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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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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.

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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.

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 (Sonnenfeld 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

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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's ice-free continental surface and the conterminous US (both up to 20% of the total area; Ford and Williams, 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 the 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 (Kačaroğlu, 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 and Gómez-Gómez, 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, 1995; 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 (Rodríguez-Martinez, 1995) compared to the well-developed karsts in Europe (Greece, Panagopoulos, 2012; Romania, Oraseanu and Mather, 2000; LaMoreaux and LaMoreaux, 1998), the eastern conterminous US (Tennessee, Wolfe et al., 1997; Arkansas, Peterson et al., 2002), 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; Göppert 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: 8710 km^2) 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 km^2 which represents 44% of the total northern karst area of 850 km^2), the lower aquifer with Lares limestone and the Cibao formation (153 km^2; 18%), confining units (166 km^2; 19%) and the alluvial valley aquifer (143 km^2; 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 and Gómez-Gómez, 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: the 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 the 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