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THEMATIC ISSUE

Effect of hydrogeological and anthropogenic factors on the spatial and temporal distribution of CVOCs in the karst system of northern Puerto Rico

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Abstract

This study evaluates factors affecting the spatial and temporal distribution of chlorinated volatile organic contaminants (CVOCs) in the highly productive aquifers of the karst region in northern Puerto Rico (KR-NPR). Historical records from 1982 to 2016 are analyzed using spatial and statistical methods to evaluate hydrogeological and anthropogenic factors affecting the presence and concentrations of multiple CVOCs in the KR-NPR. Results show extensive spatial and temporal distributions of CVOCs, as single entities and as mixtures. It is found that at least one type of CVOC is present above detection limits in 64% of the samples and 77% of the sampling sites during the study period. CVOC distribution in the KR-NPR is contaminant-dependent, with some species being strongly influenced by the source of contamination and hydrogeological characteristics of the system. Persistent presence of CVOCs in the KR-NPR system, even after contaminated sites have been subjected to active remediation, reflect the high capacity of the system to store and slowly release contaminants over long periods of time. This study shows that karst aquifers are highly vulnerable to contamination and can serve as a long-term route of contaminants to potential points of exposure.

Keywords Groundwater contamination · CVOCs · Karst aquifers · Statistical methods · Hydrogeological properties · Anthropogenic factors

Introduction

Karst aquifers serve as an important source of freshwater for human consumption, industrial, and agricultural use. They promote industrial, urban, and agricultural development, and contribute to ecological integrity of the region (Padilla et al. 2011). Karst groundwater systems provide roughly 20–25% of the global population water needs (Ford and Williams 2007; Butscher and Huggenberger 2009). Second only to unconsolidated and semi-consolidated sand and gravel aquifers, which supply nearly 80% of groundwater, karst groundwater systems are among the most important sources of groundwater in United States. They provide about 8% of all groundwater needs in the country, of which 17% is used for public supply (Maupin and Barber 2005). Other sources of groundwater come from igneous and metamorphic rocks (6%), sandstone rock (2%), sandstone, and carbonate rock (2%) (Maupin and Barber 2005).

Karst systems have unique characteristics that make them very different from other types of aquifers (Bakalowicz

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2005). They are characterized by well-developed conduit porosity and high permeability zones formed by dissolution of soluble rocks, primarily limestone (Anaya et al. 2014). Conduits and high permeability zones are well connected to sinkholes, sinking streams, and other surface features that provide for direct recharge into karst groundwater systems (Padilla and Vesper 2018). These characteristics also allow for unattenuated input and rapid transport of contaminants in the subsurface. As a result, contaminants from both point and distributed sources can be rapidly conveyed over long distances. Compared to unconsolidated porous media, in which water velocities are typically less than a meter per day, in karst aquifers, groundwater and contaminants can travel more than a kilometer per day (Green et al. 2006). Contaminants that enter the karst subsurface can also diffuse into and sorb onto rock matrix of lower relative permeability and sediments trapped in karst conduits and voids, where they can be stored and slowly released over long periods of time (Padilla and Vesper 2018; Torres et al. 2018). Rapid unattenuated transport over long distances and high storage capacity of contaminants in karst groundwater systems enables potential exposure to human and wildlife (Padilla et al. 2011, 2015) over long periods of time. Of particular concern is the contamination of karst groundwater systems with chlorinated volatile organic compounds (CVOCs). These contaminants are commonly present in the environment and have the potential to impact health (Padilla et al. 2011).

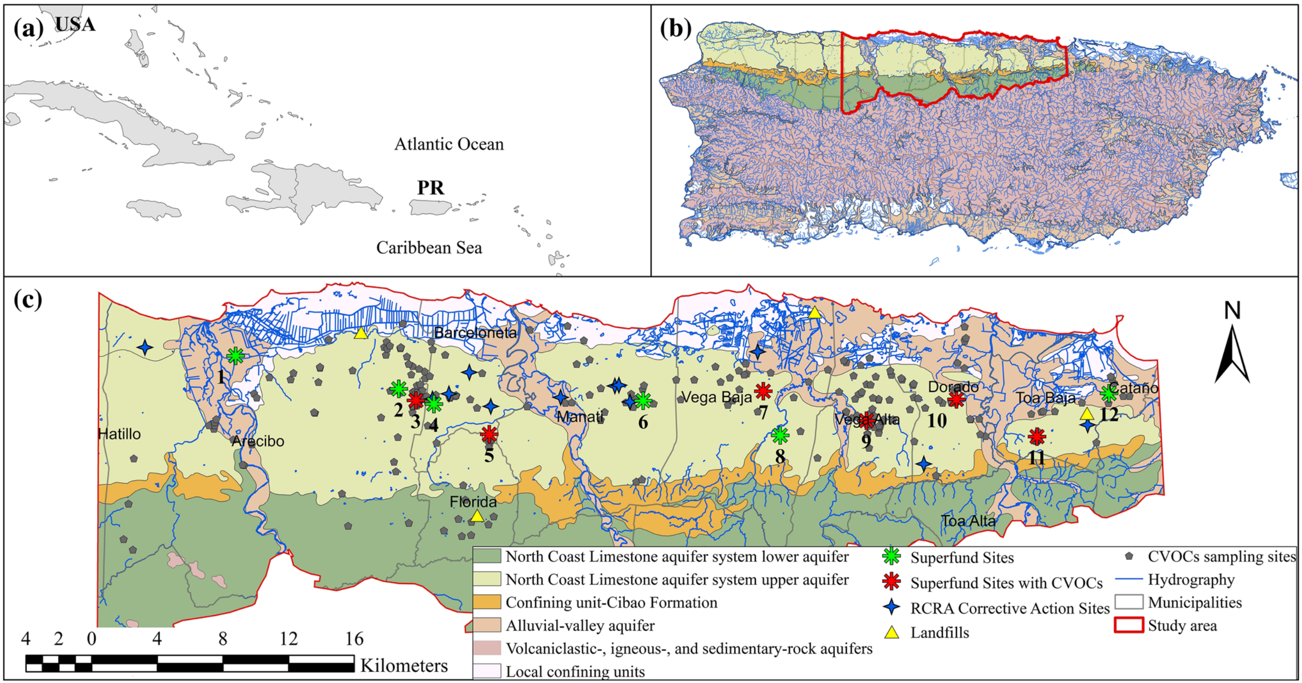
Common presence of CVOCs in the environment results from their unique properties. CVOCs have a high dissolving capacity for non-polar substances and are used in large quantities of industrial processes (Kistemann et al. 2008). They are commonly used as industrial solvents, metal surface degreaser, and paint or spot removers, and in a variety of household and consumer products, textile cleansing, and food extraction (Moran et al. 2007; Padilla et al. 2011). CVOCs are also highly volatile, slightly soluble in water (Table S1), and resistant to degradation (Huang et al. 2014). As a result, they can be transported in different subsurface fluid media over long distances and periods of time (Huang et al. 2014). These compounds are also subjected to sorption onto soil, sediments, and organic matter (Lawrence 2006). Degradation of CVOCs can occur under different environmental pathways and conditions (Rivera 2018). CVOCs generally degrade from higher order of chlorine content to lower or no chlorine content (Schiffmacher et al. 2016; Figure S1).

In urban areas, protecting and preserving groundwater supplies from CVOCs can be difficult because of the number of potential sources from homes, businesses, and industries (Squillace et al. 2004). CVOCs have been widely detected in environmental media for many years (Huang et al. 2014). Their presence has been reported in fractured, karstic, and carbonate-rock groundwater settings in West Virginia, USA (Plummer et al. 2013) and Puerto Rico (Padilla et al. 2011; 2015) and from other groundwater aquifers in the United States (e.g., Squillace et al. 2004; Moran et al. 2007; Carter et al. 2008; Howard and Gerber 2018). Groundwater contamination with CVOCs has also been reported in other countries, e.g., in Taiwan (Fan et al. 2009), Italy (Di Lorenzo et al. 2015), Korea (Lee et al. 2015), and east China (Bi et al. 2012). Due to their presence in many products and the environment, exposure to CVOCs can occur through different routes, including drinking, swimming, showering, bathing, food, or laundering (Huang et al. 2014). Exposure to CVOCs has been related to cardiac, neurological, hepatic, renal, dermal, immunological, and reproductive problems, increased birth defects, perinatal mortality, cancer, decreased birth weights (ATSDR 2011; Huang et al. 2014), and risk for preterm birth and spontaneous abortion (Lipscomb et al. 1991; Khattak et al. 1999; Ha et al. 2002).

While contamination of karst aquifer renders significant ecologic, water resources, and human health impacts, the understanding of how contaminants is transported through these systems is limited (Padilla and Vesper 2018). The distribution of contaminants in karst groundwater systems, which are very heterogeneous and highly variable in flow rates, may be influenced by changes in hydrogeological conditions and human activities. This study assesses the spatial and temporal distributions of CVOCs in the karst aquifer system of northern Puerto Rico, and evaluates the principal hydrogeological and anthropogenic factors affecting this distribution. It will improve the understanding of the factors affecting the spatial and temporal variability of CVOCs in karst aquifers, and advance the ability of scientists and engineers to predict, minimized the potential for exposure of contaminants to humans and ecosystems, and mitigate the occurrence of CVOCs in these aquifers.

Site description

The island of Puerto Rico is located in the Caribbean (Fig. 1a). It is characterized by a relatively warm and humid climate, having two major seasonal periods based on the historical monthly rainfall: a wet season (May through November) and a dry season (December through April) (Torres et al. 2018). The area of study is located in the karst region of northern Puerto Rico (KR-NPR; Fig. 1b, c), which comprises 19% and contains the most extensive and productive aquifer system of the island (Padilla et al. 2011; Maihemuti et al. 2015). The aquifer system of the KR-NPR is comprised by four major hydrogeological units: an upper aquifer, which is mostly unconfined and linked to the surface throughout most of its outcrop area (Padilla et al. 2011; Torres et al. 2018); a middle confining unit; a lower aquifer; and a basal confining unit. The lower aquifer is confined toward the coastal zone and outcrops to the south of the upper aquifer,



No.	*Site*	*Enlisted Year*	*Contaminants*
1	The Battery Recycling Company	Proposed 2016	Lead, arsenic, cadmium, and other heavy metals
2	Pesticide Warehouse I	2006	Pesticides (DDE, Dieldrin, Aldrin, Endrin, Chlordane, Diuron, Heptachlor)
3	Upjohn	1984	**CCl_4, acetonitrile, metals**
4	RCA del Caribe	1983	Ferric chloride, metals (Cr, Be, Se, Fe)
5	Barceloneta Landfill	1983	**VOCs (DCA, DCE, TCE, TCM), metals (Hg, Ni, Cr) DEHP**
6	Pesticide Warehouse III	2003	Pesticides (Malathion, Diuron, Toxophene, Heptachlor, Aldrin, Dieldrin, Encrin, Chlordane), Phthalate (DEHP)
7	Vega Baja Solid Waste Disposal	1999	**Heavy metals (As, Pb, Cr, Mn), TCM, phthalates**
8	V&M Albaladejo	1996	Heavy Metals (Sb, Cd, Cu, Ag, Pb)
9	Vega Alta Public Supply Wells	1984	**VOCs (TCE, TCA, PCE, DCE, DCA)**
10	Dorado Groundwater Contamination	2016	**TCE, PCE**
11	Scorpio Recycling	1999	**Metals (Pb, V, Ba, Cr), TCE, DEHP**
12	Naval Security Group	1988	Paints, solvents, waste oil, battery acid, pesticides, PCBs, metals (arsenic, lead)

Fig. 1 **a** Location of Puerto Rico, **b** major streams and aquifers in Puerto Rico, **c** aquifer hydrogeology of the KA-NPR study area; location of potential sources of contamination in the study area; location of CVOC sampling sites. Superfund sites are identified with numbers from 1 to 12, and the name, enlisted year and contaminants are on the shown table

where it is recharged and exposed to surface contamination. Both aquifers are characterized by highly variable porosity and permeability over short distances, reflecting the variable distribution of conduit porosity (Ghasemizadeh et al. 2012). A direct connection between the upper and lower aquifers exists along the outcrop of the confining unit, allowing groundwater flow from the unconfined part of the lower aquifer into the upper aquifer (Torres et al. 2018). The outcrop areas of the aquifer are much more vulnerable to contamination due to direct interaction with the surface (Padilla et al. 2015).

The KR-NPR is characterized by a karst topography having distinctive surface and subsurface features associated with sinkholes, springs, caves, and sinking, losing, and gaining streams. Elevation is highest toward the south, where the lower aquifer outcrops, and lowest toward the coastal area, where outcrops of the upper aquifer intermingle with surface alluvial deposits (Fig. 1c).

As an eogenetic karst aquifer (Anaya et al. 2014; Torres et al. 2018), significant flow occurs in conduits and the rock matrix (Padilla et al. 2015). Groundwater enters the system through surface infiltration and direct injection of runoff into karstic conduits via sinkholes and sinking streams. Flow in the upper and lower aquifers move regionally northward toward the Atlantic Ocean (Ghasemizadeh et al. 2012) and locally to surface streams and wetlands (Renken et al. 2002). Discharge occurs at wells, springs, and through seepage at surface features. Groundwater is mostly extracted from the upper aquifer, because is the most accessible for drilling and pumping, although several industrial and municipal wells extract water from the lower aquifer. These aquifers are the principal groundwater source of water supply in the region (Torres-González et al. 1996; Conde-Costas and Rodríguez-Rodríguez 1997; Cherry 2001).

Sinkholes, which may serve as direct input of water and contaminants into the subsurface, are widespread in the KR-NPR (Torres et al. 2018). Sinkhole density varies spatially, with the highest density generally associated with the outcrop of the upper aquifer. Hydraulic conductivities in the study area are highly variable, ranging from less than 30 to greater than 300 m/days (Renken et al. 2002; Torres et al. 2018). Major land uses in the region (Figure S2; Torres et al. 2018) include natural land (67%), developed land (18%), waters (including surface water, such as rivers, mangroves and swamps; 9%), and agriculture (6%). Developed land incorporates 62% residential, 5% industrial, and 33% construction and other uses.

Availability of water resources from the highly productive karst aquifer system of northern Puerto Rico has spawned industrial and urban development, which promotes economic growth, and increases the potential for extensive groundwater contamination. Industries in the region have relied on the use of hazardous materials, which can enter the karst groundwater from accidental spills and deliberate disposal. This region, which is among the areas with highest groundwater extraction in Puerto Rico (Molina-Rivera and Gómez-Gómez 2008), has indeed been affected by a long history of toxic spills, chemical waste, and industrial solvent release into the subsurface (Zack et al. 1987; Hunter and Arbona 1995; Padilla et al. 2011, 2015; U.S. EPA 2011). Liquid waste was also injected into the confined aquifer system prior to the 1970s (Zack et al. 1987). The unintended consequence of the industrial and urban development has, therefore, been an extensive contamination of the groundwater resources in the northern karst aquifer.

After more than 40 years, pollution persists (Padilla et al. 2015). Significant contamination from different sources in Puerto Rico has caused the inclusion of 25 Superfund sites in the EPA National Priority List (NPL) sites and 49 sites in the Resource Conservation and Recovery Act Corrective Action Corrective Action (RCRA-CA) Program around the island (U.S. EPA 2018). Since 1983, 12 Superfund sites, which comprises 48% of all superfund sites on the island, and 13 RCRA-CA sites have been included in the KR-NPR (Fig. 1c; Table S2; Padilla and Vesper 2018). Several types of contaminants have been detected at Superfund sites in Puerto Rico, including CVOCs, pesticides, heavy metals, and phthalates (Table S2) (Padilla et al. 2015). Studies in the region have reported the presence of organic contaminants in the karst groundwater system (Guzmán-Ríos et al. 1986; Padilla et al. 2011, 2015; Yu et al. 2015; Torres et al. 2018). Of particular importance is the contamination with CVOCs because of their persistent presence in the environment and potential for exposure and health impacts (Padilla et al. 2011). CVOCs are present in 50% of Superfund sites in the KR-NPR (Fig. 1c).

Methods

Data collection

Chlorinated volatile organic contaminants data from June 1982 to March 2016 were collected from historical records, obtained from governmental agencies and published reports (Padilla et al. 2011; Irizarry 2014) and the University of Puerto Rico, Mayagüez Campus (Cotto 2015; Padilla et al. 2015; Rivera 2018). The records included concentrations of different CVOC species (Table 1) in wells and springs sites, sampling dates, detection limits (DL), and site-associated spatial coordinates. A total (*n*) of 8088 samples from 326 sampling sites (Fig. 1c) incorporating data for the CVOCs listed in Table 1 were used for the analysis. CVOCs data were compiled into a central database for the Puerto Rico Testsite for Exploring Contamination Threats (PROTECT) Center at Northeastern University for current and future studies (PROTECT 2018). Ancillary data, including hydrogeological and topographic characteristics, land use, and potential sources of contamination, were also collected, as described by Torres et al. (2018).

Data analysis

Detection of CVOC concentrations was grouped into four categories, according to their DLs (Table 1) and maximum contaminant level (MCL; Table S3): not detected (ND); detected, but below DL; above DL, but below MCL; and above DL and MCL. DLs varied due to different data sources, equipment used, CVOCs species, and analysis protocols, with minimum DL ranging from 0.00002 for CCl_4 to 0.00025 mg/L for 1,1,1,2-TeCA.

The factors that affect the variability of CVOC distribution in the karst system of northern Puerto Rico were analyzed from two perspectives: (1) hydrogeological factors (aquifer system, seasonality, elevation, hydraulic conductivity, and sinkhole density) and anthropogenic factors (land use and potential sources of contamination). Hydraulic conductivity distributions from Renken et al. (2002) and sinkhole density maps from Giusti and Bennet (1976) were used to estimate values at each sampling site based on the location of the sampling sites in those maps, as described by Torres et al. (2018). Correlation with CVOC distributions was based on categorical analysis for hydrogeology (upper aquifer, lower aquifer), season (wet, dry), hydraulic conductivities (<30, 30–300, and >300 m/days), and sinkhole density (<1, 1–10, >11%). Seasonality analysis was based on the time of sample collection in relation to historically

Table 1 Name, abbreviation, number of samples, and DL of samples collected for CVOC analysis

Contaminant name	Abbreviation	Number of sample data (*n*)	Detection limit (DL) (mg/L) (mean ± confidence interval)
Trichloroethylene	TCE	5354	0.00204 ± 0.00047
Tetrachloroethylene	PCE	5106	0.00201 ± 0.00048
Chloroform	TCM (or CF)	4602	0.00225 ± 0.00051
Carbon tetrachloride	CCl_4 (or CT)	7425	0.00166 ± 0.00040
1,1-Dichloroethane	1,1-DCA	3756	0.00262 ± 0.00056
1,1-Dichloroethylene	1,1-DCE	4716	0.00228 ± 0.00050
Cis-1,2-Dichloroethylene	CIS-1,2-DCE	4254	0.00226 ± 0.00053
1,2-Dichloroethane	1,2-DCA	4908	0.00142 ± 0.00049
1,1,1-Trichloroethane	1,1,1-TCA	5022	0.00221 ± 0.00051
1,1,2-Trichloroethane	1,1,2-TCA	4792	0.00204 ± 0.00050
Dichloromethane	DCM (or MC)	5264	0.00258 ± 0.00048
1,1,2,2-Tetrachloroethane	1,1,2,2-TeCA	3496	0.00262 ± 0.00058
Trans-1,2-Dichloroethylene	Trans-1,2-DCE	4609	0.00221 ± 0.00051
Vinyl chloride	VC	4404	0.00220 ± 0.00052
Chloroethane	CA	3541	0.00262 ± 0.00062
Chloromethane	CM	3523	0.00263 ± 0.00058
1,1,1,2-Tetrachloroethane	1,1,1,2-TeCA	3302	0.00266 ± 0.00060
Bromoform	BF	3466	0.00267 ± 0.00059
Bromodichloromethane	BDCM	3535	0.00273 ± 0.00058
Chlorodibromomethane	CDBM	3494	0.002655 ± 0.00058

wet and dry seasons. The effect of anthropogenic factors on CVOC contamination was evaluated in relation to potential contamination sources and landuse (Torres et al. 2018). The effect of land use on CVOCs contamination was evaluated by extracting the major land use within a 1.6-km radius buffer at each sampling site using ArcMap 10.4, from a 2010 land use map (RIKS 2018) with respect to four categories: water coverage (which includes surface water, such as rivers, mangroves and swamp), natural (such as forests), developed, and agriculture. The spatial distribution of CVOCs was assessed by applying the kriging method of interpolation. Average concentrations, which were calculated using all concentrations above DL for each site having at least one detection for the period of analysis (as described by Torres et al. 2018) were used to perform the spatial interpolation analysis,.

Multiple statistical methods were applied to examine CVOC detections and concentration distributions and assess principal factors affecting their distributions. Temporal and statistical analyses were performed on the seven most frequently detected CVOCs in the study area: CCl_4, TCM, DCM, PCE, TCE, 1,1-DCE, and CIS-1,2-DCE, and on total CVOC (TCVOC) average concentration. TCVOC average concentration was calculated as the average of CVOC mean concentration for each species found in a sample. The statistical analyses were conducted using Minitab (v. 17, State College, PA), and included simple statistics (mean, confidence intervals, min and max), Pearson correlation, and frequency quantile analysis to evaluate trends in the data. A One-Way Analysis-of-Variance (ANOVA) testing the null hypothesis that the means of two or more populations are equal was used to assess statistical differences between mean concentrations of the different CVOCs being analyzed in the different categories. The test of equal variance was performed previous to the ANOVA test. Chi square was used to test the statistical differences between the detection frequencies of the different CVOCs analyzed in the different categories. Interval confidence of 95% [alpha (α) of 0.05] was used to test significance of the tests. *p* values of 0.05 were used to accept or reject the null hypothesis (Minitab 2017) and assert, with a probability of 95%, that mean concentrations (ANOVA) or detection frequencies (Chi square) of CVOCs in the categories analyzed were statistically equal ($p > 0.05$) or different ($p < 0.05$).

Results and discussion

The data exhibited an uneven spatial and temporal distribution resulting from the different institutions and agencies that collected the data for different objectives. For instance, the number of samples (*n*) collected and analyzed varies for each of the CVOC used in this study (Table 1). The number of samples available for the different hydrogeological units is also disproportionally higher for the upper (`=7379) than the lower ($n = 709$) aquifer. This is attributed to the higher number of wells in the upper aquifer, which is more accessible for drilling, than the lower aquifer. Different types of CVOCs species have been found in the study area; however, the results and discussion presented in this study cover the seven most frequently detected CVOCs in groundwater in the KR-NPR: CCl_4, TCM, DCM, PCE, TCE, 1,1-DCE, and CIS-1,2-DCE.

CVOCs' detection frequencies

With 64% of groundwater samples and 77% of sampled sites showing presence of CVOCs as single entities or mixtures, our analysis demonstrates that these contaminants are commonly present in the karst groundwater system of northern Puerto Rico and that this system is highly vulnerable to contamination. The high number of sites showing presence of CVOCs denotes an extensive groundwater contamination in this system. TCE, PCE, TCM, CIS-1,2-DCE, 1,1-DCE, CCl_4, and DCM are the most detected CVOCS in groundwater samples (Table 2). TCM and DCM are the most detected CVOC per site, followed by TCE and PCE. High detection frequency of these contaminants is attributed to: high number of contamination sources (Fig. 1; Table S2), high capacity of the system to rapidly transport contaminants from the source of contamination, high capacity of the system to store and slowly release contaminant over time, and the formation of contaminant by-products. TCE is the CVOC with the highest percentage of samples above MCL, followed by CCl_4, and PCE. This is because these contaminants are the principal species associated with major contamination sources (Sites Nos. 3 and 9 in Fig. 1). The high percent detection of TCM and DCM per site reflects widespread sources of these contaminants beyond well-known sources of contamination (e.g., Superfund and RCRA-CA sites).

Analysis of the data shows 53% of samples (Fig. 2a) and 45% of sites having multiple CVOCs (Table 2). The most prevalent mixtures in groundwater samples, which include PCE + TCE + 1,1DCE + CIS-1,2DCE followed by CCl_4 + TCM + DCM (Fig. 2b), indicate coexistence of various species of contaminants. Coexistence of various groups of species is attributed to multiple inputs of contaminants and the formation of different CVOC species through the degradation of parent compounds. For instance, contaminant sources in the Vega Alta Superfund site (Fig. 1) include PCE, TCE, and DCE, among other CVOCs. Many of the CVOCs could have also formed from degradation of PCE and TCE (Figure S1). Similarly, the coexistence of CCl_4 + TCM + DCM may result from the degradation of CCl_4, but could also integrate contaminants from other nearby contamination sources.

CVOCs concentrations

Analysis shows TCE, CCl_4, 1,1-DCE, PCE, CIS-1,2-DCE, TCM, and DCM to have the highest concentrations of detected CVOCs in the KR-NPR (Fig. 3a; Table 3). TCE

Table 2 Percent detection of contaminants in groundwater in the KR-NPR

CVOC type	Total number of samples	% Sample detection above DL	% Sample detection above MCL	Number of sites with detection	% Detection per site ($n = 326$)
TCE	5354	46.30	29.40	90	27.61
PCE	5106	36.09	8.17	88	26.99
TCM	4602	30.18	0.15	159	48.77
CIS-1,2-DCE	4254	27.50	0.82	33	10.12
1,1-DCE	4716	26.93	6.34	55	16.87
CCl_4	7425	24.31	18.19	57	17.48
DCM	5264	15.71	2.62	110	33.74
1,1-DCA	3756	14.86	1.06	36	11.04
BDCM	3535	4.07	0.23	53	16.26
Trans-1,2-DCE	4609	2.99	0.02	32	9.82
CDBM	3494	2.95	0.23	57	17.48
BF	3466	2.31	0.20	45	13.80
CM	3523	1.70	0.28	42	12.88
1.2-DCA	4908	0.65	0.08	22	6.75
VC	4404	0.57	0.09	12	3.68
1,1,1-TCA	5022	0.56	0.02	16	4.91
1,1,2-TCA	4792	0.36	0.00	4	1.23
CA	3541	0.20	0.00	6	1.84
1,1,2,2-TeCA	3496	0.06	0.00	0	0.00
1,1,1,2-TeCA	3302	0.00	0.00	0	0.00

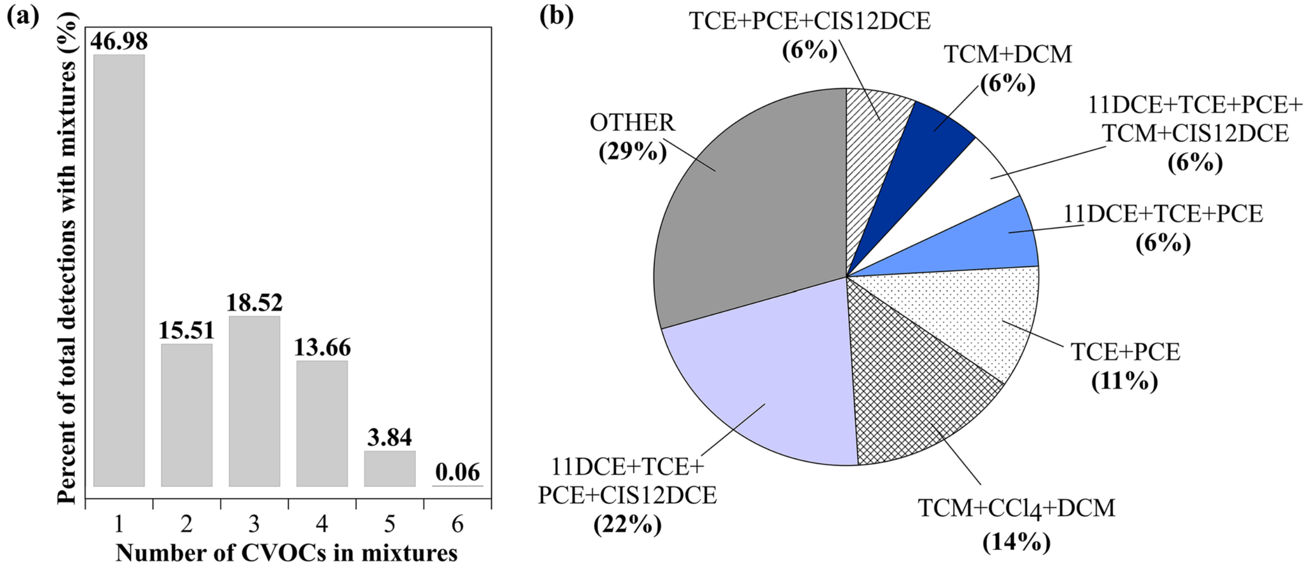


Fig. 2 **a** Percent of total samples with one or more of the 7 most detected CVOCs as single entities or mixtures, **b** most prevalent mixtures (from the total number of mixtures)

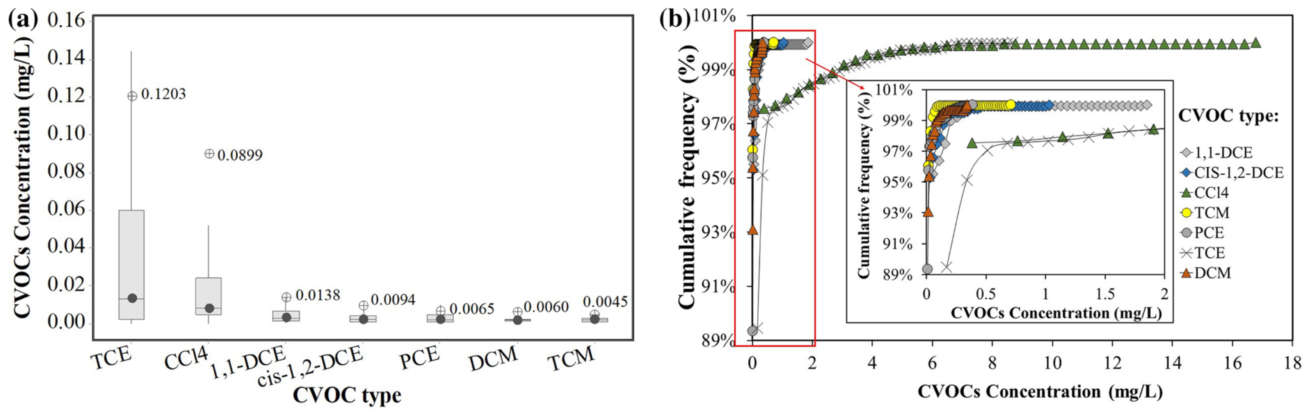


Fig. 3 **a** Box plots of CVOC concentrations; **b** cumulative frequency plot showing concentration of CVOC species

and CCl_4 show the highest concentrations ranges with maximum concentrations of 8.5 and 16.4 mg/L, respectively. PCE, TCM, CIS-1,2-DCE, 1,1-DCE, and DCM, show lower concentration ranges. The high concentrations associated with TCE and CCl_4 are attributed to the potential presence of TCE and CCl_4 non-aqueous phase liquids (NAPL) near Upjohn and Vega Alta Public Supply Wells Superfund sites (Fig. 1). Although NAPLs were never found near those areas, it is known that pure CCl_4 solvent entered the subsurface at the Upjohn site. Laboratory experiments studying fate and transport processes after TCE NAPL injection in karstified rock show maximum aqueous concentrations around 7 mg/L downstream of the injection (Carmona and Padilla 2015, 2017), and support the conjecture of potential TCE NAPLs in the study area. Cumulative frequency plots (Fig. 3b) show that most of the CVOCs species have a highly skewed distribution toward the low range. TCVOC average concentrations show a range from 0.00001 to 16.4 mg/L with a mean concentration of 0.054 ± 0.011 mg/L. ANOVA statistical analysis show that concentration means for the most detected CVOCs are statistically different from each other ($p < 0.0005$).

Spatial and temporal CVOCs occurrences

The spatial and temporal distribution of CVOCs may be influenced by sources of contamination, monitoring, and remediation of the contaminated areas, and hydrogeological properties of the system. The areas with highest concentrations (Fig. 4) are associated with known significant

Table 3 Concentration of contaminants in groundwater of the KR-NPR

CVOCs type	Min (mg/L)	Max (mg/L)	Mean ± confidence interval (95%) (mg/L)
TCE	0.00010	8.500	0.1203 ± 0.021
PCE	0.00001	0.380	0.0065 ± 0.017
TCM	0.00008	0.690	0.0045 ± 0.017
CIS-1,2-DCE	0.00005	1.000	0.0094 ± 0.003
1,1-DCE	0.00017	1.800	0.0138 ± 0.003
CCl_4	0.00002	16.396	0.0899 ± 0.028
DCM	0.00020	0.330	0.0060 ± 0.002
1,1-DCA	0.00007	0.110	0.0025 ± 0.001
BDCM	0.00025	0.056	0.0052 ± 0.001
Trans-1,2-DCE	0.00020	0.039	0.0081 ± 0.001
CDBM	0.00050	0.029	0.0042 ± 0.001
CM	0.00050	0.190	0.0053 ± 0.006
BF	0.00050	0.036	0.0048 ± 0.001
1,2-DCA	0.00014	0.026	0.0024 ± 0.002
VC	0.00041	0.380	0.0169 ± 0.031
1,1,1-TCA	0.00020	0.227	0.0131 ± 0.018
1,1,2-TCA	0.00025	0.004	0.0019 ± 0.001
CA	0.00060	0.001	0.0008 ± 0.0002
1,1,2,2-TeCA	0.00070	0.003	0.0021 ± 0.018

sources of CVOC contamination in the western and eastern sides of the study area. CCl_4 high concentrations (Fig. 4a) are located on the western side of the KR-NPR, and related to the "Upjohn" Superfund Site (Padilla et al. 2015; Yu et al. 2015). TCM and DCM are widely distributed over the study area (Fig. 4b, c). Their widespread distribution in the KR-NPR is attributed to multiple sources, including direct entrance into the subsurface from surface sources, degradation of CCl_4 to TCM and DCM, and leakage of disinfection by-product (DBPs) from chlorinated water-distribution lines, as suggested by Yu et al. (2015). High concentrations of PCE and TCE (Fig. 4d, e) are found in the Vega Alta and Dorado areas and related to Superfund sites in that region (Padilla et al. 2015; Yu et al. 2015). CIS-1,2-DCE and 1,1-DCE (Fig. 4f, g), which are degradation-by-products of PCE and TCE, have similar spatial distribution to those of PCE and TCE. Spatial distributions of total (Fig. 4h) and individual CVOCs average concentrations show that their presence extends beyond demarked sources of contamination, even after active remediation.

The temporal distributions of CVOCs for wells located near the Upjohn (Fig. 5a) and Vega Alta (Fig. 5b). Superfund sites show high variability over time. Temporal variability and trends depend on CVOC specie and space, reflecting the influence of multiple factors on their distribution. In general,

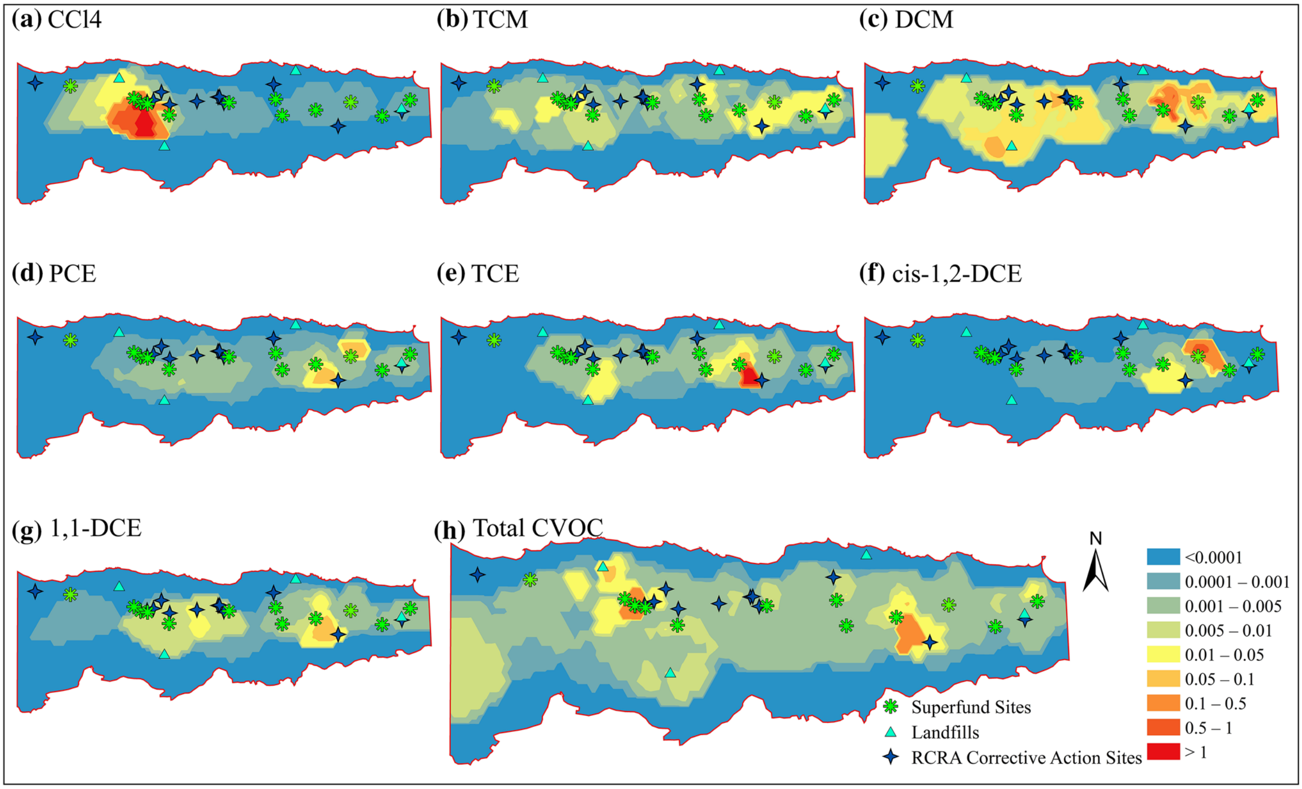


Fig. 4 Spatial distribution of **a** CCl_4, **b** TCM, **c** DCM, **d** PCE, **e** TCE, **f** CIS-1,2-DCE, **g** 1,1-DCE, and **h** total CVOC average concentrations (mg/L) in the study area (note that the legend is for all CVOCs)

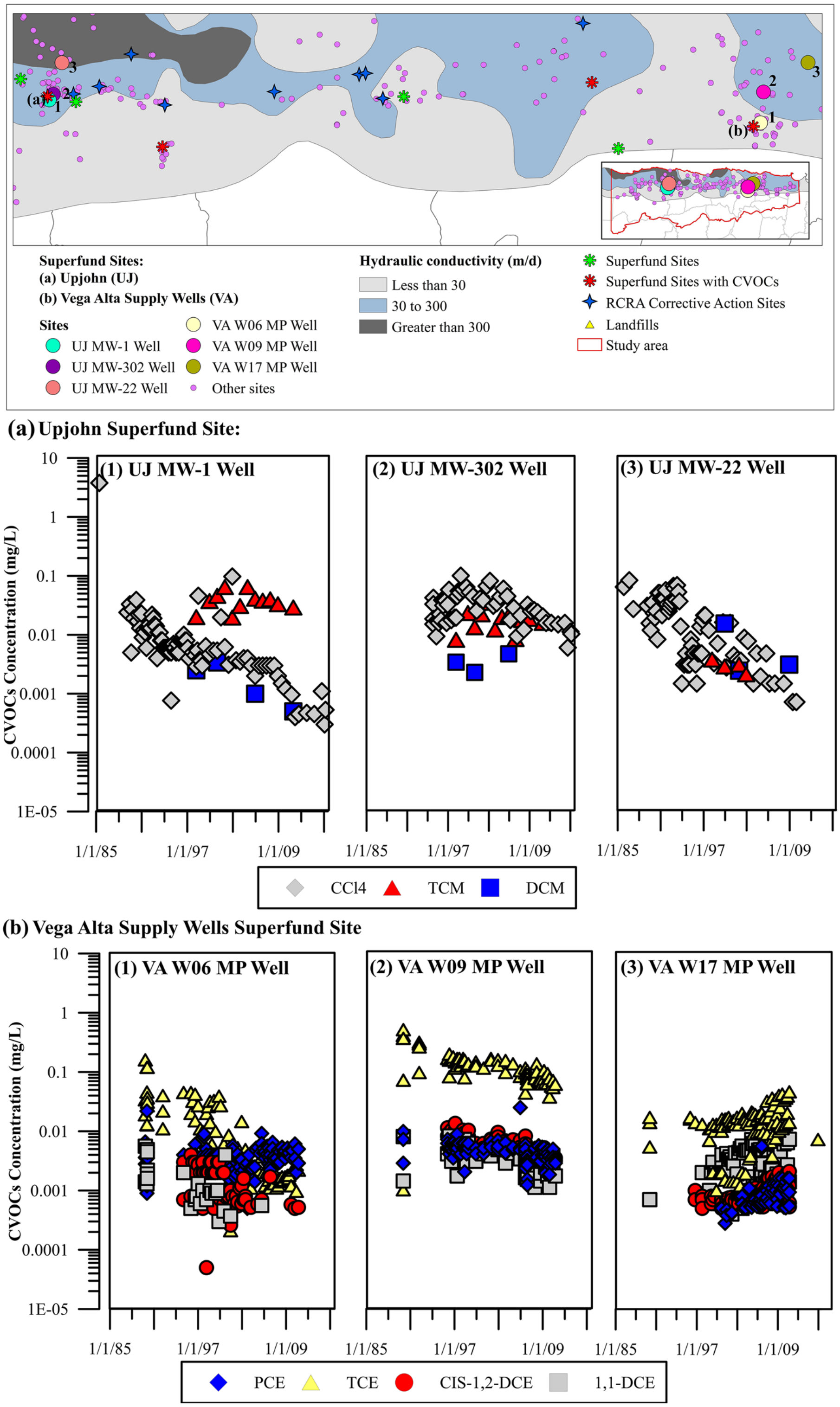


Fig. 5 Temporal distribution of CVOCs species in wells near **a** Upjohn superfund site, Barceloneta; **b** Vega Alta public supply wells superfund site, Vega Alta

there is a tendency to decrease over time, although some distributions show some broad increase during particular periods. Decreasing trends in concentrations are attributed to the active remediation activities (mostly pump and treat), as also observed by Padilla et al. (2015) and Yu et al. (2015), and natural attenuation. Under natural attenuation, CCl_4 degrades to TCM, which degrades to DCM; PCE degrades to TCE, which also degrades to 1,1-DCE, and CIS-1,2-DCE. As observed in Fig. 5b, PCE concentrations are shown to be lower than TCE, which generally shows the highest concentrations. Higher concentration of TCE than PCE is attributed to a potentially greater source of TCE and to possible degradation of PCE to TCE. Increasing concentrations of some CVOCs in different locations are attributed to differential arrival of contaminant sources, due to the heterogeneity of sources and hydrogeological characteristics, and to the formation of degradation-by-products. Persistent presence of CVOCs in the KR-NPR system over long periods of time, even after contaminated sites have been subjected to active remediation, reflects the high capacity of the system to store and slowly release contaminants.

Hydrogeological factors

Significant difference is observed on concentrations and detection frequencies between the upper and the lower aquifer. Percent detection of single or multiple species in groundwater samples is higher in the upper aquifer (69%) than the lower aquifer (16%). Results show a high number of samples with low concentrations in the lower aquifer and a higher range of concentrations in the upper aquifer (Fig. 6a). Overall, TCVOC average concentrations and detection frequencies are significantly higher in the upper than in the lower aquifer ($p < 0.0005$) (Table 4). Concentrations and detection frequencies varied among CVOC species, with PCE, TCE, CIS-1,2-DCE, and 1,1-DCE concentrations and detection frequencies showing significantly higher concentrations ($p < 0.0005$) in the upper than lower aquifers (Table 4). Although mean concentrations were not significantly different between the two aquifers for CCl_4 ($p = 0.72$), TCM ($p = 0.372$) and DCM ($p = 0.72$), their detection frequencies were significantly higher in the upper than lower

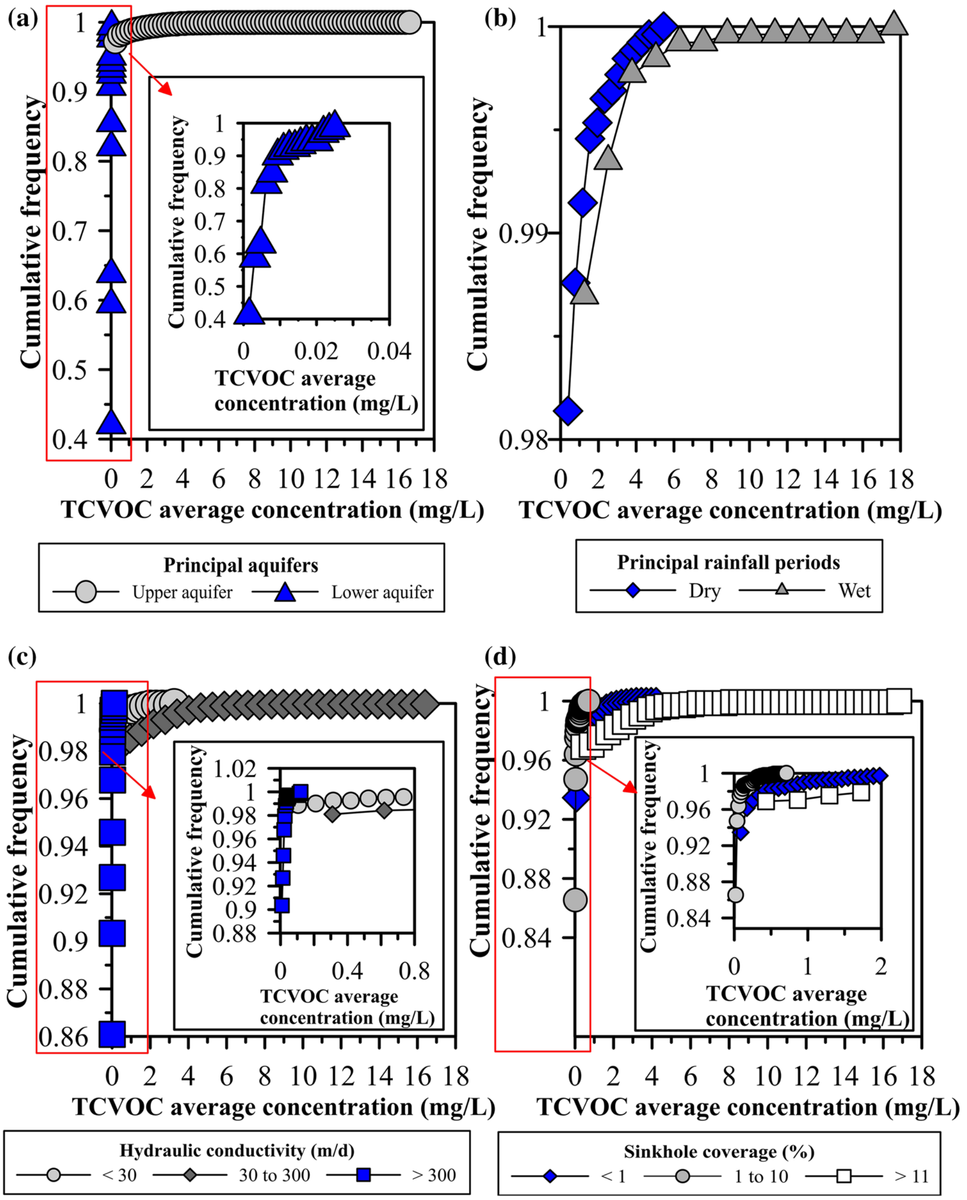


Fig. 6 **a** Cumulative frequency of TCVOC average concentrations for different aquifer types; **b** seasonal TCVOC average concentrations cumulative frequency plot, **c** TCVOC average concentrations for different hydraulic conductivities, and **d** TCVOC average concentrations for different sinkhole coverage area

Table 4 Summary of concentrations and detection frequencies of CVOCs for different hydrogeology characteristics

CVOC type	Hydrogeology				Season			
	Upper aquifer		Lower aquifer		Wet		Dry	
	Concentration (mg/L)	Detection frequency (%)	Concentration (mg/L)	Detection frequency (%)	Concentration (mg/L)	Detection frequency (%)	Concentration (mg/L)	Detection frequency (%)
TCVOC average	0.0551 ± 0.011	68.76% ($n=7379$)	0.0040 ± 0.001	16.22% ($n=709$)	0.0636 ± 0.015	61.18% ($n=4266$)	0.0443 ± 0.015	67.48% ($n=3822$)
CCl_4	0.0902 ± 0.028	26.63% ($n=6756$)	0.0016 ± 0.49	0.90% ($n=669$)	0.1301 ± 0.058	19.88% ($n=4039$)	0.0576 ± 0.021	29.59% ($n=3386$)
TCM	0.0044 ± 0.0001	31.42% ($n=4239$)	0.0068 ± 0.005	16.53% ($n=363$)	0.0040 ± 0.002	21.61% ($n=2351$)	0.0047 ± 0.001	39.27% ($n=2251$)
DCM	0.0061 ± 0.002	16.66% ($n=4725$)	0.0047 ± 0.007	7.42% ($n=539$)	0.0085 ± 0.004	4.511% ($n=2771$)	0.0056 ± 0.002	28.15% ($n=2493$)
PCE	0.0065 ± 0.001	40.28% ($n=4578$)	0.0005 ± 0.032	0.38% ($n=528$)	0.0072 ± 0.001	35.27% ($n=3000$)	0.0055 ± 0.002	37.42% ($n=2106$)
TCE	0.1205 ± 0.021	51.30% ($n=4825$)	0.0009 ± 0.0004	0.57% ($n=529$)	0.1307 ± 0.029	44.97% ($n=3024$)	0.1077 ± 0.032	47.98% ($n=2330$)
CIS-1,2-DCE	0.0094	30.95% ($n=3777$)	0.0007	0.21% ($n=477$)	0.0092 ± 0.003	27.18% ($n=2553$)	0.0098 ± 0.004	27.98% ($n=1701$)
1,1-DCE	0.0138 ± 0.003	30.20% ($n=4199$)	0.0014 ± 0.086	0.39% ($n=517$)	0.0160 ± 0.004	26.67% ($n=2760$)	0.0108 ± 0.005	27.30 ($n=1956$)

aquifer. Higher detection frequencies and concentrations in the upper aquifer are attributed to its greater outcrop area and direct connection with surface features and sources of contamination.

The analysis shows that detection frequencies of CVOCs are significantly higher ($p<0.0005$) in wells ($df=65.1\%$; $n=7930$) than springs ($df=26.5\%$; $n=147$). Although TCVOC average concentrations are higher in wells (0.0543 ± 0.011 mg/L) than springs (0.0030 ± 0.122 mg/L), they are not found to be significantly different ($p=0.412$). Higher concentrations and detection frequencies in wells than springs are attributed to the large number of wells installed and used for monitoring purposes, as well as differences in transport hydrodynamics associated with springs. Only a small number of springs, which are natural, in the study are used as monitoring stations. Many springs, although not all, are associated with high conduit flow, which would flush high concentrations. Long-term concentrations in springs are, therefore, associated with slow release from diffuse storage compartments.

Results show that concentrations, detections, and distribution of CVOCs vary among the different historical rainfall seasons. The analysis shows that detection frequency for TCVOC is significantly higher for the dry season ($p<0.0005$; Table 4). The mean concentration is slightly higher in the wet season (Fig. 6b), although not significantly different ($p=0.073$) from the dry season. Analysis shows that, for the CVOCs species analyzed (Table 4), mean concentrations of CCl_4 are significantly higher ($p=0.02$) in the wet season than those in the dry season. Although not significantly different, mean concentrations are slightly higher for DCM, PCE, TCE, and 1,1-DCE in the wet season and for TCM and CIS-1,2-DCE in the dry season. Results also show that detection frequencies are significantly higher for CCl_4, TCM, DCM ($p<0.0005$), and TCE ($p=0.029$) during dry seasons. Detection frequencies are slightly higher for PCE, CIS-1,2-DCE, and 1,1-DCE (Table 4), but not significantly different. Differences in detection frequencies and concentrations between rainfall seasons for the different CVOCs are attributed to an interplay of multiple factors, including physico-chemical characteristics of the contaminants, location of contaminant sources, and hydrogeological properties of the karst. For instance, it is observed that, except for DCM, CVOCs with higher Henry's law constant (CCl_4, 1,1-DCE, PCE, and TCE) show lower concentrations during the dry than wet seasons (Figure S3). This is attributed to higher volatilization loses of those CVOCs. It is also noted that those CVOCs with significantly higher detections during the dry season (CCl_4, TCM, DCM) are within the same anaerobic degradation pathway (Figure S1), suggesting lower degradation during drier conditions. Higher average concentrations but lower detection frequencies during wet seasons suggests greater mass release from storage compartments accompanied with higher mobility under higher flows. As observed by Anaya et al. (2014), higher flow rates during wet conditions may induce expansion of preferential flow zones into areas that are commonly stagnant during low-flow regimes. This expansion could mobilize contaminants stored in those compartments. Because they are rapidly mobilized, they are not easily detected under point-sampling schemes. As later discussed in this paper, hydrogeological properties play important roles in the distributions of CVOCs in karst systems. Specific interplay of multiple variables affecting the detection and concentrations of CVOCs under different seasons is, however, beyond the scope of this study and needs to be further studied.

TCVOC and single species mean concentrations and detections vary for different categories of hydraulic conductivities and sinkhole coverage. Mean concentrations for TCVOCs were significantly higher ($p < 0.0005$) in zones of hydraulic conductivities between 30 and 300 m/days (Fig. 6c; Table 5). Results show that CCl_4 and TCM have significantly higher concentrations in zones of hydraulic conductivities between 30 and 300 m/days ($p < 0.0005$), followed by zones having hydraulic conductivities greater than 300 m/days (Table 5). DCM, PCE, TCE, 1,1-DCE ($p < 0.0005$), and CIS-1,2-DCE ($p = 0.002$) mean concentrations are significantly higher in areas of low hydraulic conductivities (Table 5). Detection frequencies are higher in hydraulic conductivities between 30 and 300 m/days for TCVOCs ($p < 0.0005$), greater than 300 m/days for CCl_4, TCM, and DCM ($p < 0.0005$), and less than 30 m/days for PCE, TCE, CIS-1,2-DCE, and 1,1-DCE ($p < 0.0005$). In relation to percent sinkhole coverage areas, TCVOCs ($p < 0.0005$) (Fig. 6d), CCl_4 ($p < 0.0005$), TCM ($p = 0.001$), and DCM ($p = 0.001$) mean concentrations were significantly higher in areas of sinkhole coverage of more than 11% (Table 6; Figure S4) TCE, CIS-1,2-DCE, and 1,1-DCE mean concentrations were significantly higher ($p < 0.0005$) in areas with low percent of sinkhole coverage area (< 1%) (Table 6; Figure S4). Except for CCl_4, which show higher detection frequencies for sinkhole coverage areas greater than 11%, and TCE, which show higher detection frequencies for sinkhole coverage areas lower than 1%, detection frequencies of most CVOC are higher for sinkhole coverage areas between 1 and 10% (Table 6; Figure S4). Higher mean concentrations and detection frequencies of CVOCs species in regards to hydraulic conductivities and percent sinkhole coverage area are mostly related to the location of the major source of contamination (Figs. 7, 8). For instance, higher

Table 5 Summary of CVOC concentrations and detection frequencies for different hydraulic conductivities categories

CVOC type	Hydraulic conductivity (m/days)					
	< 30		30–300		> 300	
	Concentration (mg/L)	Detection frequency (%)	Concentration (mg/L)	Detection frequency (%)	Concentration (mg/L)	Detection frequency (%)
TCVOC average	0.0616 ± 0.013	60.98% ($n=2642$)	0.0638 ± 0.018	73.92% ($n=3761$)	0.0046 ± 0.001	69.98% ($n=976$)
CCl_4	0.0012 ± 0.001	0.27% ($n=2223$)	0.1226 ± 0.039	36.30% ($n=3559$)	0.0076 ± 0.001	51.44% ($n=974$)
TCM	0.0041 ± 0.001	22.26% ($n=1860$)	0.0077 ± 0.004	23.21% ($n=1741$)	0.0019 ± 0.0001	80.56% ($n=638$)
DCM	0.1950 ± 0.008	6.32% ($n=2343$)	0.0075 ± 0.003	7.58% ($n=1820$)	0.0017 ± 0.0001	89.15% ($n=562$)
PCE	0.0101 ± 0.002	39.00% ($n=2410$)	0.0027 ± 0.001	44.14% ($n=2012$)	0.0001 ± 0.0001	10.26% ($n=156$)
TCE	0.1893 ± 0.038	52.18% ($n=2593$)	0.0375 ± 0.004	54% ($n=2076$)	0.0048	0.65% ($n=156$)
CIS-1,2-DCE	0.0134 ± 0.004	27.93% ($n=2073$)	0.0056 ± 0.004	35.78% ($n=1649$)	–	0% ($n=55$)
1,1-DCE	0.0209 ± 0.007	27.05% ($n=2329$)	0.0068 ± 0.001	35.59% ($n=1790$)	0.0005	1.27% ($n=80$)

Table 6 Summary of CVOC concentrations and detection frequencies for different sinkhole coverage area

CVOC type	Sinkhole coverage area (%)					
	< 1%		1–10		> 11%	
	Concentration (mg/L)	Detection frequency	Concentration (mg/L)	Detection frequency	Concentration (mg/L)	Detection frequency
TCVOCs average	0.0419 ± 0.008	65.26% ($n=3823$)	0.0132 ± 0.002	69.50% ($n=1797$)	0.1120 ± 0.036	63.18% ($n=2246$)
CCl_4	0.0066 ± 0.006	1.22% ($n=3353$)	0.0074 ± 0.001	28.93% ($n=1673$)	0.1242 ± 0.040	58.11% ($n=2194$)
TCM	0.0040 ± 0.001	20.04% ($n=2805$)	0.0035 ± 0.002	54.09% ($n=1235$)	0.0102 ± 0.002	30.25% ($n=519$)
DCM	0.0145 ± 0.003	5.34% ($n=3239$)	0.0038 ± 0.002	42.95% ($n=1299$)	0.0034 ± 0.005	12.15% ($n=650$)
PCE	0.0072 ± 0.001	39.29% ($n=3568$)	0.0042 ± 0.0004	49.00% ($n=902$)	0.0005 ± 0.001	0.34% ($n=582$)
TCE	0.1359 ± 0.027	52.71% ($n=3747$)	0.0606 ± 0.007	52.52% ($n=933$)	0.0044 ± 0.004	2.10% ($n=620$)
CIS12DCE	0.0120 ± 0.004	27.11% ($n=2992$)	0.0037 ± 0.0003	49.6% ($n=724$)	–	0% ($n=493$)
11DCE	0.0173 ± 0.005	29.11% ($n=3284$)	0.0024 ± 0.0003	36.48% ($n=806$)	0.0148 ± 0.006	3.49% ($n=573$)

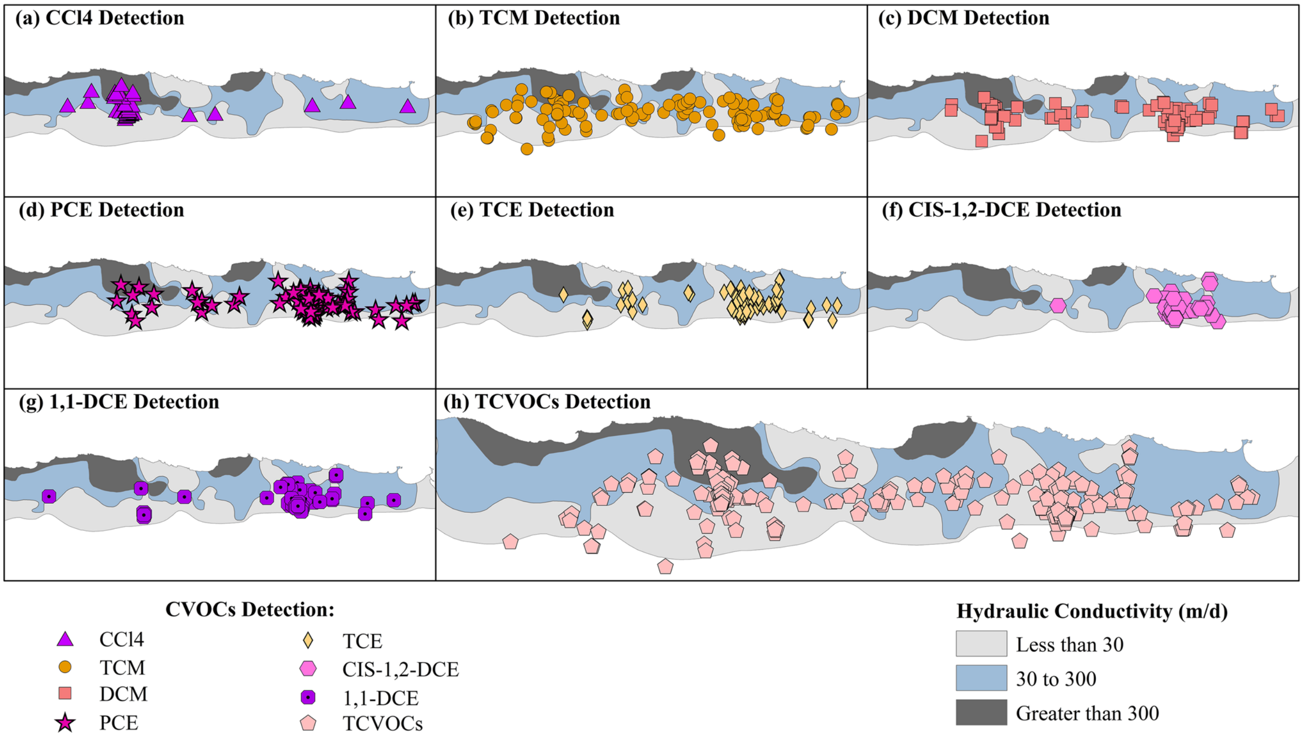


Fig. 7 CVOC detections for different hydraulic conductivities categories in the upper aquifer: **a** CCl_4, **b** TCM, **c** DCM, **d** PCE, **e** TCE, **f** CIS-1,2-DCE, **g** 1,1-DCE, and **h** TCVOC average

concentrations for CCl_4 and TCM are found in the range of hydraulic conductivities (between 30 and 300 m/days) and sinkhole coverage area (> 11%), where the Upjohn Superfund site is located (Figs. 1, 7). Higher detection frequencies for CCl_4, TCM, and DCM are, however, found at zones of higher hydraulic conductivities (> 300 m/days) downstream of the site, and suggest that this zone is influencing the movement toward that area. Greater detection frequency of DCM in that zone is attributed to the formation of TCM degradation-by-products away from the source. The influence of hydraulic conductivities and percent sinkhole coverage can also be observed on the spatial distributions of the CVOC detections (Figs. 7, 8). Detection distribution of CCl_4 and related degradation-by-products associated with areas of higher hydraulic conductivities and sinkhole coverage near the Upjohn superfund sites tend to be elongated toward the north, which is toward where regional groundwater flows. Detection of PCE and TCE and related by-products associated with the lower hydraulic conductivities and sinkhole coverage near the Vega Alta Superfund site, on the other hand, tends to follow a more transverse distribution in relation to the regional groundwater flow.

Pearson correlation analysis between elevation and CVOC concentrations shows weak, but significant correlation between elevation and CCl_4, DCM, CIS-1,2-DCE, and TCVOCs concentrations. Correlation between PCE, TCE, TCM, and 1,1-DCE concentrations is not significant. Positive (although weak) correlation coefficients for TCVOC and CCl_4 indicate increasing concentration with elevation, whereas those with negative coefficients (CIS-1,2-DCE, DCM) reflect increasing concentrations at lower elevations. Although not statistically significant, TCM concentrations show a decreasing trend with elevation. The influence of elevation on concentrations depends on the location of the contamination sources. In general, for widely distributed species, such as TCM and DCM, concentrations tend to be higher at lower elevations, reflecting cumulative transport from higher to lower elevations. Because most of the sources of contamination are located at lower elevations, higher percent detections and concentrations are found at lower elevations.

Anthropogenic factors

The analysis shows that TCVOC concentrations and detection frequencies vary with different land uses in the KR-NPR. TCVOC, CCl_4, and TCM mean concentrations are found to be statistically higher ($p < 0.0005$) in agricultural land use, while DCM mean concentrations are not statistically different ($p = 0.680$) for the different land uses. PCE, TCE, and CIS-1,2-DCE show significantly higher concentrations ($p < 0.0005$) in areas with natural land use, whereas

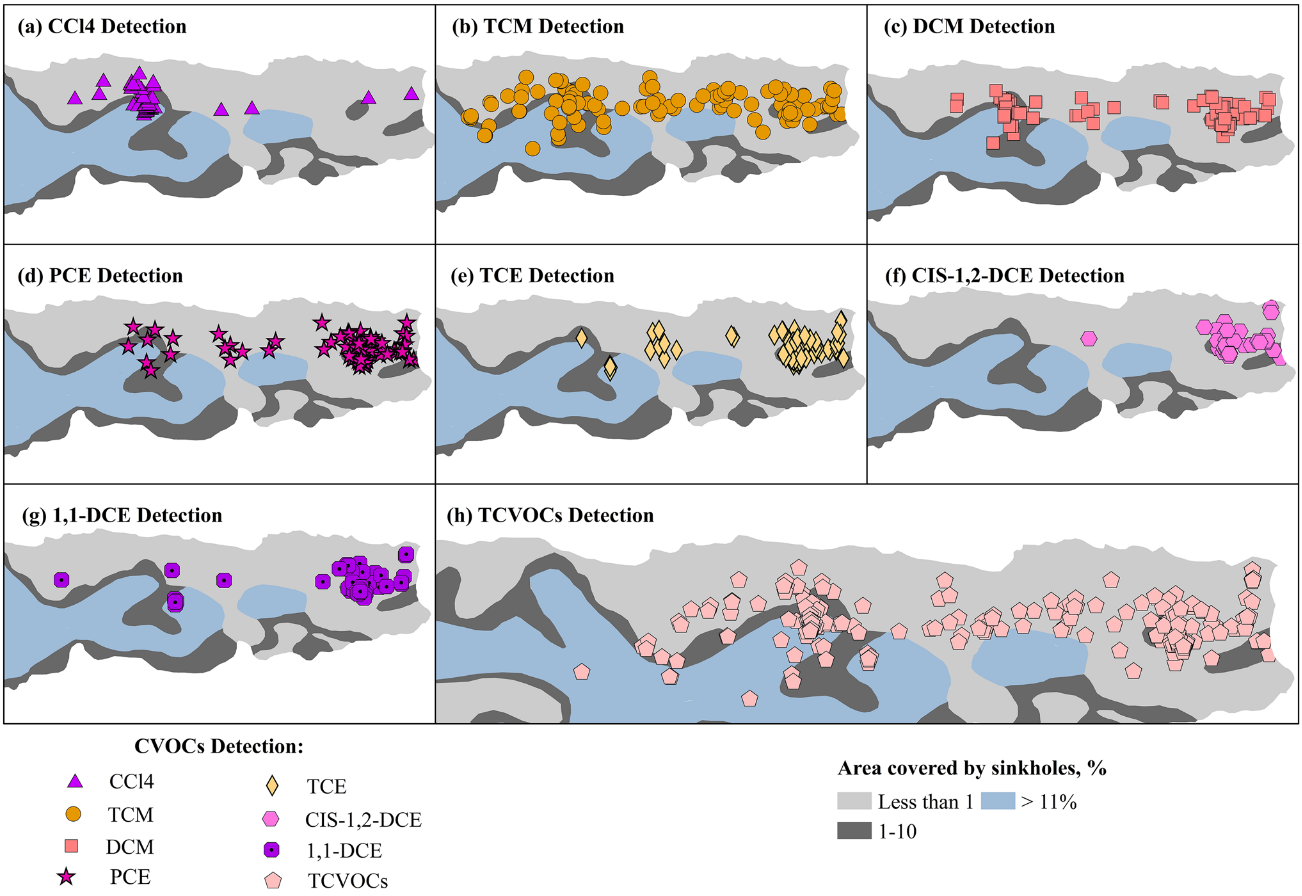


Fig. 8 CVOC detection for different sinkhole coverage area categories: **a** CCl_4, **b** TCM, **c** DCM, **d** PCE, **e** TCE, **f** CIS-1,2-DCE, **g** 1,1-DCE, and TCVOC average

1,1-DCE ($p = 0.013$) show higher concentrations in construction and other areas. Detection frequencies were significantly higher ($p < 0.0005$) in agricultural land use for TCVOC and CCl_4, in natural land use for DCM, TCE, and CIS-1,2-DCE, and in construction and other uses for TCM, PCE, and 1,1-DCE. Although different land uses are associated with significant higher concentrations and detection of the different CVOC species, the effect of land use is more related to the mobility of the contaminants away from the source than to the source. For instance, although most contaminant sources are located on industrial areas, most detection and high concentrations are associated with agricultural and natural land uses.

The results from the analysis shows that although the source of contamination may be related to a particular land use, the movement of CVOC contaminants through different pathways in the karst groundwater system is mainly influenced by the hydrogeological properties of the system. For instance, high concentration distributions of CCl_4 in the western part of the study area (Fig. 4a) are attributed to the "Upjohn" Superfund Site (No. 3 in Fig. 1c), which is located in an area of industrial land use. Greater association of high CCl_4 presence and concentrations with agricultural land use reflects its movement beyond the contamination zone. This movement is influenced by the high hydraulic conductivities and sinkhole coverage (Figs. 7, 8). High CVOC concentrations and detections in high sinkhole coverage and hydraulic conductivities areas (mostly for TCVOC and CCl_4) reflect a high amount of contaminant mass entering and moving through the groundwater when in coexistence with an available source. This is observed in the distribution of CCl_4 related to the "Upjohn" Superfund Site. This distribution (Figs. 4a, 7a) follows a northwestern path, which is influenced by flow gradients toward areas of high hydraulic conductivities (Fig. 7a). High frequency of CVOC detections and concentrations (mostly for PCE, TCE, CIS-1,2-DCE, and 1,1-DCE) in low hydraulic conductivities areas coincides with low sinkhole coverage areas, and suggests that there is a lower diluting flow through these regions. As a consequence, CVOCs in the groundwater system become concentrated.

Multiple factors influence the widespread CVOC contamination beyond sources of contamination. In addition to the known sources, there may be unknown sources of contamination in the region. The heterogeneity and anisotropy of the system contribute to the movement of the contaminants to other areas. As a result, traditional remediation techniques are less efficient in karst aquifers (Field 2018) than other aquifers. The movement of dense NAPLs (DNAPLs), of which most of the CVOCs in this study are classified under, through karst aquifers is poorly known (White 2018). As a consequence, monitoring of DNAPLs and associated solutes in these aquifers is not adequate and remediation designs fail to capture and contain contaminants from further spreading. Lack of rapid response to characterize, monitor, and remediate the sites, in addition to the high capacity of karst systems too rapidly convey water and contaminants, results in widespread contamination beyond the sources of contamination (Padilla et al. 2015). For the Vega Alta Superfund Site (No. 9 in Fig. 1), for instance, monitoring and remediation efforts in the site were implemented long after the contamination occurred. In addition, the complexity of the hydrogeology of the area resulted in transport of contaminants to other areas, which were discovered at later states of the remedial action implementation (Padilla et al. 2015). This has resulted in widespread contaminations spatially and temporally.

Conclusions

Analysis of CVOC presence and concentrations in the KR-NPR indicate that there is an extensive spatial and temporal contamination of CVOCs as single entities and as mixtures in the area of study. In addition to a large number of contaminant sources, extensive contamination is attributed to the high capacity of the karst groundwater system to rapidly convey contaminants through preferential flow zones in conduits and highly transmissivity zones and to the large capacity of the system to store and slowly release these contaminants. The high number of mixtures having CCl_4, TCM, DCM and PCE, TCE, CIS-1,2-DCE, or 1,1-DCE suggests strong coexistence of those contaminants. This is attributed to the presence of multiple contaminants in many sites and to the formation of degradation-by-products.

The presence and distribution of many of the CVOC contaminants in the KR-NPR groundwater system are significantly influenced by hydrogeological characteristics, sources of contamination, and properties of the contaminants. Sinkhole coverage, hydraulic conductivity, and rainfall seasonality affect the load of contaminants entering the system, their mobility, distributions, and concentrations. Unlike for contaminants associated with disperse sources, such as those studied by Torres et al. (2018), the distribution of contaminants associated with heavily contaminated sources is influenced to a greater extent by the location of these sources than the overall distribution of hydrogeological properties. Still, the distribution from these sources is influenced locally by these properties. Greater percent detection of CVOCs is associated with drier conditions, but the effect of rainfall seasons on concentrations varies among the different CVOCs. The effect of rainfall seasons on contaminant distribution is found to be compounded by other variables, including source location, hydrogeological, and physico-chemical characteristics of the contaminants. The interplay among these variables must be further studied. Results from this study provide further evidence of the factors that make karst groundwater systems highly vulnerable to contamination and likely routes for long-term exposure to Superfund-related contaminants.

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