SPATIOTEMPORAL RESPONSE OF CVOC CONTAMINATION AND REMEDIAL ACTIONS IN EOGENETIC KARST AQUIFERS

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Abstract

The northern karst region of Puerto Rico has a long and extensive history of toxic spills, chemical waste, and industrial solvent release into the subsurface. High potential for exposure in the region has prompted aggressive remediation measures, which have extended for over 40 years. Of particular concern is contamination with chlorinated volatile organic compounds (CVOCs) because of their ubiquitous presence and potential health impacts. This work evaluates historical groundwater quality data to assess the spatiotemporal distribution of CVOC contamination in the karst aquifer system of northern Puerto Rico, and its response to remedial action in two superfund sites contaminated with CVOCs. Historical data collected from different information sources with different monitoring objectives is evaluated spatially and temporally using Geographic Information System (GIS) and statistical analysis. The analysis shows a significant extent of contamination that comes from multiple sources and spreads beyond the demarked sources of pollution. CVOCs are detected in 65% of all samples and 78% of all sampled wells. Groundwater shows continued level of contamination over long periods of time, demonstrating a strong capacity of the karst groundwater system to store and slowly release contamination. Trichloroethene and Tetrachloroethene are the most frequently found, although other CVOCs (e.g., Trichloromethane, Dichloromethane, Carbon Tetrachloride) are detected as well. The spatial and temporal distributions of CVOCs seem to be highly dependent upon the monitoring scheme and objectives, indicating that the data does not adequately capture the contamination plumes. Targeted remedial action using pump and treat (air stripping) and soil vapor extraction in two superfund sites has reduced concentrations over time, but the spatial and temporal extent of the contamination reflect inability to completely capture the heterogeneous plumes.

Introduction and Background

The northern karst region (Figure 1) contains two of the most extensive and productive freshwater aquifers in Puerto Rico (Lugo et al., 2001). These aquifers promote industrial, agricultural, and population growth (PRDNER, 2008), and contribute to the ecological integrity of the rivers, springs, wetlands, and estuaries (Padilla et al., 2011).

The northern karst aquifer system comprises three major hydrogeological units (Figure 1): the upper aquifer, which is mainly composed of the Aymamon and Aguada Limestone Members; the lower aquifer, which is formed by the Lares and Montebello Limestone Members; and a confining unit that separates the upper and lower aquifer, which is comprised by the Cibao formation. (Renken et al., 2002). The upper aquifer is unconfined and also linked to the surface throughout most of its outcrop area. The lower aquifer is confined toward the coastal zone and outcrops to the south of the shallow aquifer, where it is recharged. The outcrop extents are much more vulnerable to contamination due to direct interaction with the surface.

The karst aquifers of northern Puerto Rico have developed in carbonate rocks that have not undergone deep burial and are under active meteoritic diagenesis, thus considered eogenetic aquifers (Vacher and Mylroie, 2002). In addition to well-developed conduit networks, these aquifers have high primary porosity and permeability and significant flow components through the rock matrix. As a result, both conduit and matrix flow contribute flow in these aquifers. These flow characteristics allow for extensive water production from the aquifers and make the systems highly vulnerable to pollution (Göppert and Goldscheider, 2008). The highly heterogeneous distribution of flow characteristics in karst systems also imparts an enormous capacity to store and convey contaminants from sources to potential expo-

sures zones. Consequently, karst aquifers may serve as an important route for long-term contaminant exposure to humans and wildlife.

The northern karst region of Puerto Rico has had a long and extensive history of toxic spills, chemical waste, and industrial solvent release into the subsurface (Padilla et al., 2011; Hunter and Arbona, 1995; Zack et al., 1987).

Liquid-waste was also injected into the confined aquifer system prior to the 1970s (Zack et al., 1987). After 40 years of high potential exposure and remediation measures, pollution persists. Since 1983, twelve superfund sites, which comprise 55% of all superfund sites on the island and 13 Corrective Action (RCRA CA) sites have been included in the study area (Figure 1). Several types of contaminants have been detected at superfund sites in Puerto Rico, including: chlorinated volatile organic compounds (CVOCs), pesticides, heavy metals, and contaminants of emerging interest, such as pharmaceuticals and phthalates. Of particular concern are the CVOCs due to their ubiquitous presence in the environment, potential for exposure, and health impacts. CVOCs are present in 58% of superfund sites in the study area, and include: Trichloroethene (TCE), Tetrachloroethene (PCE), Chloroform (Trichloromethane, TCM), Carbon tetrachloride (CCl_4), Methylene Chloride (DCM), 1,1-Dichloroeth-

ane (1,1-DCA), 1,1-Dichloroethylene (1,1-DCE), and 1,2-Cis-dichloroethylene (cis 1,2-DCE). These pollutants are commonly used as industrial solvents, degreasers, and paint removers; and have been known to cause cancer and reproductive problems (ATSDR, 2011).

This work evaluates historical groundwater quality data to assess the spatiotemporal distribution of CVOC contamination in the karst aquifer system of northern Puerto Rico (Figure 1) and its response to remedial action in two superfund sites: The Upjohn Company (UJ) and Vega Alta Public Supply Wells (VA-PSWs). Historical data collected from different information sources was evaluated spatially and temporally using GIS and statistical analysis.

In 1982, the Upjohn Company reported a 57.92m³ accidental spill of CCl_4 from an underground storage tank (USEPA, 1984). Shortly after the incident, the company installed monitoring wells in the surroundings, established recovery well for CCl_4 extraction, and provided an alternative water supply to the population. The UJ facility was listed in the Superfund sites in 1984. In 1985, the tank farm area was covered with fiber glass-reinforced concrete to contain the contamination and prevent the infiltration into the subsurface. A total of 45.42 m³ (78.4% of total reported volume) of CCl_4 had been removed by

Figure 1. Hydrogeology of Puerto Rico and associated superfund, RCRA CA, and landfill sites (Irizarry, 2014; Torres, 2013).

1985 using 19 vacuum extraction wells in the soil and a groundwater extraction well installed down gradient of the spill area (USEPA, 1988). The company ceased CCl_4 use and applied a pump and treat technology with air stripping water treatment (1988). Recent 5-year evaluations and review reports suggest that potential human exposure is under control (USEPA, 2014).

In 1983, the United States Geological Survey (USGS) reported TCE and PCE contamination (Guzmán and Quiñones, 1984) in the Puerto Rico Aqueduct and Sewer Authority (PRASA) wells of the Vega Alta region. Although the time of contaminant release is unknown, it is suspected that contamination had been present for a long time. The VA-PSWs site was listed in 1984 in the Superfund program, and an air stripper was immediately installed in one of the PRASA wells, which operated only until 1985 due to technical problems. In 1987, EPA selected the following actions: closure of private wells within the contaminated area; investigation of contamination sources; water softening pretreatment of PRASA wells; and installation and operation of 4 air strippers. The treated effluent was to be discharged to the PRASA distribution system for public use and to Honda creek. The groundwater treatment started in 1994, but due to changes in pumping conditions the plume of the contamination was no longer captured by the treatment wells and the EPA required the installation of extraction wells for treatment in a new location. Remedial actions, including pump and treat and soil vapor extraction (SVE) in the source, began operations in 2002 (almost 20 years after pollution was reported). Since December 2002, approximately 75,708 m^3 of water has been treated each month (USEPA, 2014).

Data Collection and Analysis

Historical and spatial groundwater quality data were compiled to assess the CVOC contamination in the karst aquifers of northern Puerto Rico. The study area (Figure 1) extended from the municipalities of Toa Baja and Toa Alta on the east to the Municipality of Arecibo on the west. Water quality data included temporal CVOC concentrations spanning from 1982 through 2013 in the study area. Historical data was collected from different information sources with different scope and monitoring objectives. Water quality, site information, and site location were collected from: Steele (2011), U.S. Geological Survey data base (USGS, 2008) and reports (Guzmán, et al., 1986; Guzmán and Quiñones, 1984; Guzmán and Quiñones 1985; Sepulveda, 1999; Conde and Rodríguez, 1997), EPA data base (USEPA, 2008), Caribbean Environmental Protection Agency (CEPA) local office, Puerto Rico Environmental Quality Board (PREQB) (PREQB, 2011), University of Puerto Rico at Mayaguez (UPRM),

and Puerto Rico Department of Health (PRDoH). Data from EPA included water quality results from superfunds and RCRA CA sites in the study area (Figure 1). The PRDoH data included water quality for PRASA and NON-PRASA drinking water systems. PRASA data included water quality for point water sources in the distribution system, and was collected quarterly for compliance with drinking water regulations. NON-PRASA drinking water systems have been defined as those that are not supplied by PRASA and contain more than 25 people and 5 connections; most of this data came from industries. Data from the PREQB included water quality measurements from their monitoring stations (Steele, 2011), but they only had a few monitoring wells within the study area and the records were for a brief period of time. The PREQB, superfund division provided some special monitoring events of Scorpio Recycling and limited amount of data from Pesticide Warehouse I. Since 2011, the UPRM has been collecting current groundwater samples from 17 wells in the study area twice a year. The samples have been analyzed for target contaminants and the results have been entered into a database. Once collected, data is classified and categorized into data characteristics representing categories and indices used to describe historical distribution of contaminants in the area of study. Characteristic parameters include: aquifer system (lower, upper), contaminant presence (or absence) and concentration ranges, contaminant types (e.g., chlorinated hydrocarbons, phthalates), detection limits, and information source (e.g., UPRM, USGS, EPA, Reports).

Spatial analysis was performed using GIS technologies (ArcGIS 10.1; ESRI 2012). Spatial distributions of CVOCs were analyzed as average detected concentrations over a period of time for the unconfined karst aquifer system of northern Puerto Rico. Although contamination has been detected in the confined aquifer, this work focuses on the unconfined system because of its direct connection to the surface. Average concentration distributions were developed for individual species and total CVOCs, defined herein as the sum of TCE, PCE, CCl_4 , TCM, and DCM average concentrations. These species are among the five major CVOCs found in the northern karst region. Isotropic interpolation of concentrations using the Inverse Distance Weighted (IDW) method produced raster spatial distributions of the contaminants. The interpolation method did not, however, take into account groundwater flow direction. Basic statistical analysis was performed to obtain contaminant detection frequencies for groundwater samples and groundwater sites in reference to the total number. Groundwater sites refer to sampling sites (wells/springs). Because many groundwater sites have multiple temporal measure-

ments, the number of groundwater samples is greater than the number of sites. Differences in their basic statistical characteristics reflect on the detection variability within each site.

Results and Discussion

Analysis of the data indicates widespread presence of CVOC contamination in the study area (Figure 2) during the 31-year period between 1982 and 2013 (Figure 3). Temporal distributions data (Figure 3a) shows a high percentage of detection over the period of analysis, with 90% of samples surpassing 50% detection on a yearly basis. Similar temporal trends are observed for detection in groundwater sites, except with higher detection frequencies than groundwater samples. Over the entire period of analysis, CVOCs were detected in 65% of all groundwater samples (Figure 3. Total numbers of CVOCs samples and detections per year (a) (Irizarry, 2014) and overall percent detection of CVOC by number of samples (b) and wells (c) for the period of analysis.b) and 78% of all sampled groundwater sites (Figure 3c). Lower detection frequencies of groundwater samples over groundwater sites reflect temporal detection variability at sampling sites and indicate that some sites had both detection and no-detection of contaminants. This behavior is indicative of dynamic fate and transport processes that affect the rate at which contaminants reach potential exposures points.

The most prevalent CVOCs in the study area is TCE (52.5%), followed by PCE (39.0%), 1,1-DCE (30.4%), cis1,2-DCE (30.2%), CCl_4 (26%), TCM (22%), 1,1-DCA (15.3%), and DCM (9%). The detection distribution among the different CVOCs is generally associated with major sources of contamination, although data analysis suggests other potential sources of CVOC contamination. Some CVOCs may also be formed by degradation (e.g., DCE, TCM, DCM) or disinfection processes (e.g., disinfection-by-products, DBPs, such as TCM). The highest CVOC concentration is for CCl_4 , followed by TCE, 1,1-DCE, TCM, DCM, and PCE. TCE shows higher number and percentage of samples above MCL, followed by CCl_4 , PCE, 1,1-DCE and DCM.

CVOC Spatiotemporal Distribution

Spatial distributions of TCE, CCl_4 , TCM, and total CVOCs over the entire period of analysis (1982-2013) show widespread contamination of CVOCs in the study area that extend beyond known sources of contamination (Figure 2). Although generally detected over the entire area of study, high percent detection and concentrations of TCE (Figure 2a) are associated with the VAPWS superfund site, whereas those for CCl_4 (Figure 2b) are associated with the UJ site. Presence of CVOCs in other areas indicates other potential sources of CVOC contamination, including the formation of degradation and disinfection by-products. The spatial concentration

Figure 2. Spatial Concentration Distribution for TCE (a), CCl_4 (b), TCM (c) and total CVOCs (d). (Irizarry, 2014).

Figure 3. Total numbers of CVOCs samples and detections per year (a) (Irizarry, 2014) and overall percent detection of CVOC by number of samples (b) and wells (c) for the period of analysis.

distribution of TCM (Figure 2c) shows that this contaminant is found widely distributed throughout the study area. The highest TCM concentrations are found near the UJ site and near the Naval Security superfund site in the Toa Baja area. These high concentrations are most likely associated with the CCl_4 contamination, either as an additional source or as a degradation by-product of CCl_4 . The widespread presence of TCM may also be attributed to other potential sources of contamination, as well as its formation as a disinfection by-product. Spatial concentration distributions of total CVOCs (Figure 2d) show widespread contamination of CVOCs over the study area.

Temporal concentration distributions of TCE in a well near the VA-PSW superfund site (Figure 4) and CCl_4 in a well near the UJ site (Figure 5) show an overall decrease-

ing trend. The decrease is mostly associated with active remediation activities of the major superfund sites, but is also due to degradation processes. Degradation of TCE and CCl_4 is reflected in the increasing concentrations of their degradation by-products, DCE (Figure 4) and TCM (Figure 2c) near the VA PWS and UJ superfund sites, respectively. It is important to note that, even under active remediation, concentrations have not reached regulatory levels and a significant number of samples still have concentrations above the maximum contaminant level (MCL).

Spatiotemporal data of total CVOC concentrations show widespread CVOC distributions that vary in space and time (Figure 6). The variability of CVOC spatiotemporal distributions is attribute to: (1) changes in contamination input sources; (2) dynamic fate and transport processes;

Figure 4. Temporal distribution of TCE and DCE concentrations in a Vega Alta well.

Figure 5. Temporal distribution of CCl_4 concentrations in an Upjohn well (Irizarry, 2014).

Figure 6. Spatial Distributions of Total CVOC Concentrations for 1984 (a), 1990 (b), 1996 (c), 2000 (d), and 2009 (e) (Irizarry, 2014).

(3) variation in remedial and monitoring schemes; (4) differences in spatial and temporal data resolution; and (5) changes in groundwater use. Changes in contaminant input result from addition or removal of contaminated sites. Fate and transport processes (e.g., advection, dispersion, sorption, degradation, mass transfer) affect the mobility and persistence of the contaminants. In karst systems, these processes are influenced by the mode of transport (i.e., conduit vs. diffusive flow) and by the heterogeneities of the systems. As a result, fate and transport processes are also influenced by time-dependent

hydrogeological conditions. Changes in water extraction practices driven by hydrological and water quality conditions further accentuate the variability in spatiotemporal concentration distributions. The effect of monitoring scheme and data resolution (density) variations on the apparent spatiotemporal concentration distribution can be observed when comparing spatial concentrations distributions for different years. Total CVOC concentration distributions for 1990 (Figure 6b) appear to be of lower extent and concentration ranges than that for 1984 (Figure 6a), suggesting a decrease in the contamination

plume. Comparison of the 1990 distributions with 1996 and 2000 (Figure 6c and 6d), however, show a stronger and much widespread contamination at a later time. The apparent increase is not caused by higher contamination, but by an increase in the amount of spatial data available for the analysis from the period between 1993 and 2000, which showed the greatest amount of data collected (Figure 3a). Changes in monitoring well locations also captured higher concentrations near the VA-PWS superfund site that were previously unnoticed. The smaller extension of the contamination in 2009 (Figure 6e) is not only attributed to decreasing concentrations due to natural attenuation and remediation, but also to the lower amount of data resolution available. This data shows that the difficulty in defining concentration distribution patterns in karst region result from, not only the complex processes influencing the mobility and persistence of contaminant, but also the observation and management schemes of the contaminated sites.

Response to Remedial Action

The response of eogenetic karst aquifers to remedial actions is evaluated with respect to two superfund sites in northern Puerto Rico: the UJ and VAPSW superfund sites. These sites, although not representative of all sites in eogenetic karst systems, have been subjected to extensive temporal and spatial contamination, and provide valuable information regarding factors influencing the distribution and cleanup of contamination. Spatial concentration distribution of TCE (Figure 2a), CCl_4 (Figure 2b), and Total CVOCs (Figure 2d and 6) show that the contamination extended beyond demarked superfund sites. Extensive spatial contamination is attributed to rapid transport through conduit networks of heterogeneous character, and to the lack of rapid response to characterize, monitor, and remediate the sites. This can be seen when comparing CVOC concentration distributions associated with the VA-PWS and UJ superfund sites. Both sites show contamination extending kilometers beyond the delineated superfund sites, long temporal tailing distributions, and high capacity to store and slowly release contamination over long periods of time. Long tailing is associated with mass transfer limitations and heterogeneous distribution of variable-capacity transport regions and storage compartments for contaminants in the eogenetic karst system. The TCE concentration distribution (Figure 2a) related with the VA-PWS site, however, shows a more extensive contamination area than that of CCl_4 (Figure 2b) associated with the UJ superfund site. Although contamination in both of these sites was reported at about the same time (1982-1983), it is suspected that contamination in the VA-PWS site occurred long before it was reported. Monitoring and remediation efforts in this site were implemented long

after the contamination occurred. Poor characterization and monitoring efforts, in conjunction with the hydrogeological complexity of the VA-PWS site, resulted in transport areas of unknown concentrations. Some of these areas were discovered at later stages of the remedial action implementation. Rapid response to contamination events in the UJ site, on the other hand, incited prompt implementation of site characterization, monitoring, and remediation activities. As a result, the areal extent of the UJ-related contamination was smaller than of the VA-PWS. The rapid response in the UJ site also resulted in a faster decrease of CVOC initial concentrations than in the VA-PWS site, at which concentrations are still at concerning levels (Figure 4 and 5). Comparative analysis of remedial response actions for the UJ and VA-PWS superfund sites indicate the importance of proper site characterization and design of monitoring scheme, particularly for complex sites, such as those in karst systems.

Conclusions

Analysis of the historical contamination data in the northern karst groundwater system shows a significant extent of contamination that comes from multiple sources and extends beyond the demarked sources of contamination. Groundwater quality data shows sustained level of contamination over long periods of time, suggesting that the complexity and the heterogeneity of the karst give the system a strong capacity to store and slowly release contamination. Spatial and temporal distributions of CVOCs show to be highly dependent upon the site characterization, monitoring scheme and objectives, indicating that the data does not adequately capture the contamination plumes. Although the selected remedial action (pump and treat combined with air stripping and soil vapor extraction) in two superfund sites has reduced concentrations over time, the spatial and temporal extent of the contamination reflect inability to completely capture the heterogeneous plumes in the complex karst system. The comparison and contrast of the initial response time in two superfunds shows the early response of remediation results in a rapid reduction of the contaminants concentration and more control in the extent of the contamination plume.

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