withdrawal wells, 10% were domestic wells, and 10% were observation wells. The CDPH database lists wells used for public drinking water supplies, and includes wells from systems classified as community (such as cities, towns, and mobile-home parks), nontransient, noncommunity (such as schools and workplaces), and transient, noncommunity (such as campgrounds and parks). About 45% of the wells in the NWIS data were public-supply or other types of production wells, 22% were domestic wells, and 33% were monitoring wells.

Because GAMA data were collected from wells that were randomly selected from spatially distributed grid cells covering priority groundwater basins (stratified random design), and had low LRLs and associated QA
data (Belitz et al., 2003, 2010), GAMA data were used for evaluating occurrence and distribution of hydrocarbons and gasoline oxygenates in California groundwater. The more extensive CDPH data, with higher method detection levels (MDLs), were used for assessing the distribution at higher concentrations and to evaluate explanatory relations identified using the GAMA data. The detection frequencies based on CDPH data need to be regarded with caution because the MDLs were not always recorded in the database; the detection frequencies in this study are reported relative to the most common MDLs. The NWIS data, with low LRLs similar to GAMA for most of the data, have a more clustered spatial distribution than the GAMA and CDPH data; the NWIS data are primarily for wells located in Southern California and the Central Valley. As a consequence, the NWIS data were not used for the purpose of evaluating distribution, but were used for assessing relations to explanatory variables.

### Analytes

Because of expected low detection frequencies of hydrocarbons in public-supply wells (Hadley and Armstrong, 1991; Williams et al., 2002; Zogorski et al., 2006; Kulonoski et al., 2010; Landon et al., 2010; Bennett et al., 2011; Burton et al., 2011), this study compiled data for 17 hydrocarbons and seven gasoline oxygenates or degradates included in standard USGS VOC analyses (Bender et al., 1999) (Table S1) in an attempt to have sufficient statistical mass to evaluate variables explaining detections. Detection frequencies of the gasoline oxygenate methyl tert-butyl ether (MTBE) have been slightly higher than for individual hydrocarbons in Southern California (e.g., Shelton et al., 2001; Hamlin et al., 2005) and nationally (Zogorski et al., 2006). Benzene and MTBE were selected as the primary dependent variables for hydrocarbons and oxygenates, respectively, because they were: (1) the most commonly occurring hydrocarbon and oxygenate in the GAMA data, (2) the most reliably measured constituents based on QA analysis. The sum-of-hydrocarbons concentration was selected as a secondary dependent variable (Table 1) because of the common co-occurrence of multiple hydrocarbons.

### Data Processing

A single analysis at each well was selected to avoid biasing the data to those wells having many analyses over time. About 90% of the wells sampled by GAMA were visited once; for the 10% of wells sampled more than once, the sample date with the most complete data was selected. The GAMA data included 1,973 wells sampled during May 2004 through August 2010 (median of November 2006). For CDPH data, the most recent concentration of each VOC and other target constituents was selected and evaluated using the QA steps described below. The CDPH data included 12,417 wells sampled between July 1984 and August 2010 (median of March 2005); >75% of the data was

---

### Table 1. Detection Frequencies for Benzene and Sum of Hydrocarbons in GAMA and CDPH Data.

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Benzene</th>
<th>Sum of Hydrocarbons</th>
<th>MTBE</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAS number</td>
<td>71-43-2</td>
<td>na</td>
<td>1634-04-4</td>
</tr>
<tr>
<td>Threshold type</td>
<td>MCL-CA</td>
<td>na</td>
<td>MCL-US</td>
</tr>
<tr>
<td>Threshold value (µg/l)</td>
<td>1</td>
<td>na</td>
<td>13</td>
</tr>
<tr>
<td>Maximum</td>
<td>0.013</td>
<td>na</td>
<td>0.08</td>
</tr>
<tr>
<td>LT-MDL (µg/l)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**GAMA**

<table>
<thead>
<tr>
<th>Number of wells</th>
<th>1,972</th>
<th>1,973</th>
<th>1,972</th>
</tr>
</thead>
<tbody>
<tr>
<td>Detections at or above LT-MDL</td>
<td>33</td>
<td>53</td>
<td>114</td>
</tr>
<tr>
<td>Detection frequency (LT-MDL), %</td>
<td>1.67</td>
<td>2.69</td>
<td>5.78</td>
</tr>
<tr>
<td>Detections at or above CDPH MDL</td>
<td>4</td>
<td>na</td>
<td>1</td>
</tr>
<tr>
<td>Detection frequency (CDPH MDL), %</td>
<td>0.20</td>
<td>na</td>
<td>0.05</td>
</tr>
<tr>
<td>Detected concentrations, maximum, µg/l</td>
<td>78.9</td>
<td>79.8</td>
<td>28.3</td>
</tr>
<tr>
<td>Detected concentrations, median, µg/l</td>
<td>0.024</td>
<td>0.09</td>
<td>0.10</td>
</tr>
<tr>
<td>Detections above threshold</td>
<td>3</td>
<td>na</td>
<td>1</td>
</tr>
<tr>
<td>Detection frequency above threshold, %</td>
<td>0.15</td>
<td>na</td>
<td>0.05</td>
</tr>
</tbody>
</table>

**CDPH**

<table>
<thead>
<tr>
<th>Number of wells</th>
<th>12,417</th>
<th>12,441</th>
<th>10,792</th>
</tr>
</thead>
<tbody>
<tr>
<td>Most frequent MDL, µg/l</td>
<td>0.5</td>
<td>0.5</td>
<td>3</td>
</tr>
<tr>
<td>Detections at or above CDPH MDL</td>
<td>16</td>
<td>71</td>
<td>32</td>
</tr>
<tr>
<td>Detection frequency (CDPH MDL), %</td>
<td>0.13</td>
<td>0.57</td>
<td>0.30</td>
</tr>
<tr>
<td>Detected concentrations, maximum, µg/l</td>
<td>140</td>
<td>200</td>
<td>500</td>
</tr>
<tr>
<td>Detected concentrations, median, µg/l</td>
<td>3.45</td>
<td>0.60</td>
<td>8.60</td>
</tr>
<tr>
<td>Detections above threshold</td>
<td>11</td>
<td>na</td>
<td>15</td>
</tr>
<tr>
<td>Detection frequency above threshold, %</td>
<td>0.09</td>
<td>na</td>
<td>0.14</td>
</tr>
</tbody>
</table>

**Note:** GAMA, Groundwater Ambient Monitoring and Assessment; CDPH, California Department of Public Health; MTBE, methyl tert-butyl ether; CAS, chemical abstract service; LT-MDL, USGS long-term method detection level; MCL-CA, California Department of Public Health maximum contaminant level; MCL-US, U.S. Environmental Protection Agency maximum contaminant level; na, not available; µg/l, micrograms per liter.
from the 2000s. For NWIS data, the sample date having the most complete data was selected for each well. The NWIS data included 1,105 wells sampled between August 1984 and June 2010 (median of March 2001); >70% of the data was from the 2000s.

Study-specific reporting levels (SRLs) for individual VOCs were developed by the GAMA program on the basis of evaluation of blank samples (Fram et al., 2012). These SRLs for VOCs were used in this study to exclude GAMA results with a reasonable likelihood of being false positives. GAMA SRLs were applied to NWIS data to maintain consistency in the analysis of GAMA and NWIS data. Application of GAMA SRLs resulted in analytical detections at low concentrations of toluene, ethylbenzene, o-xylene, m- and p-xylene, and 1,2,4-trimethylbenzene being treated as nondetections in 290 GAMA and 155 NWIS samples (see Supporting Information); these constituents were detected in blanks at concentrations and frequencies that overlapped with environmental samples (Fram et al., 2012). Hydrocarbons other than the five listed above were not detected in GAMA blank samples and the interpretation of detections of these constituents was not affected by application of SRLs. In 25 GAMA and 51 NWIS samples, data for the five constituents were not screened to SRLs because of independent evidence that detections of these compounds were likely to be environmental rather than sampling artifacts. The evidence included: detection of one or more co-occurring hydrocarbons that were not censored based on detections in blanks, historical detections of hydrocarbons in that well in the CDPH database, or concentrations of the five constituents above SRLs.

Because the CDPH data are collected for regulatory purposes at thousands of wells by different individuals and laboratories, there is not an opportunity to review the quality of these data as rigorously as the GAMA data. Following CDPH recommendations, a single detection of a constituent is not considered to represent an actual occurrence until the detection is verified by subsequent sample results. For all CDPH wells with hydrocarbon detections in the most recent sample, the historical data were evaluated for previous detections. If there were previous detections, the most recent result was used to represent that well. Single detections of a single constituent with no other historical detections were treated as nondetections in the most recent CDPH data to avoid false positives; results from wells with only a single analysis were retained in the CDPH data analyzed. The screening procedures resulted in apparent detections being treated as nondetections in 55 samples; 29 of these samples had single detections of toluene only in the most recent sample. This screening was done to remove detections from the data that were not likely to represent aquifer conditions.

### Explanatory Factors

Potential explanatory variables were organized into three conceptual groups: source, transport, and receptor variables. Source variables include direct or proxy measures of the density of sources of fuel constituents at or near the land surface within areas surrounding wells or the proximity of these sources to wells. Transport variables include factors that affect the hydrogeologic conditions between the recharge area and a sampled well, including geochemical conditions, groundwater age, groundwater pumping and recharge, geology, density of public-supply wells, soil properties, and depth to water. Receptor variables are characteristics of the sampled well (receptor) itself, including well construction and well type.

Table 2 lists 19 continuous potential explanatory variables discussed in this study. Data for many of the explanatory variables have been used in previous studies in California (Johnson and Belitz, 2009; Jurgens et al., 2010; Wright and Belitz, 2010; Fram and Belitz, 2011; Landon et al., 2011). Leaking Underground Fuel Tank (LUFT) density and proximity and population density were selected because they have been found to be important in previous studies of VOCs (Moran et al., 2005). Relations to land use were assessed using data in 30-m cells interpreted from early 1990s satellite imagery and aerial photography (Nakagaki et al., 2007) and subsequent calculations of the percent of the total land area within 500 m of each well in selected categories including urban, commercial, and high-intensity residential land use (Johnson and Belitz, 2009). The commercial land-use category represents commercial/industrial/transportation areas consisting of roads, railroads, and highly developed areas (constructed materials account for >80% of area) not classified as high-intensity residential (apartment complexes and row houses). Land-use data from the 1990s were used rather than more recent data because water entering the perforations of wells is more likely to be influenced by land use two or more decades ago than current land use; the 1990s land-use data represented the earliest comprehensive land-use data available across the entire state. A Geographic Information System was used to attribute GAMA, CDPH, and NWIS wells with ancillary spatial data. Additional continuous and categorical variable data compiled for this study that did not indicate consistent relations with hydrocarbon distribution are described in the Supporting Information.

GAMA data were classified on the basis of groundwater age, well depth, reduction-oxidation (redox) conditions, and proximity to oil and gas fields; detection frequencies were compared between the resulting data bins. For tritium ($^3$H), a tracer of groundwater recharged by precipitation during the period of above
Table 2. Spearman’s ρ Correlation Test Results Between Primary Continuous Explanatory Variables and Concentrations of MTBE, Benzene, and Sum of Hydrocarbons.

<table>
<thead>
<tr>
<th>Variable, Units (reference)</th>
<th>GAMA Old gw Benz HC</th>
<th>GAMA Recent gw Benz</th>
<th>CDPH Benz</th>
<th>CDPH MTBE</th>
<th>NWIS MTBE</th>
<th>NWIS Benz</th>
<th>NWIS HC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Source</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anthropogenic</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6LUFT density, no./km²</td>
<td>+1</td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
<td>+1</td>
<td>+1</td>
<td>+1</td>
</tr>
<tr>
<td>6Distance to nearest LUFT, m</td>
<td>+1</td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
<td>+1</td>
<td>+1</td>
<td>+1</td>
</tr>
<tr>
<td>6Population density, people/km²</td>
<td>+1</td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
<td>+1</td>
<td>+1</td>
<td>+1</td>
</tr>
<tr>
<td>6Commercial land use, %</td>
<td>+1</td>
<td>+1</td>
<td>ns</td>
<td>ns</td>
<td>+1</td>
<td>+1</td>
<td>+1</td>
</tr>
<tr>
<td>8Urban land use, %</td>
<td>+1</td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
<td>+1</td>
<td>+1</td>
<td>+1</td>
</tr>
<tr>
<td>Geogenic</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6Distance to nearest oil or gas field, m</td>
<td>ns</td>
<td>-2</td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
</tr>
<tr>
<td>Receptor</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10,11,12Depth to top of perforations, m bls</td>
<td>-4</td>
<td>ns</td>
<td>-2</td>
<td>ns</td>
<td>ID</td>
<td>ID</td>
<td>ns</td>
</tr>
<tr>
<td>10,11,12Well depth, m bls</td>
<td>ns</td>
<td>+2</td>
<td>ns</td>
<td>ns</td>
<td>ID</td>
<td>ID</td>
<td>-4</td>
</tr>
<tr>
<td>Transport</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Age/depth indicators</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10,11,12pH, standard pH units</td>
<td>-4</td>
<td>ns</td>
<td>-2</td>
<td>ns</td>
<td>-4</td>
<td>+2</td>
<td>-4</td>
</tr>
<tr>
<td>10,12Tritium, pCi/l</td>
<td>+4</td>
<td>-2</td>
<td>-2</td>
<td>ns</td>
<td>ID</td>
<td>ID</td>
<td>ns</td>
</tr>
<tr>
<td>10Carbon-14, pmc</td>
<td>+4</td>
<td>-2</td>
<td>-2</td>
<td>ns</td>
<td>ID</td>
<td>ID</td>
<td>ID</td>
</tr>
<tr>
<td>Aquifer stress/aquifer characteristics</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11CDPH well density, wells/km²</td>
<td>+5</td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
<td>+5</td>
<td>ns</td>
</tr>
<tr>
<td>13Soil permeability, cm/h</td>
<td>-5</td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
</tr>
<tr>
<td>14Groundwater recharge minus pumping</td>
<td>-5</td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
</tr>
<tr>
<td>Oxidation-reduction conditions</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10,12Dissolved oxygen, mg/l</td>
<td>ns</td>
<td>-3</td>
<td>-3</td>
<td>ns</td>
<td>ID</td>
<td>ID</td>
<td>-3</td>
</tr>
<tr>
<td>10,11,12Nitrate, mg/l as N</td>
<td>ns</td>
<td>-3</td>
<td>-3</td>
<td>ns</td>
<td>+4</td>
<td>-3</td>
<td>ns</td>
</tr>
<tr>
<td>10,12Manganese, μg/l</td>
<td>ns</td>
<td>+3</td>
<td>-3</td>
<td>ns</td>
<td>+3</td>
<td>+3</td>
<td>ns</td>
</tr>
<tr>
<td>10,12Iron, μg/l</td>
<td>ns</td>
<td>+3</td>
<td>-3</td>
<td>+3</td>
<td>ns</td>
<td>+3</td>
<td>ns</td>
</tr>
</tbody>
</table>

Notes: +, significant positive correlation; −, significant inverse correlation; ns, correlation not significant; ID, insufficient data to evaluate correlation; significant correlations were determined on the basis of ρ values (significant level of the Spearman’s test) less than the threshold value (z) of 0.05; GAMA, Groundwater Ambient Monitoring and Assessment; CDPH, California Department of Public Health; NWIS, National Water Information System; MTBE, methyl tert-butyl ether; Benz, benzene concentrations; HC, sum-of-hydrocarbon concentrations; gw, groundwater; km², square kilometers; no., number; m, meters; %, percent; LUFT, Leaky Underground Fuel Tank; pCi/l, picocuries per liter; pmc, percent modern carbon; cm, centimeters; mg/l, milligrams per liter; μg/l, micrograms per liter; bls, below land surface; N, nitrogen.

Group of relations:
1Correlations with anthropogenic source variables consistent with increasing concentrations with increasing source density and proximity.
2Correlations of benzene with variables indicating increasing concentrations with proximity to oil and gas fields and greater depth and age.
3Correlations with redox conditions indicating increasing concentrations with reducing groundwater.
4Correlations of MTBE with variables indicating increasing concentrations with shallower and younger groundwater.
5Correlations of MTBE with variables indicating increasing concentrations with greater aquifer stress and permeability.

Sources:
8Nakagaki et al. (2007); Johnson and Belitz, 2009.
13USDA (1994).
14California Department of Water Resources (2005).
ground nuclear testing that began after 1950, a threshold activity of 1 pCi/l was selected for distinguishing water that was likely to have recharged aquifers prior to 1950 (old groundwater, <1 pCi/l) from post-1950 water (recent-age groundwater, ≥1 pCi/l) (Michel, 1989; Plummer et al., 1993; Michel and Schroeder, 1994; Clark and Fritz, 1997; Manning et al., 2005). Well depths were classified into three bins, <30, 30-180, and >180 m. These depth values were selected to separate upper and lower parts of the depth distributions from most of the interquartile range (Figure S1) while using consistent threshold values for all three datasets. Three depth bins were used because of the observation of a bimodal relation of hydrocarbon occurrence to well depth; these three bins were further simplified to a binary classification of ≥180 m (deep) and <180 m (shallow and intermediate) for use with other variables. Redox conditions were classified based on measured concentrations of dissolved oxygen (O$_2$), nitrate (NO$_3$), manganese (Mn$^{+2}$), iron (Fe$^{+2}$), and sulfate (McMahon and Chapelle, 2008; Jurgens et al., 2009). The redox categories ofoxic, suboxic, mixed, and anoxic (McMahon and Chapelle, 2008) were further lumped into a binary redox classification of oxic, and reducing, the latter of which included suboxic, mixed, and anoxic categories, for testing the variation in frequency of detection of contaminants (Table S2). Based on analysis of the relation between hydrocarbon occurrence and minimum distance to the nearest oil and gas field, a threshold value of 5 km was identified for binary classification. Density of CDPH wells (wells/km$^2$) is considered an indicator of aquifer utilization for supply (aquifer stress), although groundwater withdrawals for irrigation dwarf those for public supply in California. However, the locations and withdrawals from irrigation wells throughout California are not available. Additional proxy variables for assessing relations to aquifer stress were areal mean groundwater recharge, pumping, and recharge minus pumping rates (cm/yr), which were computed from estimated annual volumes and areas reported by California Department of Water Resources (2005) for 56 planning areas covering the state.

Statistical Methods

Nonparametric rank-based methods were used for statistical analysis because these techniques are generally not affected by outliers and do not require that the data follow a normal distribution (Helsel and Hirsch, 2002). The significance level ($p$) used for hypothesis testing was compared to a threshold value ($x$) of 5% ($x = 0.05$) to evaluate whether the relation was statistically significant ($p < x$). Correlations were investigated using Spearman’s method to calculate the rank-order correlation coefficient ($\rho$) between concentrations and continuous explanatory variables. The Wilcoxon rank-sum test was used to evaluate the differences between two groups (Helsel and Hirsch, 2002). The Kruskal-Wallis test was used to test differences among more than two groups (Conover, 1980). A Pearson’s chi-square ($\chi^2$) contingency table test was used to evaluate whether two categorical variables are related. All statistical analysis was done using S-PLUS for Windows, version 8.1, Professional Edition (TIBCO Software Inc., Somerville, Massachusetts).

Principal components analysis (PCA) was also used to distinguish the characteristics of wells in which benzene and other hydrocarbons were detected. PCA is a multivariate statistical technique that reduces the number of variables into a smaller number of components (Kshirsagar, 1972; Gnanadesikan, 1997; Manly, 2005). The transformed variables, known as principal components, are uncorrelated linear combinations of the original variables. PCA provides an objective way to combine variables to account for as much of the variability in the data as concisely as possible. The magnitude and direction (positive or negative) of the contribution of each variable to the principal component score is described by an eigenvector (Manly, 2005). PCA was applied iteratively based on conceptual models of important variables developed from initial nonparametric statistical analysis. Although both correlation and covariance matrices are calculated, PCA results based on correlation matrices are presented in this study. PCA was conducted using GAMA data that excluded samples with missing data for one or more variables; the data analyzed included 1,473 samples for benzene and sum of hydrocarbons and 1,461 samples for MTBE. PCA was conducted using both ranked and log-transformed data; results for these two datasets were similar and only results for log-transformed data are reported in this study. PCA was performed using the Multivariate Statistical Package (MVSP) v. 3.13p by Kovach Computing Services (Kovach, 2007).

RESULTS

Both the GAMA and CDPH data primarily represent depth zones of aquifers used for public supply across California, whereas the NWIS data generally represent shallower groundwater in more urban settings. The median well depth was 120 m for the GAMA data, 140 m for CDPH data, and 92 m for NWIS data (Figure S1). Public-supply wells are primarily perforated at depths sufficient to protect the wells from
surface contamination and are located in or near the communities that they serve. The GAMA data are primarily collected from randomly selected wells within cells spatially distributed across entire groundwater basins (Belitz et al., 2010) and are not always located in or near communities, as CDPH wells generally are. Studies in which VOC data were collected and entered into the NWIS database by USGS have primarily been conducted in urban areas using samples from a variety of monitoring, domestic, and supply wells to meet the objectives of local studies. These differences in the spatial distribution of wells result in significant differences in well depth and urban land-use percentage (within 500 m of well) between the datasets. Well depths were significantly greater for CDPH data than for GAMA data (Wilcoxon test statistic $Z = 36.3$, $p < 0.0001$) and well depths were significantly greater for GAMA data than NWIS data (Wilcoxon $Z = 6.3$, $p < 0.0001$). Similarly, urban land-use percentage was significantly greater for CDPH data than for GAMA data (Wilcoxon test statistic $Z = 16.7$, $p < 0.0001$) and urban land use was significantly greater for NWIS than CDPH data (Wilcoxon $Z = 12.8$, $p < 0.0001$) (Figure S2).

**Occurrence of Oxygenates and Hydrocarbons**

Based on the GAMA and CDPH data, detection frequencies and concentrations of gasoline oxygenates and hydrocarbons were generally low in public-supply aquifers of California. Spatial weighting of the data could result in slight changes in the detection frequencies reported below, but raw frequency estimates rarely fall outside the 90% confidence intervals of spatially weighted estimates (Belitz et al., 2010).

MTBE was detected in about 5.8% of the GAMA data (Table 1) and was the most frequently detected oxygenate. Four other oxygenates were detected in the GAMA data at frequencies $\leq 0.5\%$ (Table S1). One or more oxygenates were detected in 6.2% of GAMA samples. The median detected concentration for MTBE was 0.10 $\mu$g/l (Table 1). Oxygenates were detected above a regulatory threshold in one GAMA sample, a frequency of 0.05%; this well had MTBE above the California Maximum Contaminant Level (MCL) of 13 $\mu$g/l. MTBE detections are distributed across several agricultural and natural areas of California as well as densely urbanized areas of Southern California.
MTBE rarely co-occurred with other oxygenates; of the GAMA samples in which MTBE was detected, only 2.6% (3 of 114) had detections of other oxygenates.

Benzene was detected in about 1.7% of the GAMA data (Table 1) and was the most frequently detected hydrocarbon. Fifteen other hydrocarbons were detected in the GAMA data at frequencies ≤ 1.0% (Table S1). One or more hydrocarbons were detected in about 2.7% of GAMA samples. The median detected concentration was 0.024 l/g for benzene and 0.09 l/g for sum of hydrocarbons (Table 1). Hydrocarbons were detected above a regulatory threshold in three GAMA samples, a frequency of detection of 0.15%; these wells had benzene concentrations above the California MCL of 1.0 l/g and were located in the southwestern portion of the Central Valley (Figure 1b, Table S1). Benzene detections were widely distributed across California, but were especially prevalent in parts of the Central Valley and Southern California (Table S3).

CDPH MDLs were 2-100 (median 20) times higher than the GAMA long-term method detection levels (LT-MDLs); consequently, detection frequencies for the CDPH data were lower than for the GAMA data. However, when GAMA data were censored to the most common MDLs of the CDPH data, detection frequencies of hydrocarbons for the GAMA data were generally similar to those in the CDPH data (Tables 1 and S1). Detected concentrations in the CDPH data were higher than in the GAMA data, reflecting higher MDLs and sample numbers about 10 times larger for CDPH, but the frequency of detections above regulatory thresholds were similar for both datasets. In the CDPH data, four hydrocarbons or gasoline oxygenates were detected above regulatory thresholds (detection frequency above threshold): benzene (0.09%), toluene (0.01%), MTBE (0.14%), and tert-butyl alcohol (0.05%) (Table S1). CDPH wells with MTBE concentrations above the MCL were widely distributed across California (Figure S3a). CDPH wells with benzene concentrations above the MCL were primarily located in inland southern California, the southern Central Valley, and Central California coastal areas (Figure S3b), a similar distribution to GAMA data.

Hydrocarbons and oxygenates rarely co-occur (Figure 2). In the CDPH data, hydrocarbons and oxygenates were not detected together (0% frequency of co-occurrence in 10,792 samples). At or above the CDPH MDLs of 0.5 μg/l, hydrocarbons and gasoline oxygenates evidently do not co-occur. At LT-MDLs for the USGS analyses, which are one to two orders of magnitude lower than CDPH MDLs, hydrocarbons and oxygenates sometimes co-occur. For GAMA data, there was co-occurrence in 9 of 166 (5.4%) wells with detection of either class of compounds; for NWIS data, there was co-occurrence in 16 of 141 (11.3%) wells with detection of either class of compounds. The frequency of co-occurrence may increase at lower concentrations as a result of mixing of water of different ages and source areas in supply wells, producing relatively low concentrations. Co-occurrence also increases at shallower aquifer depths, as the NWIS data represent shallower groundwater than the GAMA and CDPH data. The rare co-occurrence of hydrocarbons and oxygenates implies that these constituents can be treated as being independent of each other for the purposes of statistical analysis.

Relation to Explanatory Variables

In GAMA and CDPH data, MTBE and benzene were related to different variables or had opposing relations to variables (Table 2), indicating fundamental differences in the sources and processes controlling occurrence of these compounds at aquifer depths used for public supply. Consequently, relations of MTBE and benzene to explanatory factors are discussed sequentially below. Results of different nonparametric tests, correlations, and tests for differences in values of explanatory variables between wells with and without detections, generally indicated the same relations of benzene or MTBE prevalence to explanatory variables (Tables S4 and S5). Although statistical correlation between variables does not indicate causality, analysis of correlations with many variables provides insight concerning controlling variables in a regional context.

**MTBE**

Higher MTBE concentrations were correlated with increasing density and proximity of sources, younger groundwater age (higher values of 3H and 14C), increasing density of public-supply wells, higher soil
permeability, more negative water balance (recharge-pumping), and shallower perforations in receptor wells. Thus, MTBE is related to source, transport, and receptor variables, although relations with source and transport variables are strongest. These relations are consistent with expectations that MTBE is related to anthropogenic sources. Relations were most evident for GAMA and NWIS data; fewer relations were evident from analysis of CDPH data.

For the GAMA data, MTBE concentrations were significantly correlated with many source variables, including increasing concentrations with increasing urban, high-intensity residential, and commercial land use, density of LUPTs, and population density, and decreasing distance to the nearest LUPT (Table 2). Nearly all source terms are correlated with each other, including positive correlations of LUPT density, population density, and percentages of urban, high-intensity residential, and commercial land use (Table S6); distance to the nearest LUFT was negatively correlated with the source density variables. MTBE was also significantly related to several transport variables, including positive correlations with 3H and 14C (decreasing age), density of CDPH wells, and soil permeability, and a negative correlation with recharge minus groundwater pumping (Table 2). Among receptor variables, MTBE concentrations were negatively correlated with depth to the top of perforations (Table 2). MTBE concentrations were also negatively correlated with pH, which may serve as a surrogate for depth; pH usually increases from recharge at the water table to greater depths in a groundwater flow system with increasing residence time (Koh et al., 2006; Jurgens et al., 2008). In the GAMA data, pH is negatively correlated with 3H and 14C, and positively correlated with well depth (Table S6).

For the CDPH data, higher MTBE concentrations were significantly correlated with increasing source proximity (but not density as for GAMA) and indicators of younger groundwater age (decreasing pH, increasing NO3\(^-\)). There were fewer relations evident from analysis of CDPH than GAMA data. In both the CDPH and GAMA data, there was a negative correlation with pH and with distance from the well to the nearest LUFT (Table 2). As with the GAMA data, increasing pH is a surrogate for increasing groundwater age and depth in the CDPH data; pH is available at many more CDPH wells than depth or age. Two other variables, NO3\(^-\) and Mn\(^{+2}\), were positively correlated with MTBE in the CDPH data but not in the GAMA data. The correlation of increasing MTBE with increasing NO3\(^-\) in the CDPH data may reflect that relatively younger, shallower groundwater with elevated NO3\(^-\) concentrations from surficial sources is also vulnerable to MTBE. The positive correlation of MTBE and Mn\(^{+2}\) in the CDPH data is consistent with the fact that MTBE is more readily biodegraded under oxic than anoxic conditions (Landmeyer et al., 2001; McMahon and Chapelle, 2008). It is not possible to evaluate the relations of MTBE to receptor variables given limited CDPH well construction data. Other source and transport variables with significant relations for GAMA data were not significant for CDPH data (Table 2). The relative scarcity of the relations for the CDPH data compared to the GAMA data probably reflects that the CDPH data have the following: (1) higher MDLs, (2) greater spatial clustering, and (3) more limited ancillary variable information.

For NWIS data, relations of MTBE to explanatory variables followed expected patterns, with concentrations increasing with increasing source proximity and density, decreasing depth, increasing well density, more negative water balance, and more reducing groundwater conditions (Table 2). For NWIS data, MTBE was correlated with the same source density and proximity variables as for the GAMA data. MTBE was negatively correlated with well depth for the NWIS data, similar to the negative correlation with depth to the top of the perforations for the GAMA data (Table 2). MTBE and pH were negatively correlated for both the NWIS and GAMA data, reflecting that pH is positively correlated with depth (Tables 2 and S6). MTBE was positively correlated with density of CDPH wells and negatively correlated with recharge minus groundwater pumping. These relations of MTBE with indicators of aquifer stress were significant for both the GAMA and NWIS data. The correlation of increasing MTBE with these variables is reasonable as greater pumping and aquifer development would be expected to increase groundwater velocities and MTBE movement to wells. However, density of CDPH wells (positive) and recharge minus groundwater pumping (negative) also were correlated with LUFT density and other source density variables (Table S6). Therefore, it is possible that the relations of MTBE concentrations to well density and negative water balance may result from cross-correlations between source and aquifer stress variables. MTBE was negatively correlated with O2, and positively correlated with Mn\(^{+2}\), indicating higher MTBE concentrations under anoxic conditions. McMahon and Chapelle (2008) also noted higher detection frequencies of MTBE under anoxic than oxic conditions. These patterns are consistent with the observation that MTBE is more readily biodegraded under oxic than anoxic conditions (Landmeyer et al., 2001). It is possible that the association of MTBE and anoxic conditions could be influenced by the source of MTBE, gasoline spills, which often result in anoxic water near the source as a result of abundant organic carbon from gasoline as an electron donor, and transport of both MTBE and anoxic water to downgradient wells. However, plumes near gasoline spills are
typically localized near the spill site (Rice et al., 1995) and are unlikely to commonly affect ambient groundwater redox conditions in downgradient production wells represented by the GAMA, CDPH, and most NWIS wells.

**Benzene and Other Hydrocarbons**

The explanatory variables for benzene generally differed from those for MTBE, which include variables related to anthropogenic sources. Benzene was correlated with fewer explanatory variables (Table 2) and exhibited more complex relations with controlling variables than MTBE. Concentrations of benzene and sum of hydrocarbons were correlated with each other (ρ = 0.78, \( p < 0.0001 \)) and were correlated with the same explanatory variables in most cases (Table 2). Detections of benzene and other hydrocarbons in California groundwater appear to be related to both geogenic sources and anthropogenic surficial fuel sources.

The presence of benzene and other hydrocarbons in old (\( ^3H < 1 \text{ pCi/l} \)), deep (>180 m), and brackish (specific conductance >1,600 \( \mu \text{S/cm} \)) groundwater in aquifers used for public supply in California was attributed to geogenic sources (Landon and Belitz, 2012). Evidence that many of the detections of benzene and other hydrocarbons in groundwater are related to geogenic rather than anthropogenic sources includes: higher concentrations and detection frequencies of benzene and sum of hydrocarbons with increasing well depth, groundwater age, and proximity to oil and gas fields; and geochemical evidence, including salinity and chloride/iodide ratios, that old groundwater samples with detections of benzene and other hydrocarbons have interacted with oilfield brines. Detection frequencies of benzene were highest (20%) in samples with brackish, old, and reducing groundwater in proximity (<5 km) to oil or gas fields, and in nonbrackish, old, deep, and reducing groundwater <5 km from oil or gas fields (15.4%); benzene detected in these settings is likely to be geogenic and accounts for about 45% of detections of benzene in the same GAMA data analyzed in this study (Landon and Belitz, 2012). Of the remaining benzene detections in the GAMA data, those in recent-age groundwater (\( ^3H \geq 1 \text{ pCi/l} \)) at shallow to intermediate depths (<180 m) account for about 27% of detections; anthropogenic sources may explain many of these detections (Landon and Belitz, 2012). The remaining detections (28%) occur in groundwater with mixed age and depth characteristics and may result from geogenic, anthropogenic, or a mixture of sources. The results below emphasize analysis of relations of benzene to explanatory variables in recent-age groundwater, which includes samples representing a mixture of groundwater ages.

**GAMA Data.** Benzene concentrations and detection frequencies were strongly correlated with lower concentrations of \( O_2 \) and \( NO_3^- \) and higher concentrations of \( Mn^{2+} \) and \( Fe^{2+} \) (Tables 2 and S7). Samples classified as reducing (including redox categories of suboxic, mixed, and anoxic, Table S2) had a significantly higher (\( \chi^2 = 19.1, p < 0.0001 \)) benzene detection frequency (4.1%) than samples classified as oxic (0.9%) (Figure 3). Benzene and sum-of-hydrocarbon concentrations and detection frequencies were higher in reducing than oxic groundwater in both old (\( ^3H < 1 \text{ pCi/l} \)) and recent-age (\( ^3H \geq 1 \text{ pCi/l} \)) groundwater (Tables 2, S4, and S7). These results indicate that redox conditions influence hydrocarbon persistence across a range of groundwater residence times. The relation to redox conditions is expected because hydrocarbons readily biodegrade under oxic or aerobic conditions (Howard et al., 1991; Suarez and Rifai, 1999); biodegradation rates under reducing or anaerobic conditions are substantially lower than those under oxic conditions (Kauffman and Chapelle, 2010).

Benzene detections exhibited a bimodal relation with respect to well depth, with significantly higher detection frequencies for wells <30 m (3.13%) and >180 m (3.92%) than for wells with intermediate depths (30-180 m) (1.1%) (\( \chi^2 = 13.7, p = 0.0011 \)) (Landon and Belitz, 2012). These bimodal relations are consistent with two sources of hydrocarbons, deep and shallow, to groundwater.

In recent-age groundwater samples, benzene and hydrocarbon concentrations and (or) detection frequencies are significantly correlated with commercial land use. Among GAMA samples of recent-age groundwater, benzene concentrations were positively correlated with commercial land-use percentage (Table 2); in addition, the detection frequency for benzene (3.2%) in wells with commercial land use >10% was higher (\( \chi^2 = 9.3, p = 0.0023 \)) than the detection frequency (0.7%) in wells with commercial land use <10%.
Among GAMA recent-age samples that were also reducing, the benzene detection frequency for wells with commercial land use >10% was 7.1%, higher ($\chi^2 = 7.8, p = 0.0053$) than for wells with commercial land use <10% (1.1%) (Figure 4b). Similarly, detection frequencies of sum of hydrocarbons were higher for wells with commercial land use >10% and reducing conditions than other recent-age groundwater samples (Table S7). Concentrations of sum of hydrocarbons in GAMA recent-age samples were also positively correlated with another land-use surrogate, high-intensity residential (Table S4), which was correlated with other indicators of urban land use, including commercial land use (Table S6).

The results of PCA were consistent with the non-parametric statistical analysis of correlations and detection frequencies described above and indicated that benzene detections occurred in two different groups of wells with contrasting characteristics, (1) wells that sample old, deep, and (or) brackish groundwater and (2) wells that sample recent, shallow to intermediate depth, and nonbrackish groundwater (Figure 5). For benzene, the first two PCA axes accounted for 46% of the variance in the data. The first principal axis separated samples by location and depth variables (well depth, distance to oil and gas fields, and commercial land-use percentage). The second principal component is mostly influenced by groundwater age and water quality variables (tritium, dissolved oxygen, and specific conductance).

![Figure 4](image1.png)  
**FIGURE 4.** Detection Frequency of Benzene in Groundwater Ambient Monitoring and Assessment Samples Categorized by Commercial Land-Use Percentage for (a) Recent-Age Groundwater and (b) Recent-Age and Reducing Groundwater.

![Figure 5](image2.png)  
**FIGURE 5.** Principal Components Analysis Plot of Groundwater Ambient Monitoring and Assessment Data Showing Characteristics of Water Samples from Wells with Benzene Detections, Organized into Two Major Groups: Old, Deep, and Brackish Samples (purple polygon) and Recent, Shallow to Intermediate Depth Samples (orange polygon). Variables contributing to principal component axes 1 and 2 are shown: tritium concentration (Trit), well depth, salinity (SPC), commercial land use (commpct), dissolved oxygen (DO), and distance to nearest oil and gas field (OnG_DIST_m).
**CDPH Data.** The higher MDLs of the CDPH data and generally low frequency of occurrence of hydrocarbons limit the use of these data to discern relations to explanatory variables. In the CDPH data, there were fewer statistically significant relations between benzene concentrations and explanatory variables than for the GAMA or NWIS data, and some important variables such as age-tracer concentrations and perforation depth were absent or infrequent in the CDPH data. However, Landon and Belitz (2012) noted that the positive correlation of benzene to pH, a surrogate for depth, and higher detection frequency of benzene in wells <5 km from oil and gas fields than in wells ≥5 km away was consistent with evidence from the GAMA data that many detections in public-supply wells are related to geogenic sources of petroleum. The negative correlation of benzene and sum-of-hydrocarbon concentrations with \( \text{NO}_3^- \) and positive correlation of sum of hydrocarbons with \( \text{Mn}^{2+} \) and \( \text{Fe}^{2+} \) (Tables 2 and S4) are consistent with relations indicating persistence of hydrocarbons in reducing groundwater noted in the CAMA data.

**NWIS Data.** The NWIS data generally exhibited different relations between hydrocarbons and explanatory variables than those indicated by the GAMA and CDPH data, likely as a consequence of representing shallower and more urban settings. A commonality with the GAMA and CDPH data is that analysis of the NWIS data indicated that benzene concentrations were greater in more reducing groundwater, with a negative correlation with \( \text{NO}_3^- \) and a positive correlation with \( \text{Mn}^{2+} \) (Table 2).

In contrast to the GAMA data, benzene and sum-of-hydrocarbon concentrations for the NWIS data were not significantly correlated with depth, groundwater age (\( \text{3H} \) and \( \text{14C} \)), or proximity to oil and gas fields (Table 2). Although the NWIS data had a bimodal relation for benzene and well depth similar to the GAMA data, the higher detection frequencies for well depth <30 m (4.0%) and >180 m (3.8%) than for wells 30-180 m deep (2.6%) were not significantly different. Thus, in contrast to results of analysis of GAMA and CDPH data, analysis of the NWIS data did not yield statistical evidence for benzene occurring in some deep groundwater as a result of geogenic sources. This difference is likely to reflect the more limited spatial distribution of the NWIS data (Figure S4b).

For NWIS data, benzene was related to more source variables than in the GAMA and CDPH data. Benzene concentrations and detection frequencies were significantly correlated with source density and proximity (Table 2). The relations to increasing density and proximity of fuel sources suggest that anthropogenic sources explain most detections of benzene in the NWIS data. Commercial land use, the single measure of source density correlated with benzene concentrations in GAMA recent-age groundwater data, also was significantly correlated with benzene and sum of hydrocarbons for NWIS data (Table 2). In the NWIS data, benzene detection frequency was significantly higher (contingency table \( \chi^2 = 8.4, p = 0.0038 \)) among wells with commercial land use >10% (5.1%) than among wells with commercial land use <10% (1.8%). The larger number of relations for the NWIS data compared to the GAMA data probably reflects that NWIS data have similar LRLs to GAMA but is more clustered in shallow and urban settings.

Analysis of the NWIS data indicated that MTBE and benzene and other hydrocarbons were related to a number of common variables, particularly source term and redox variables (Tables 2 and S4). Although relations of benzene and sum of hydrocarbons to source variables were statistically significant for the NWIS data, greater absolute values of Spearman’s \( \rho \), smaller \( p \) values, and visual plots of data indicated that MTBE concentrations had stronger relations to source terms than benzene and sum of hydrocarbons did (Table S4). MTBE and benzene in the NWIS data were generally related to different receptor and transport variables, with the exception of a positive correlation of both constituents with \( \text{Mn}^{2+} \), consistent with expected greater persistence of both compounds under more reducing conditions. In the NWIS data, higher concentrations of MTBE were negatively correlated with well depth and groundwater recharge minus pumping and positively correlated with CDPH well density (Table 2), the latter two variables serving as proxy indicators of increased aquifer stress. In contrast, benzene and sum of hydrocarbons were not significantly related to receptor and transport variables other than redox conditions.

The relations of MTBE and benzene and other hydrocarbons to common source term variables observed for the NWIS data contrast with the results of analyses of the GAMA and CDPH data, which indicated common relations to only one source variable, commercial land use. This contrast likely reflects differences in the areal and vertical distribution of wells between the different datasets (Figures 1, S3, and S4). The NWIS data are primarily restricted to Southern California basins, Bay area, Central Valley, and a few samples in the Southern California Desert. Thus, the NWIS data are more focused on urban and agricultural areas more likely to be affected by anthropogenic activity than the more widely distributed GAMA and CDPH data.

Although co-occurrence of hydrocarbons and MTBE was more common in the NWIS data than in the GAMA and CDPH data, co-occurrence was still relatively infrequent, occurring in about 1.5% of NWIS samples (Figure 2) and about 11.4% (16 of 141) of
samples that had detections of either hydrocarbons and (or) MTBE. Thus, correlations with the same source variables in the NWIS data do not indicate co-occurrence of hydrocarbons and MTBE. The wells in which co-occurrence did occur did not have significantly different characteristics from wells with detections of either hydrocarbons or MTBE without co-occurrence.

**DISCUSSION AND CONCLUSIONS**

The infrequent co-occurrence of oxygenates with benzene and other hydrocarbons in samples from aquifer depths used for public supply (GAMA and CDPH), and the divergent relations of these constituents to explanatory variables, provide insight regarding the differing variables that control their occurrence. MTBE followed a pattern expected for a constituent derived from anthropogenic surficial sources, with larger concentrations associated with: proximity and density of sources; aquifers with younger-age groundwater, increasing public-supply well density, more negative water balance (recharge-pumping), and larger soil permeability; and receptor wells with shallower perforations. Benzene and other hydrocarbons followed a pattern expected for constituents derived from both anthropogenic and geogenic sources, with concentrations positively correlated with commercial land use, but also with depth, groundwater age, and proximity to oil and gas fields. Larger concentrations and detection frequencies of benzene were also associated with reducing conditions regardless of groundwater age.

Differences in the spatial distribution of MTBE and hydrocarbons indicate that these compounds have different transport characteristics and sources. MTBE has lower biodegradation rates under oxic and anoxic conditions than hydrocarbons (Landmeyer et al., 2001), and is expected to move faster to supply wells when spilled fuel products containing both sets of constituents reach groundwater (Kauffman and Chapelle, 2010). Detection frequencies of MTBE in California — about five times greater than benzene and two times greater than all hydrocarbons combined (Table 1) — are consistent with results from across the U.S. (Zogorski et al., 2006) and reflect the differing physiochemical properties of these constituents. MTBE also has a different use history and source distribution than gasoline hydrocarbons (Moran et al., 2005). MTBE was a fuel additive in use during the early 1990s through the mid 2000s (Shih et al., 2004; Zogorski et al., 2006), a much shorter period of use than gasoline, which has been used for more than 100 years. MTBE in groundwater may also result from nonpoint sources such as partitioning from the atmosphere to recharge water (Squillace et al., 1998; Baehr et al., 1999; Belitz et al., 2004; Zogorski et al., 2006). For example, in confined aquifers of the coastal plain of Southern California, which receive little vertical recharge from the overlying landscape, the distribution of MTBE is predominantly controlled by lateral movement of groundwater along flow paths away from artificial recharge areas toward pumping centers (Shelton et al., 2001; Dawson et al., 2003); the artificial recharge primarily comprised surface water that contained MTBE that may have been derived from atmospheric or other surficial sources.

In groundwater shallower than that typically used for public supply, represented by the NWIS data, common relations to source variables and more frequent co-occurrence (about 11%) imply that the conditions permitting co-occurrence of MTBE and hydrocarbons become more prevalent closer to sources of these compounds near the land surface. In the NWIS data, MTBE and benzene were both related to source strength and proximity variables and were both more prevalent under reducing than oxic conditions.

There are multiple lines of evidence indicating that detections of hydrocarbons in some groundwater are related to geogenic (geologic reservoirs of petroleum) rather than anthropogenic sources (Landon and Belitz, 2012). Concentrations and detection frequencies of benzene and sum of hydrocarbons are positively correlated with well depth, groundwater age, and other depth/age proxies such as pH; also, concentrations and detection frequencies in old groundwater are greater in proximity to oil or gas fields (Landon and Belitz, 2012). Geochemical evidence, including salinity and CI/I ratios, indicate that old groundwater with detections of benzene and other hydrocarbons have interacted with oilfield brines (Landon and Belitz, 2012). In addition, PCA indicates that wells with benzene and other hydrocarbon detections occurred in two different groups of wells with contrasting characteristics: one group of wells that sample old, deep, and (or) brackish groundwater and another group of wells that sample recent, shallow to intermediate, and nonbrackish groundwater. These results support the nonparametric statistical analysis indicating both geogenic and anthropogenic sources of hydrocarbons to groundwater used for public supply in California.

The higher detection frequencies of benzene and other hydrocarbons in reducing groundwater, significant negative correlations with $O_2$ and $NO_3^-$, and significant positive correlations with $Mn^{2+}$ and $Fe^{2+}$ in all evaluated data (GAMA, CDPH, NWIS) are consistent with laboratory and field studies indicating that biodegradation rates of hydrocarbons are typically lower.
under anoxic than oxic conditions (Howard et al., 1991; Kazumi et al., 1997; Weiner and Lovley, 1998; Suarez and Rifai, 1999; USEPA, 1999; Kauffman and Chapelle, 2010). Within a plume of dissolved hydrocarbons from spilled petroleum, more reducing conditions develop in the interior of the plume as a result of organic carbon serving as electron donors for redox reactions (Baedecker et al., 1993; Chapelle et al., 2003). The resulting redox zonation can vary over small spatial scales (McNab, 1999; Bekins et al., 2001). Previous studies noting that plumes from fuel spills are generally of limited extent (Rice et al., 1995) and infrequently reach public-supply wells in California (Hadley and Armstrong, 1991) have attributed these results to the effects of microbially facilitated biodegradation. In this study, the measured redox parameters are representative of the ambient conditions of the groundwater system, often at the depths used for public supply, rather than the zone of altered redox that often occurs around spill sites.

In recent-age groundwater ($^{3}H \geq 1 \text{ pCi/l}$), benzene and hydrocarbon concentrations and (or) detection frequencies are positively correlated with commercial land use. Wells having a combination of >10% commercial land use within 500 m of the well and reducing groundwater conditions had the highest detection frequency of benzene (7.1%) and hydrocarbons (11.9%) among any combination of variables in GAMA recent-age samples. In the NWIS data, representing shallower and more urban groundwater than the GAMA data, benzene and hydrocarbon concentrations were more strongly correlated with commercial land use and were related to five additional source strength variables, including LUFT density, distance to the nearest LUFT, population density, percent urban land use, and percent high-intensity residential land use. These variables are proxy measures for fuel source strength and proximity. In shallow groundwater (NWIS data), relations of benzene and other hydrocarbons to source terms were as strong as relations to redox indicators; in deeper groundwater (GAMA and CDPH), hydrocarbons were more strongly correlated with redox indicators than with source terms.

Differences and similarities of results of analyses of the three datasets provided greater insight regarding explanatory variables than would have been possible with analysis of any single dataset. Analysis of GAMA data, with lower reporting limits and more extensive ancillary, age, and chemistry data than available for the CDPH data, provided greater insight regarding variables explaining occurrence of hydrocarbons and MTBE in public-supply wells (Table 2). Relations to explanatory variables identified from analysis of the much larger CDPH data were consistent with analysis of the GAMA data, but fewer relations to source, transport, and receptor variables were evident (Table 2). Comparison of analyses of GAMA and NWIS data indicated that effects of anthropogenic sources of hydrocarbons are more evident in shallow groundwater than in deeper groundwater, and that deeper groundwater is affected more by geogenic sources of hydrocarbons than by anthropogenic sources. For MTBE, the similarity of relations identified using the GAMA and NWIS data reflects that MTBE followed patterns expected for a mobile constituent with surficial anthropogenic sources; in both datasets, larger concentrations were associated with greater source proximity and density, shallower depths, younger groundwater age, and increasing aquifer pumping. For benzene, with a more complex distribution of geogenic and anthropogenic sources, differences in explanatory relations identified between the GAMA and NWIS data reflect that the GAMA data are from wells that are deeper and less commonly in urban areas; in the GAMA data, relations to both geogenic and anthropogenic sources were detected, whereas the shallower, more urban NWIS data were primarily suited for detecting relations with anthropogenic sources.

Occurrence of benzene in public-supply wells in California is infrequent (1.7%) and these occurrences are related more to natural variables — ambient reducing groundwater conditions and proximity to geogenic sources — rather than anthropogenic variables. It is possible that anthropogenic source control/remediation and groundwater protection activities contribute to these relations. The limited impact of fuel spills on aquifers used for public-water supply in California is notable given the widespread distribution of petroleum storage and distribution systems across the landscape; the number of leaking gasoline tanks in California has been estimated to exceed 11,000 or 6.5% of underground tanks in the state (Hadley and Armstrong, 1991). Hadley and Armstrong (1991) concluded that the most likely explanation of infrequent occurrence of benzene in public-supply wells was biodegradation of spilled petroleum near its source. In a simulation study of VOC transport in selected principal aquifers in the U.S., Kauffman and Chapelle (2010) determined that simulated aquifers in the western U.S. had low vulnerability to VOCs, particularly petroleum hydrocarbons such as benzene and toluene because of low-recharge rates, long travel times, and the predominantly oxic conditions, which facilitated biodegradation of the hydrocarbons before reaching public-supply wells. The results of this study are consistent with these interpretations, but clarify the geogenic and anthropogenic variables that explain the occurrence of hydrocarbons in wells in those cases where they occur.
SUPPORTING INFORMATION

Additional Supporting Information may be found in the online version of this article, including: supplemental methods description, description of occurrence of selected constituents, relations to secondary explanatory variables, and supporting figures and tables.

Figure S1. Well-depth distribution for CDPH, GAMA, and NWIS data.
Figure S2. Urban land use distribution around CDPH, GAMA, and NWIS wells.
Figure S3. (a) Map showing results of analyses for MTBE in CDPH data overlain on land use. (b) Map showing results of analyses for benzene in CDPH data overlain on land use.
Figure S4. (a) Map showing results of analyses for MTBE in NWIS data overlain on land use. (b) Map showing results of analyses for benzene in NWIS data overlain on land use.
Figure S5. (a) Map showing estimated areal average groundwater pumping for 2,000 (cm) in 56 planning areas (California Department of Water Resources, 2005) and CDPH wells with detections of any hydrocarbon (blue) or no detections (black). (b) Map showing estimated areal average groundwater recharge for 2,000 (cm) in 56 planning areas (California Department of Water Resources, 2005) and CDPH wells with detections of any hydrocarbon (blue) or no detections (black). (c) Map showing estimated areal average groundwater recharge minus pumping for 2,000 (cm) in 56 planning areas (California Department of Water Resources, 2005) and CDPH wells with detections of any hydrocarbon (blue) or no detections (black).

Table S1. Hydrocarbons and gasoline oxygenates included in study, comparative thresholds, reporting information, and detection frequencies relative to selected thresholds.
Table S2. Criteria and threshold concentrations for identifying redox processes in groundwater (Jurgens et al., 2009; McMahon and Chapelle, 2008) and distribution of wells by redox category and redox process.
Table S3. Detections of MTBE and benzene by lumped hydrogeologic province in GAMA and CDPH data.
Table S4. Spearman’s ρ and significance levels for correlation tests between continuous explanatory factors and benzene, sum of hydrocarbons and MTBE.
Table S5. Results of Wilcoxon nonparametric tests for differences in explanatory variables between wells with and without detections of MTBE and benzene, GAMA data.
Table S6. Spearman’s correlation coefficients (ρ) between explanatory variables for GAMA data.
Table S7. Detection frequencies of benzene and summed hydrocarbons in GAMA data by explanatory variable categories.

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