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Spatiotemporal changes of CVOC concentrations in karst aquifers: analysis of three decades of data from Puerto Rico

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Abstract

We studied the spatial and temporal distribution patterns of Chlorinated Volatile Organic Compounds (CVOCs) in the karst aquifers in northern Puerto Rico (1982-2013). Seventeen CVOCs were widely detected across the study area, with the most detected and persistent contaminated CVOCs including trichloroethylene (TCE), tetrachloroethylene (PCE), carbon tetrachloride (CT), chloroform (TCM), and methylene chloride (DCM). Historically, 471 (76%) and 319 (52%) of the 615 sampling sites have CVOC concentrations above the detection limit and maximum contamination level (MCL), respectively. The spatiotemporal patterns of the CVOC concentrations showed two clusters of contaminated areas, one near the Superfund site “Upjohn” and another near “Vega Alta Public Supply Wells.” Despite a decreasing trend in concentrations, there is a general northward movement and spreading of contaminants even beyond the extent of known sources of the Superfund and landfill sites. Our analyses suggest that, besides the source conditions, karst characteristics (high heterogeneity, complex hydraulic and biochemical environment) are linked to the long-term spatiotemporal patterns of CVOCs in groundwater.

Keywords

Karst; Groundwater contamination; CVOC; Spatiotemporal patterns; Puerto Rico (USA)

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1. Introduction

The United States Environmental Protection Agency (US EPA) developed a national primary drinking water regulation (NPDWR) to control the carcinogenic Volatile Organic Compounds (cVOCs) in 2011, where a number of Chlorinated Volatile Organic Compounds (CVOCs) were included in the cVOC drinking water standard. The occurrence of CVOCs in groundwater systems poses a serious environmental threat to both natural ecosystem integrity and human water uses (Lapworth et al., 2012; Anaya et al., 2013). Exposure to CVOCs is potentially harmful to human health and may contribute to adverse reproductive outcomes (Sonenfeld et al., 2001; Forand et al., 2012), as well as damage to the nervous system (Bale et al. 2011), liver and kidney (Lash et al., 2000), immune system (Cooper et al., 2009) and lungs (Odum et al., 1992; Chiu et al., 2013). CVOCs typically have long residence times (hundreds to thousands of years) in groundwater due to their low solubility, persistence in the environment due to low degradation rates, and immobility (Heron et al., 2009; Liu et al., 2010). Understanding the occurrence, transport and source of CVOCs in the environment is of significant scientific and engineering importance. However, studies on the spatial and temporal distributions of CVOCs in karst aquifers are notably underrepresented when compared to those of other types of aquifers and surface water systems.

Karst aquifers are developed from limestone geology through dissolution and surface drainage. Groundwater in the karst aquifers typically flows more rapidly than the fissured and porous alluvial aquifers due to the existence of swallow holes and underground conduits and drains. As hydrogeological conditions within karst aquifers are highly heterogenic and anisotropic with complex networks of cracks, caverns, conduits and channels, water flows are primarily stochastic (Ghasemizadeh et al., 2012). Groundwater in karst aquifers is important for the integration of natural ecosystems and anthropogenic water uses. Karst terrain is a significant topography in the Earth ice-free continental surface and the conterminous US (both up to 20% of the total area; Ford and William, 2007; Padilla et al., 2011). Groundwater from the karst aquifers consists about 20-25% of the anthropogenic water use globally and over 40% of the drinking water use in US (Veni et al., 2001). The karst area is usually highly productive because of its high permeability characteristics, and is also vulnerable to contamination because of rapid transport and low natural attenuation of the contaminants (Karl, 1999). Consequently karst aquifers are important routes of contaminant exposure for humans and wildlife. The northern region of Puerto Rico is characterized as karst topography, and as of 2005, groundwater from the karst aquifers provides 8% of the total water production in Puerto Rico (Molina-Rivera et al., 2008). However, the karst groundwater in this region is threatened with contamination by CVOCs and other organic contaminants (OCs) from industrialization activities, especially the effluents and/or exudates from pharmaceutical companies in the past century (Hunter and Arbona, 1993; US EPA, 2013). Recent effective remediation activities and strict discharge controls have resulted in substantial removal of contamination from source zones in this region. However, considering the downward movement of contaminants and spatial dispersion in the highly heterogeneous aquifers, the concentrations of OCs in karst aquifers may not directly respond to source depletion in the contamination zones (Wang et al., 2012).

The karst aquifer of northern Puerto Rico is relatively young with high permeability and heterogeneity (Rodriguez-Martinez, 1995) compared to the well-developed karsts in Europe (Greece, Panagopoulos, 2012; Romania, Oraseanu, 2000; LaMoreaux and LaMoreaux, 1998), the eastern conterminous US (Tennessee, Wolfe et al., 1996; Arkansas, Peterson, 2003), and parts of southern China (Lu et al., 2006). The study of contaminant concentrations and distribution in this kind of aquifer is challenging as a matter of the aforementioned heterogeneity and anisotropy as well as the unknown geology of potential conduit network along which rapid transport spreads the contaminants (Scanlon et al., 2003; Goppert and Goldscheider, 2008; Ghasemizadeh et al., 2012; Ronayne, 2013). Contaminant storage occurs in the rock matrix and epikarst, but contaminant transport occurs mostly along preferential pathways that are typically inaccessible, which makes it difficult to model the dynamics (or functioning) of a karst system. Therefore, surveying the concentrations from associated wells and springs is still the most direct and effective method in analyzing the distribution and spreading patterns of the contaminants for the northern karst region of Puerto Rico (Veni, 1999).

The concentrations of contaminants are expected to be decreasing due to waste management and remediation activities. However, the spatial patterns of concentrations and their variations during this period are yet to be known. In this study, we analyzed the concentrations of dissolved CVOCs in the northern karst aquifers of Puerto Rico from multiple sites over three decades using a number of previous studies, surveys and data collected by various agencies. The main objective of this study is to investigate the spatial and temporal patterns of concentrations of various types of CVOCs and evaluate the long-term and spatial extent patterns of the contamination in the karst aquifers.

2. Methods

2.1. Study sites

We chose eight counties in the northern karst region of Puerto Rico (17°55'-18°33'N, 65°33'-67°17'W; total area: 8,710 km²) that were heavily affected by CVOC contamination. The counties are Arecibo, Florida, Dorado, Barceloneta, Vega Baja, Manatí, Toa Baja, and Vega Alta (Fig. 1). About 10% (0.41 million people) of the 3.72 million people who live in Puerto Rico reside within the study area (US Census 2010). The land is largely covered by evergreen forest (39%), followed by grassland/pasture/scrub (30%), urban and developed land (17.5%), wetlands (7%), crops (4%), open water (1.5%), and barren land (1%). The terrain of the study region principally consists of the north coast limestone aquifer-upper system with the Aguada and Ayamon limestone formations (surface outcrop area is 371 km² which represents 44% of the total northern karst area of 850 km²), the lower aquifer with Lares limestone and the Cibao formation (153 km²; 18%), confining units (166 km²; 19%) and the alluvial valley aquifer (143 km²; 17%). Groundwater extractions for domestic, industrial, agricultural, and public supply purposes are largely from the upper aquifer due to easier accessibility for drilling and pumping, though there are several wells that withdraw from the lower aquifer for industrial and public water supply (Molina-Rivera et al., 2008).

There are four major rivers flowing across the study region: Rio Grande de Arecibo, Rio Grande de Manatí, Rio Cibuco and Rio de la Plato (from west to east; Fig. 1). The elevation

of the study area ranges from sea level to 440 m above sea level toward the middle mountainous areas of the island. The groundwater flow pattern is northward toward the Atlantic Ocean with higher hydraulic heads near the middle and lower heads near the northern coastal area. The hydraulic conductivities are generally higher in the more karstified aquifers near the coast than areas near the southern mountains (Giusti, 1978).

There is a long history of improper disposal of toxic waste across Puerto Rico as a result of the industrial development and population expansion coupled with a lack of proper waste disposal, monitoring and management practices (Hunter and Arbona, 1995). Since authorization of the Superfund Act, EPA has listed 10 Superfund sites (Table 1) on the National Priority List (NPL) and 291 corrective action sites on the Resource Conservation and Recovery Act (RCRA) within the study area (Fig. 1). The densely distributed NPL and RCRA sites highlight the need for detailed studies of groundwater contamination in this region (Padilla et al., 2011).

2.2. Data acquisition

We collected concentrations of various types of dissolved CVOCs at 615 sites from all currently available studies and surveys in this region, including data from the following sources: US Geological Survey (USGS), EPA, NPL, Puerto Rico Environmental Quality Board (PREQB), Puerto Rico Department of Health (PRDOH), Puerto Rico Department of Natural and Environmental Resources (PRDNER), Puerto Rico Aqueduct and Sewer Authority (PRASA), and Puerto Rico Testsite for Exploring Contamination Threats (PROTECT) (Fig. 1). The data period covered January 1982 through December 2013, corresponding to the rapid industrial developments, increased awareness of groundwater contamination, and ongoing pollution remediation and control activities. Among all the wells, 239 wells were used for public supply, 141 were the PROTECT monitoring wells, and other wells were used for stock, industrial, irrigation, commercial, domestic or unused purposes. Note that all the wells used for public supply were discontinued after 2005. Small errors may be introduced from the sampling such as pump maintenance (lubricant, tubing and piping, etc.) and new equipment takes time to equilibrate with the aquifer. These sampling errors may not be important for the large values of the older data before 2000. Since 2010 the field data we collected in PROTECT were following strict sampling protocols for the purpose of minimizing sampling errors.

The precipitation and temperature data were collected from National Oceanic and Atmospheric Administration's (NOAA) National Climatic Data Center (NCDC, 2013). The surface land use data were obtained from the National Land Cover Dataset (NLCD) for 2001 (Fry et al., 2009). The elevation and stream flow data were extracted from digital elevation model (DEM) data from USGS. The water use data for Puerto Rico were obtained from the National Water Information System of USGS. The population data were obtained from US Census Bureau (US Census, 2010).

2.3. Data analysis

We performed initial screening of the raw data before any statistical analysis because the data were collected from a number of sources and covered three decades. A potential

limitation with this data is that different methodologies were used in analyzing CVOC concentrations from various sources, especially due to the advancements of analytical methods in the past decades. This variance may be reflected by different detection limits (DL) for the analysis of the same type of CVOCs. Therefore, we used the same criteria from the original data sources to determine the DL and the site contamination status. Another limitation of the data is that at many sites the sampling frequencies were quite sporadic with missing data aperiodic, which makes their temporal analyses impractical. A site was considered contaminated when at least one sample was detected to contain CVOC concentration exceeding the maximum contamination level (MCL).

We used Statistical Analysis System (SAS 9.3, SAS Institute Inc., Cary, NC) software to perform the data analysis. The tools PROC MEANS, PROC FREQUENT, PROC CORR, PROC REG, PROC GLM, PROC NLIN, PROC TABULATE and ANOVA were used to analyze the simple statistics, correlation, regression, and group means comparison. The spatial analysis of the concentrations was conducted using Geographic Information System (ESRI ArcGIS 10.2) software. Geospatial analysis using GIS and statistics has proven to be powerful in analyzing spatiotemporal patterns (Kistemann et al., 2008; Chien et al., 2013). We explored the distribution patterns of CVOC concentrations by inverse distance weighted (IDW) interpolation, whereas the interpolation was confined to the extent of the study region. Note that artifacts may be generated during the interpolation processes as a result of two intrinsic limitations of our datasets: (1) the data are highly left skewed, i.e. most of the values are in the low range; and (2) the observation points are highly unevenly distributed. In statistical analysis and interpolation processes, the outliers were detected using SAS PROC UNIVARIATE and subjective judgment, with p-values of <0.05 considered as significant.

Based on our analysis on the long term precipitation intensities and a study on climatological conditions in Puerto Rico by Daly et al. (2003), we determined that the wet season period begins in June and lasts through November, as during this time, the average temperatures and precipitation intensities are generally greater than dry season; the remaining months of the year were considered to be dry season. We explored the comparative relationships among CT, TCM, and DCM, and also PCE, TCE, 1,2-DCE (full names and abbreviations of contaminants are presented in Table 2) using ternary diagrams, which were constructed by their relative contribution to the total concentrations at each site.

3. Results and Discussion

3.1. CVOCs detections

The detected CVOCs, MCLs, sampling frequencies (F_s), sampling frequencies with concentrations above zero (F_a), frequencies exceeding DLs (detection frequency, F_d), frequencies exceeding MCLs (contaminated frequency, F_c), mean and median concentrations and concentrations coefficients of variation (CV) are presented in Table 2. All seventeen CVOCs were detected to have concentrations above DLs and MCLs. TCE, TCM, DCM, PCE, 1,1-DCE, cis-1,2-DCE, 1,1,1-TCA, 1,1-DCA and CT were the most frequently detected CVOCs, with more than 20% of the sampling sites showing concentrations above DL ($F_d > 200$; Table 2). TCE, TCM, DCM, PCE, 1, 1-DCE and CT

concentrations were detected to be above MCLs more frequently among the sampling wells, with the number of contaminated sites of 162, 129, 102, 60, 59, and 58, respectively.

Contaminant detection decreased over time, with only CT, PCE, TCE and TCM detected after 2011. CVOCs with concentrations above MCLs were CT and TCM in 2011, TCE and TCM in 2012, and PCE, TCE and TCM in 2013. Fig. 2 presents the temporal patterns of the site detections for the most frequently detected CVOCs, i.e. TCE, DCM, PCE, 1,1-DCE, CT and TCM. By 2013, DCM, 1,1-DCE and CT were not detected to have concentrations above DL and MCL at any site, and TCE and PCE were detected with concentrations above DL and MCL at only a few sites ($n < 5$). However, there remained many sites ($n = 30$) with detected TCM at concentrations above DL and MCL. Note that although there are a decreasing number of sites with detected CVOCs, the sampling frequencies have also decreased significantly over recent years. The sites not sampled are very likely to have smaller concentrations of CVOCs than those of the earlier years due to source depletion, natural attenuation, and stricter monitoring management; however, there is still a need for additional sampling to cover more areas and resolve the spatial uncertainties.

3.2. CVOCs spatial patterns

The CVOCs detected with relatively higher concentrations include CT, TCE, 1,1-DCE, TCM, cis-1,2-DCE, PCE, DCM and 1,1-DCA, where their mean concentrations were 0.0543, 0.0436, 0.0037, 0.0026, 0.0026, 0.0022, 0.0019, 0.0017, and 0.0011 mg L^{-1} , respectively (Table 2). CM, trans-1,2-DCE, CV, cis-DCE, 1,1,1,2-TeCA, 1,1,1-TCA, 1,1,2-TCA, and 1,2-DCA showed quite similar spatial distribution patterns of the concentrations, and CA, 1,1,2,2-TeCA, 1,1-DCA, and 1,1-DCE showed moderately similar patterns. The spatial patterns of total CVOC concentrations showed two clusters of contamination: the contamination of CT, TCM and DCM in area near “Upjohn” in the borders of Arecibo and Barceloneta, and the contamination of TCE and PCE in area near the “Vega Alta Public Supply Wells” Superfund site in Vega Alta and Dorado.

There are notable decreasing trends in the values and areas of higher concentrations of total CVOCs ($> 0.2 \text{ mg L}^{-1}$) on the temporal scale (Fig. 3). However, the areas with total CVOC concentrations greater than MCLs did not show a noticeable decrease over time. There was also a general northward moving trend of the CVOCs over time, e.g. in the areas near “Upjohn” and “Vega Alta Public Supply Wells”, which indicated continuous toxic releases, spills and contamination spreading due to hydrological transport. CVOCs have also been observed in areas where no Superfund and RCRA sites nor landfills were in proximity, which indicates the existence of unidentified waste disposals or transport of the contaminants through unknown flow path.

3.3. CT-TCM-DCM

The spatial distribution patterns of the contaminated areas are largely in proximity to the Superfund sites. Most of the sites contaminated by CT were located near the “Upjohn” Superfund site. Pharmaceutical companies in the “Upjohn” site discharged approximately 60 metric tons of waste material, including CT, in the early 1980s (US EPA, 2013). The disposal of CT was continually documented by EPA, with the last documented release of

227 kg occurring in 1987. There were two more sites with CT samples exceeding MCL in the alluvial valley aquifer connecting to the aquifer where “Upjohn” located, which may be due to the hydrological transport of the contaminants through the aquifer and/or the surface streams, i.e. the Rio de la Plato stream system. The spatiotemporal distributions of CT concentrations are presented in Fig. 4. CT concentrations decreased rapidly in the first few years following by slow rate of decrease, which probably reflects the immediate cleanup actions from “Upjohn” after the detection of CT release. In 1982, “Upjohn” pumped the contaminated groundwater until 1985 and used a soil vacuum extraction (SVE) system to remove CT vapors from the unsaturated zones until 1988. The remediation actions are still ongoing for a few nearby sites. Our analysis showed that CT concentrations at all sites near “Upjohn” decreased significantly during the study period.

Once disposed of, the CVOCs were transported into the karst aquifers, followed by slow, natural attenuation and transport processes and biodegradation through microbial activities. The fact that CT concentrations were far from its solubility (805 mg L^{-1} ; Davis et al. 2003) suggests that the limiting factor for removing CT is the releasing capability of CT from karst matrix to groundwater, whereas the releasing capability is controlled by the geological conditions and groundwater flow velocities. Excluding those exceedingly high concentrations of CT ($>0.12 \text{ mg L}^{-1}$), the mean CT concentration in the dry season ($0.0080 \pm 0.015 \text{ mg L}^{-1}$, $n=5645$) was significantly higher than that in the wet season ($0.0074 \pm 0.014 \text{ mg L}^{-1}$, $n=5734$; ANOVA Tukey's method, $p=0.02$). The small difference in concentrations during the dry and wet seasons was expected because concentrations decrease with increasing recharge to the aquifer due to precipitation infiltration which results in lower concentrations during wet seasons (dilution effect), especially in shallow wells. Other studies have also attempted to examine the relationship between spring discharges with extreme rainfall events, which influence the pollutant concentrations (e.g. Adamski et al., 1996) as springs in highly karstified aquifers can connect to permeable channels and/or fractures that are directly impacted by recharge events. However, the impact of extreme rainfalls is damped in deep aquifers. Therefore, the observed small seasonal change is justified because the aquifer hydrodynamics in those locations are not highly impacted by conduit/channel flow. Furthermore, more intense hydrological activities due to increasing water recharge from precipitation might indicate that greater amounts of CT stored in the karst matrix was lost due to hydrological transport.

Historically, there were many sites contaminated by DCM and TCM of which the spatial distribution generally fell into clusters, with one located in the lower aquifer and one located near the Superfund sites of “Upjohn”, “Pesticide Warehouse III” and “Vega Alta Public Supply Wells”. The detections of DCM and TCM far from the industrial release areas (i.e. the Superfund sites and landfills) likely originated from household waste, as DCM is used in paint remover, industrial solvent and grain fumigant, and TCM is a byproduct of chlorinated drinking water. We explored the relationship among CT, TCM and DCM, which demonstrates a comparative description of the occurrence of these contaminants and represents how different contaminants co-exist at the study sites and possible degradation processes of CT to TCM and TCM to DCM (Fig. 5a). For example, the diagram suggests that TCM tends to exist when there is less CT available, and DCM tends to exist more often at very low relative TCM concentrations. The sides of the ternary diagram represent three

projected binary systems (two-phase relative concentrations) when the third concentration is zero. The number of point data on binary lines for TCM-DCM, CT-TCM, and DCM-CT pairs demonstrate that their two-phase coexistence decreases respectively, with the most binary coexistence between TCM and DCM, and the least binary coexistence for DCM and CT. The distribution of data within small areas at the corners of TCM and DCM in the diagram suggests the high correlation between the existence of CT, the existence of two other components, and the degradation of CT to the lesser chlorinated compounds. These findings support the natural degradation of CT to TCM and DCM as daughter products which, over time, achieve complete dechlorination of the parent CT. Microbial processes may be the major mechanisms for the degradation of CT, since the rate of abiotic degradation (such as hydrolysis) is diminutive (Penny et al., 2010). The intrinsic karst properties such as rapid flow, existence of many fractures, conduits and wide channels coupling with the tropic climate of Puerto Rico are favorable to microbial activities to degrade the organic contaminants. Therefore, conditions that affect the hydrological transport of CT (such as high heterogeneity and complex hydraulic behavior of the karst aquifers; Ghasemizadeh et al., 2012) and the biodegradation processes (such as low-high redox environment, and microorganism activities; Davis et al., 2003) are linked to the spatiotemporal patterns of CT in the karst in addition to its source origin (toxics release locations and quantities, and source-zone depletion).

3.4. PCE-TCE-DCE

TCE, PCE and DCEs (trans-1,2-DCE, cis-1,2-DCE, 1,1-DCE) were also frequently detected. The sites contaminated with TCE and PCE were mainly distributed in Vega Alta and Dorado counties where the Superfund site “Vega Alta Public Supply Wells” is located. The release of TCE was documented in Manatí by Du Pont Electronics Microcircuits ITS Industries LTD. The documented amounts of TCE released were around 5,000 kg per year in the 1980s, and then decreased to 1,600 kg per year until 1997. The spatiotemporal distribution patterns showed a considerably decreasing trend of TCE concentrations, but there were still detections and contaminations of TCE in 2012 (Fig. 4). It is also noted that there were detections of TCE in areas where no known sources (Superfund, RCRA, or landfill sites) nearby, which may point to undocumented sites, unidentified waste disposals or accident spills. Otherwise unexplained CVOC contamination of the low level values may be caused by sample contamination, well equipment, residential septic system and drain fields. Note the concentrations of TCE and PCE were strongly correlated ($r=0.93$, $p<0.0001$, $n=82,071$), but the concentrations of TCE were about an order of magnitude greater than PCE. This suggests that TCE did not form from the degradation of PCE but came largely from the source release. A similar phenomenon was reported by Kurtzman et al. (2012) for sequential multilevel data from a contaminated Mediterranean coastal aquifer. The fact was coincident with the distribution patterns of the ternary plot PCE-TCE-DCE (Fig. 5b). Most of the data were located near the corner of TCE. There was a high coexistence tendency for PCE and TCE, a medium coexistence tendency for TCE and DCE, and an insignificant tendency for PCE and DCE. Pecoraino et al. (2008) also suggested there might be common origins of the contaminants due to human activities in groundwater of Sicily, Italy.

The temporal patterns of TCE concentrations near the source location (i.e. Vega Alta Industrial Park) of “Vega Alta Public Supply Wells” varied from site to site (Fig. 6). These sites in Fig. 6 are located in the unconfined limestone karst aquifer in the Vega Alta County, which is bounded by the Atlantic Ocean coast in the north, the river Rio de la Plata in the west and the river Rio Indio in the east (Renken et al., 2002; Ghasemizadeh et al., 2014). This karst aquifer is a typical eogenetic limestone terrain with moderately karstified formation containing unknown preferential flow path and complex network of fractures, conduits and channels. In Vega Alta aquifer, the flow path is roughly northeast (Sepulveda, 1996; Lugo et al., 2001) and toward the deeper aquifer (Ghasemizadeh et al., 2014). TCE concentrations at sites closer to the source area (Sites 1, 3, 4, and 5) decreased consecutively in the study period. This decreasing trend of TCE concentrations reflected the source depletion activities, natural attenuation and hydrologic transport. In contrast to site 1, TCE concentrations in Site 2 increased over time. Note that Site 2 was underneath Site 1, which indicates that downward TCE transport toward deeper aquifer is one of the reasons of the increasing trend in concentrations at Site 2. Site 3 is closer to the Superfund site (Vega Alta Public Supply Wells) but Site 1 is very close to the TCE release source, which is an industrial park on the right of the Superfund site (Lugo et al., 2001). The concentrations of TCE at Sites 6, 8 and 9 were all less than the MCL ($<0.005 \text{ mg L}^{-1}$). Concentrations at these sites may be affected by the hydrological conditions after a recent rainfall, measurement precision, or variation in sample collection methods. The temporal TCE concentrations at Sites 7, 10 and 11 initially increased to peak concentrations and subsequently decreased slowly. This temporal pattern indicates that TCE was accumulated at these locations because initially greater amounts of TCE from the source zones were carried to and stored in these sites than the amount transported away, then a lesser amount of TCE was introduced to these sites due to source depletion. The TCE time series after 1995 in Site 10 is similar to that in Site 1 though in lower magnitudes, suggesting the presence of a discrete preferential path for low dilution of TCE during the plume transport (Kurtzman et al., 2005). There were no clear temporal variations of TCE concentrations at Site 12, which indicated that this site was, to a lesser degree, affected by water flow causing transport of TCE from the source zone to the sampling well. Finally, TCE concentrations at sites further from the source area (Sites 13, 14 and 15) increased consecutively during the study period. This pattern indicated that the attenuation rate of TCE at these sites was smaller than the enriching rate of TCE due to hydrological transport of contaminant from the source zones and the in-situ releasing of the stored contaminant. Moreover, Site 15 is more contaminated than Sites 13 and 14 which are located at different depths at the same location. With northeastern movement of TCE plume, concentrations in Site 13 increased gradually over time. However, Site 15 is located at the right of the TCE plume and is affected only after the plume had progressed enough (after 2005), which may further confirm the anisotropy of the karst aquifers.

4. Conclusion

The karst aquifers in northern Puerto Rico were historically contaminated by various CVOCs. The most detected CVOCs include TCE, PCE, CT, TCM, and DCM. All the seventeen CVOCs were detected at concentrations exceeding DLs and MCLs. There was a correlation between occurrences of parent CT and daughter products (TCM and DCM),

suggesting the highest coexistence between CT and TCM. Our analysis shows a decreasing trend in concentrations and general northward movement of the contaminants. We also noted that there may be undocumented landfill sites, accidental spills, unidentified waste disposals, or residential septic systems because CVOCs were also detected beyond the known source extent. The spatial and temporal distribution patterns of the CVOCs in the karst aquifers were largely related to the hydrogeological conditions of the karst (intrinsic properties of the karst and the biological environment) in addition to the source origin. There are still areas that are contaminated, such as sites near “Upjohn” as well as areas that have not been surveyed in this study. The long-term persistence of the contaminants in the aquifers has already significantly impacted both society and environment; for example, the use of groundwater as a source of public water supply in the study region was discontinued as of 2005 (Molina-Rivera et al., 2008). Monitoring of the CVOC concentrations should be continuous and more ubiquitous, and the impacts of CVOCs on the sustainability of water resources in Puerto Rico should be further evaluated.

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Highlights

- The eogenetic karst of north Puerto Rico is heavily affected by CVOCs historically.
- The contamination of CVOCs showed two spatial clusters near Superfund sites.
- CVOC concentrations decreased considerably over time.
- CVOCs were detected to spread northward and also beyond known source extent.
- Spatial distributions of COVCs depend on source origin and karst characteristics.

Fig. 1. Site location maps of Puerto Rico (upper left panel), study area (upper right panel), Resource Conservation and Recovery Act (RCRA), National Priority List (NPL) Superfund sites, aquifers, and the sampling wells (lower panel). The four rivers in the upper right plot refer to Rio Grande de Arecibo, Rio Grande de Manatí, Rio Cibuco and Rio de la Plato (from west to east), and the high and low values represent elevation ranges (unit: m). The Superfund site number for Upjohn and Vega Alta were 2 and 8 respectively.

Fig. 2.
Site sampling frequencies for the most frequently detected CVOCs.

Fig. 3.

The spatiotemporal patterns of the total CVOC concentrations. Due to the notably irregular sampling patterns, site distributions, highly skewed data, and heterogeneous hydrogeological conditions, concentrations in some areas especially in the south may not be accurate.

Fig. 4. The spatiotemporal distribution of historically measured CT (plots above the horizontal line) and TCE (plots below the horizontal line) concentrations.

Fig. 5.

a) Ternary plot of CT-TCM-DCM; b) ternary plot of PCE-TCE-DCE, where DCE referred to 1,1-DCE.

Fig. 6. Temporal variation trends of TCE concentrations at sites near Superfund site “Vega Alta Public Supply Wells”. The temporal plots referred to the relationships between TCE concentrations (y-axis; unit: mg L^{-1}) and date (x-axis; unit: year). Sites 1 and 2, sites 3, 4 and 5, sites 6 and 7, sites 10 and 11, and sites 13 and 14 were located in the same locations respectively but in different elevations. The different colors represent different aquifer types as shown in Fig. 1.

Table 1

Information of the Superfund sites in the study region summarized from US Environmental Protection Agency (EPA).

Site	No	Enlisted year	County	State	Contaminant
Pesticide Warehouse I	1	2006	Arecibo	Active	Pesticides (DDE, Dieldrin, Aldrin, Endrin, Chlordane, Diuron, Heptachlor
Pharmacia & Upjohn	2	1984	Barceloneta	Active	Carbon Tetrachloride, Acetonitrile, metals
RCA del Caribe	3	1983	Barceloneta	Inactive	Ferric chloride, metals- Cr, Be, Se, Fe
Barcloneta Landfill	4	1983	Florida	Inactive	VOCs (DCA, DCE, TCE, Chloroform), metals(Hg, Ni, Cr), DEHP
Pesticide Warehouse III	5	2003	Manatí	Active	Pesticides (Malathion, Diuron, Toxophene, Heptachlor, Aldrin, Dieldrin, Encrin, Chlordane, Phthalate (DEHP)
V&M/Albaladejo	6	1996	Vega Baja	Inactive	Heavy Metals (Sb, Cd, Cu, Ag, Pb)
Vega Baja Solid Waste Disposal	7	1999	Vega Baja	Active	Heavy metals (As, Pb, Cr, Chloroform, Mn), Chloroform, phthalates
Vega Alta Public Supply Wells	8	1984	Vega Alta	Active	VOCs (TCE, TCA, PCE, DCE, DCA)
Scorpio Recycling, INC	9	2000	Toa Baja	Active	Metals (Pb, V, Ba, Cr), TCE, DEHP
Naval Security Group Activity	10	1989	Toa Baja	Inactive	Paints, solvents, waste oil, battery acid, pesticides, PCBs, metals -arsenic, lead

Table 2

Types, short names, maximum contamination levels (MCL), total sampling site frequencies (F_s), site frequencies with concentrations above zero (F_a), above detection limit (F_d), and above MCL (F_c), mean and median concentrations (mg L^{-1}), and concentrations coefficients of variation (CV%).

CVOC	Name	MCL	F_s	F_a	F_d	F_c	Mean	Median	CV
Chloroethane	CA	0.012 *	480	298	175	22	0.0008	0.00025	8.7
Carbon tetrachloride	CT	0.005	615	366	222	58	0.0543	0.00025	8.9
Chloromethane	CM	0.0027 *	480	282	170	25	0.0009	0.00025	8.4
Methylene Chloride	DCM	0.005	615	338	252	102	0.0017	0.00025	6.3
Tetrachloroethylene	PCE	0.005	615	390	233	60	0.0019	0.00025	5.9
Trans-1,2-dichloroethylene	trans-1,2-DCE	0.1	615	308	184	43	0.0010	0.00025	7.5
Trichloroethylene	TCE	0.005	615	377	267	162	0.0436	0.00050	7.1
Chloroform	TCM	0.07 **	615	422	358	129	0.0026	0.00025	6.3
Vinyl Chloride	VC	0.002	615	299	173	23	0.0008	0.00025	8.9
Cis-1,2-dichloroethylene	cis-1,2-DCE	0.07	610	273	137	35	0.0022	0.00025	7.3
1,1,1,2-Tetrachloroethane	1,1,1,2-TeCA	0.001 *	475	273	129	22	0.0008	0.00025	9.1
1,1,1 Trichloroethane	1,1,1-TCA	0.2	480	319	159	27	0.0010	0.00025	9.3
1,1,2,2-Tetrachloroethane	1,1,2,2-TeCA	0.001 *	480	296	173	20	0.0008	0.00025	8.7
1,1,2-Trichloroethane	1,1,2-TCA	0.005	615	299	172	22	0.0008	0.00025	8.7
1,1-Dichloroethane	1,1-DCA	0.005	480	306	184	34	0.0011	0.00025	7.4
1,1-Dichloroethylene	1,1-DCE	0.007	480	305	194	59	0.0037	0.00025	12.6
1,2-Dichloroethane	1,2-DCA	0.005	615	300	175	24	0.0006	0.00025	8.6

Note

***HBL: water health based limits. All these standards were considered as MCL in this study.

* HAL: health advisory level

** MCLG: maximum contaminant level goal