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The influence of hydrogeological and anthropogenic variables on phthalate contamination in eogenetic karst groundwater systems☆

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Abstract

This study investigates the occurrence of six phthalates and distribution of the three most-detected phthalates in the karst region of northern Puerto Rico (KRNPR) using data from historical records and current field measurements. Statistical data analyses, including ANOVA, Chi-Square, and logistic regression models are used to examine the major factors affecting the presence and concentrations of phthalates in the KRNPR. The most detected phthalates include DEHP, DBP, and DEP. At least one phthalate specie is detected above DL in 7% of the samples and 24% of the sampling sites. Concentrations of total phthalates average 5.08 ± 1.37 μg L^{-1}, and range from 0.093 to 58.4 μg L^{-1}. The analysis shows extensive spatial and temporal presence of phthalates resulting from dispersed phthalate sources throughout the karst aquifers. Hydrogeological factors are significantly more important in predicting the presence and concentrations of phthalates in eogenetic karst aquifers than anthropogenic factors. Among the hydrogeological factors, time of detection and hydraulic conductivities larger than 300 m d^{-1} are the most influential factors. Persistent presence through time reflects continuous sources of phthalates entering the aquifers and a high capacity of the karst aquifers to store and slowly release contaminants for long periods

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Appendix A. Supplementary data
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of time. The influence of hydraulic conductivity reveals the importance of contaminant fate and transport mechanisms from contamination sources. This study improves the understanding of factors affecting the spatial variability and fate of phthalates in karst aquifers, and allows us to better predict their occurrence based on these factors.

Keywords

Groundwater contamination; Phthalates; Karst aquifers; Logistic regression model

1. Introduction

Phthalate acid esters, also known as phthalates, are widely used in many consumer products (U.S. EPA, 2012; Zota et al., 2014). High molecular weight phthalates, such as Di-(2-ethyl hexyl) phthalate (DEHP), butyl benzyl phthalate (BBP), and di-*n*-octyl phthalate (DnOP), are used as plasticizers to impart flexibility and durability to plastics (Stanley et al., 2003; Godwin, 2010). DEHP is among the most frequently used plasticizers in the market (Stanley et al., 2003), and is commonly used in flooring tiles, hoses, paint lacquers, medical devices and materials, shoes, food and beverage packaging, and wiring cables (Godwin, 2010). Low molecular weight phthalates, such as di-*n*-butyl phthalate (DBP), di-ethyl phthalate (DEP) and di-methyl phthalate (DMP), are commonly used as solvents in many consumer products and pharmaceuticals (Stanley et al., 2003) to help solubilize necessary ingredients or in application of the product (Godwin, 2010). They are commonly used in cosmetics creams, fragrances, candles and shampoos, among other uses. Because phthalates are not chemically bound to plastics (Navarro et al., 2010) and other phthalate-containing products, they can be released in the environment. Exposure to phthalates may occur by ingestion, inhalation and dermal exposure, and could pose a serious threat to human health (Latini, 2005; Schettler, 2006; Wittassek et al., 2011).

The toxicity of phthalates depends on the chemical structure, time of exposure and life stage (Howdeshell et al., 2008), and may include endocrine disruption (Ponzo and Silvia, 2013), male reproductive system malformation, and developmental impairment (Gray et al., 2000; Lyche et al., 2009; Braun et al., 2013). Because of their toxicity, prevalence in the environment, widespread use, and potential human exposure, phthalates are of particular concern. The US Environmental Protection Agency (U.S. EPA) includes 6 phthalates as priority pollutants for the current management plan: DEHP, BBP, DBP, DnOP, DEP, and DMP (U.S. EPA, 2012). Therefore, it is imperative to document the concentration distributions of phthalates, evaluate occurrence patterns, and examine factors controlling the presence of phthalate in the environment.

Widespread use and the relatively long residence times result in ubiquitous presence and long-term potential exposure of phthalates in aquatic systems. Presence of phthalates in water systems has been reported worldwide, both in rural and urban surface waters (Hashizume et al., 2002; Wang et al., 2008; Sirivithayapakorn and Thuyviang, 2010; He et al., 2013; Sun et al., 2013; Domínguez-Morueco et al., 2014; Zheng et al., 2014). Fewer studies have reported their presence in ground water. Liu et al. (2010) reported DEHP and total phthalate concentrations of 0.1 μg L^{-1} and 6.35 μg L^{-1}, respectively, in wells impacted by landfill leachate in Wuhan, China. Sorensen et al. (2015) reported DEHP (dry season: 22 μg L^{-1}; wet season: 5 μg L^{-1}) and total phthalate (dry: 45 μg L^{-1}; wet: 5.1 μgL^{-1}) concentrations in urban groundwater in Africa. Huang et al. (2012) and Zhang et al. (2009) reported presence of multiple phthalates in different areas of China, with total phthalate concentrations ranging from no detection to 6.7 μg L^{-1}. DEHP and DBP were the most detected phthalates, and their source was mostly attributed to surface water.

Extensive use of phthalates results in spatially-widespread sources that are difficult to identify. Although the presence of phthalates may be related to land use patterns, their detection and concentrations in groundwater are also influenced by system characteristics. A spatial study of measured detection and concentrations provides insight into sources of contamination, extent and severity of contamination, and system vulnerability to contamination. It is, therefore, important to understand the historical and spatial patterns of phthalates in aquifers.

Because of the high potential for contamination, it is particularly important to assess phthalate contamination in eogenetic karst aquifers. These aquifers are formed by dissolution of carbonate rocks and characterized by the presence of conduits in rock matrices having high primary porosity and permeability. They are found throughout the world in islands, such as Barbados, Guam and Puerto Rico, and continental settings (Anaya et al., 2014). Strong connections between surface and subsurface features associated with sinkholes, sinking streams, caves, conduits, springs, and highly transmissive zones provide for direct recharge into karst aquifers. These characteristics make groundwater systems in karst areas highly productive and important freshwater resources for human consumption and ecological integrity of streams, wetlands, and coastal zones. These same characteristics facilitate entry of pollutants and make karst aquifers highly susceptible to contamination.

Groundwater contamination in Puerto Rico has indeed become a major problem affecting the management of water resources of the island, and has resulted in a significant decrease of groundwater use as a public drinking water source since 2005 (Molina-Rivera and Gómez-Gómez, 2008). Padilla et al. (2011) reported potential high risk of phthalate exposure due to groundwater contamination, particularly in the northern karst region. Cantonwine et al. (2014) documented prevalent detectable concentrations of phthalate metabolites among pregnant women in northern Puerto Rico. Presence of phthalate metabolites in pregnant women have previously been related to high rates of preterm birth (Meeker et al., 2009a, 2009b), and are suspected contributors to the high preterm birth in Puerto Rico (Cordero et al., 2012).

In this study, we assess the occurrence of phthalates in karst aquifers of northern Puerto Rico, explore the spatial distribution patterns of their concentrations, and evaluate factors affecting the spatial variability of phthalate detections and concentrations. It is hypothesized that: (i) widespread use of phthalates and their relative easy entry into karst subsurface environments fosters extensive distribution of these contaminants in karst aquifers of eogenetic character; and (ii) presence and concentration distributions of phthalates in karst groundwater are associated with hydrogeological characteristics, land use, and potential sources of contamination. This study, which is the first to evaluate phthalate detections and concentrations in eogenetic karst aquifers, improves our understanding of the factors affecting spatial variability and fate of phthalates in karst aquifers. It further advances our ability to predict the occurrence of phthalates in these aquifer, and provide tools to study possible link between phthalate contamination in groundwater and potential health impacts.

2. Site description

The island of Puerto Rico (PR) is located in Caribbean (Fig. 1). It has a relatively warm and humid climate with average monthly temperatures ranging from 19.4 to 29.6°C and an average annual precipitation of 1700 mm. The full year can be generally categorized as having two seasonal periods based on the amount of monthly rainfall: the wet (May through November) and dry (December through April) seasons (Cherry, 2001; Yu et al., 2015).

The karst region of northern Puerto Rico (KRNPR; Fig. 1) covers 19% of the island and contains two of the most extensive and productive freshwater aquifers in PR (Lugo et al., 2001). It contains three major hydrogeological units (Fig. 1): an upper aquifer system, a lower aquifer, and a confining unit that separates most of the upper and lower aquifer systems (Renken et al., 2002). The upper aquifer system is mostly unconfined and 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 upper aquifer, where it is recharged. Outcrop areas are much more vulnerable to contamination due to direct interaction with the surface (Padilla et al., 2015). A direct connection between the upper and lower aquifer exists along the outcrop of the confining unit, allowing groundwater flow from the unconfined parts of the lower aquifer into the upper aquifer (Torres-González et al., 1996). Groundwater flows regionally toward the north, and locally to surface streams and wetlands (Renken et al., 2002). The five major streams flowing through the KRNPR study area (Fig. 1) are hydraulically connected to the aquifer systems (Torres-González et al., 1996; Cherry, 2001). Stream density over this region is lower than the rest of the island (Fig. 1) due to the large subsurface drainage capacity of the karst and high number of sinking streams.

Sinkholes, which may serve as direct input of water and contaminants into the subsurface, are widespread in KRNPR. The density distribution of sinkholes varies spatially (Fig. 2), with the highest density generally associated with the outcrop of the upper aquifer. The KRNPR aquifers are characterized by highly variable hydraulic conductivities ranging from less than 30 to greater than 300 m d^{-1} (Renken et al., 2002, Fig. 2).

High aquifer productivity and water availability in KRNPR, among other reasons, prompted the settlement of many pharmaceutical, chemical, and manufacturing industries, with subsequent growth in population and urban development. It also fostered the development of agricultural activity. About 14% (532,350) of the island population live within the study area, which includes the municipalities of Arecibo, Barceloneta, Florida, Manatí, Vega Baja, Vega Alta, Dorado, and Toa Baja (Fig. 1). Major land uses in the region (Fig. S1) include natural land (67%), developed land (18%), waters (9%), and agriculture (6%). Developed lands incorporate 62% residential, 5% industrial, and 33% construction and other uses. Many of the settled industries have relied on the use of hazardous materials, which can enter the karst groundwater from accidental spills and deliberate disposals. Population and associated urban growth brought construction of unlined municipal landfills and clandestine waste disposal sites. Many of the clandestine sites have been developed in sinkhole depressions, which serve as a direct route of contaminants into the underlying karst formations. The unintended consequence of the industrial and urban development has therefore been an extensive contamination of the groundwater resources in the northern karst system. The degradation of this important resource has subsequently resulted in a reduction of the extraction capacity and an increase of the environmental cost of water use (Padilla et al., 2011).

The high potential for contamination in the KRNPR is reflected in a high density of Resource Conservation and Recovery Act (RCRA) and Superfund sites in the region. RCRA sites are active facilities that manage solid and/or hazardous waste. Superfund sites are highly contaminated sites that pose significant risk to the population and the environment. At this time, the KRNPR contains 291 RCRA sites (U.S. EPA, 2015a) in the area. Serious contamination with toxic chemicals has prompted inclusion of 12 superfund and 15 RCRA Corrective Action (RCRA-CA) sites in KRNPR (Fig. 1) (Padilla et al., 2011; Irizarry, 2014; Yu et al., 2015), making the study area one with the highest densities of Superfund sites in the nation (Irizarry, 2014). Eight of the Superfund sites are active, but the others could have contributed to contamination at the system level. Four of the sites (Barceloneta Landfill (1), Pesticide Warehouse III (2), Scorpio Recycling (3), and Vega Baja Solid Waste Disposal (4)) have reported phthalate contamination (Fig. 1), mostly with DBP and DEHP, although BBP, DNOP, and DEP have also been reported at the Vega Baja Solid Waste Disposal (Padilla et al., 2011; Irizarry, 2014; U.S. EPA, 2015b; Yu et al., 2015).

3. Methods

3.1. Data collection

Phthalate data were collected from both historical records and our own field sampling campaign. Historical records were obtained from various sources, including the U.S. Geological Survey (USGS), U.S. EPA, and Puerto Rico Department of Health (PRDOH) (Padilla et al., 2011; Irizarry, 2014; Yu et al., 2015). Although not all samples (n = 1803) were analyzed for all these phthalates, the data records show analyses for DEP, DBP, DEHP, BBP, DMP and DNOP. The historical survey sites include 197 well sites and 4 spring sites, with data ranging from 1981 to 2013.

Our own field sampling campaign involved collecting 201 samples in 4 springs and 17 wells (Fig. 1), and analyzing for DEP, DBP, and DEHP. The sampling sites were selected based on proximity to potential contamination sources, accessibility, and spatial representation (Irizarry, 2014). Samples and duplicates at each site were collected in the spring and fall of each year, from 2011 through 2013. The analysis of collected samples and blanks followed modified procedures of U.S. EPA methods 3510C and 8270D (Cotto, 2015; Table S1). Limitations from these procedures are provided in Table S2. Detection limits were set at the instrument detection limit (IDL), which was assumed as the lowest point in the calibration curve that the instrument measures. Generally, the IDL for phthalates was 1 $\mu g\ L^{-1}$.

Ancillary data, including hydrogeological and topographic characteristics, groundwater quality, population information, land use, and potential sources of contamination were collected for our analyses. Population data was obtained from the City Population Website (City Population, 2016). Land elevation, land use, and hydrogeology were obtained from Giusti (1978), Renken et al. (2002), USGS (2008), and Kwast et al. (2011). Seasonal variations were based on the historical rainfall patterns reported by Cherry (2001). Potential sources of contamination included Superfund, RCRA-CA, and landfill sites (Irizarry, 2014; U.S. EPA, 2015a, 2015b). Phthalate data was compiled into a central database for the Puerto Rico Testsite for Exploring Contamination Threats (PROTECT) Center in Northeastern University for current and future studies (Cordero et al., 2012).

The high diversity of data sources used in this study strengthened the analysis by increasing the number of data points. Because various agencies and institutions collected the data for different objectives, the sampling frequencies varied. This resulted in an uneven distribution of data in space and time, and uneven total numbers of samples (n) analyzed for the different target contaminants and water quality parameters: DBP (n = 295), BBP (n = 89), DEHP (n = 1995), DEP (n = 302), DMP (n = 96), and DNOP (n = 102).

3.2. Data analysis

For the analysis, detections of phthalate concentrations were grouped into four levels: not detected (ND), detected but below DL, above DL and below maximum contaminant level (MCL) for DEHP, and above MCL for DEHP. The MCL for DEHP in drinking water is 6 μg L^{-1} (U.S. EPA, 1995). MCL values for other phthalates have not been established by the U.S. EPA. DLs varied due to differences in data sources, equipment used, phthalates species, and analysis protocols and ranged from 0.03 to 22 μg L^{-1}. We used the DLs reported in the data, for both the historical data sets and our own field data.

Principal factors affecting the variability of phthalate distribution were analyzed from two perspectives: hydrogeological factors (time, hydraulic conductivity, elevation, sinkhole density, aquifer system, and seasonality), and anthropogenic (population, land use, and potential sources of contamination). Hydraulic conductivity distributions and sinkhole density (Fig. 2) were used to estimate values at each sampling site. Correlation with phthalate distributions were based on categorical analysis for hydraulic conductivities (<30, 30–300, and >300 m d^{-1}), sinkhole density (<1, 1–10, 11–20, and >21%), population (increments of 25,000 persons), population density (increments of 300 persons per km^2), and topographical elevation (increments of 50 m). Seasonality analysis was based on the time of sample collection in relation to historically wet and dry seasons. The effect of land use on phthalate contamination was evaluated by extracting the major land use within a 1.6-km radius buffer at each sampling site using ArcMap 10.4. The information was extracted from a 2010 land use map (Kwast et al., 2011) with respect to 4 categories: water coverage, natural, developed, and agriculture. We also applied a proximity analysis to known potential sources of contamination, including Superfund sites, RCRA-CA sites, and landfills. The proximity analysis involved creating 1.6, 3.2, 4.8, 6.4, and 8-km radius buffers around each potential source of contamination, and calculating the number and percent detection of phthalates downstream of the site for each radius buffer along distance intervals of 1.6 km.

For spatial analysis, we applied Inverse Distance Weighting (IDW) method of interpolation using the Spatial Analyst Tool in the software ArcMap 10.4. Average concentrations at each site were used to perform the spatial interpolation analysis. They were calculated using all concentrations above DL for each well/spring site having at least one detection for the period of analysis. Samples having concentrations below detection limit were considered as ND, and were not included in the average calculations. Wells and springs having ND throughout the entire analysis period were considered to have zero concentration. The IDW method was applied for sites located in the upper aquifer and lower aquifer separately. The southern and northern physical boundaries were integrated as zero concentration data points because the aquifers do not extend beyond these limits. The coastal line was delineated as the northern boundary. The southern boundary was delineated as the southern limit of the lower aquifer outcrop (i.e., contact between volcanoclastic/rock and the limestone lower aquifer; Fig. 1).

Multiple statistical methods were applied to examine phthalate detection and concentration distributions, and assess principal factors influencing their distributions. DEHP was used as the main phthalate species to perform temporal and statistical analysis of phthalate detections and concentrations because of its dominant presence. The statistical analyses were conducted using Minitab (v. 17, Minitab, State College, PA). We used simple statistics (mean, confidence intervals, min and max), Pearson Correlation, and frequency quantile analysis to evaluate trends in the data. One-way Analysis of Variance (ANOVA) and Chi-Square tests were used to test the statistical differences between the mean concentrations and detections of the different phthalates being analyzed, respectively, using an alpha (α) of 0.05 to test significance. Multiple logistic regression models were applied to assess the association between multiple hydrogeological and anthropogenic factors and the detection of phthalates. A logistic regression model of the form

$$logit[p(x)] = \log\left[\frac{p(x)}{1 - p(x)}\right] = a + \sum_{i=0}^{n} bixi$$

was applied to assess the influence of multiple independent variables including aquifer type, sinkholes density, hydraulic conductivity, seasonality, elevation, population, land use, distance from potential contamination sites, number of potential contaminated sites per municipality, and time, on predicting the presence of phthalates (dependent variable). The influence was tested among: individual categories within each variable; all hydrogeological variables; all anthropogenic variables; and all variables. In this model, "p" is the probability of detection, "a" is the constant of the equation and "b_i" represents the coefficients associated with each of the predictor variables "x_i" (Burns and Burns, 2009). We defined a site with no phthalate detection as ND (0) and a site with at least one detection above DLs as detected (1).

4. Results

4.1. Phthalate detection frequencies

Among the sampled phthalates (DBP, BBP, DEHP, DEP, DMP and DNOP), only DBP, DEHP, DEP, and DNOP were detected above DLs, as single entities and mixtures. BBP and DMP were only reported at concentrations below DLs. The most detected phthalate was DEHP, which was present in 61% of the samples that were analyzed for DEHP, 4% above DL and 1% above MCL. The least detected phthalate was DEP, which was detected in only 29% of the samples that were analyzed for DEP, with 9% above DL. Although DNOP was detected in about 38% of the samples analyzed for DNOP, only 1% showed a concentration above DL. Overall, 35% of the total samples showed no phthalates detection, 58% were below DL, 7% above DL and less than 1% above MCL. Out of 197 total sampling sites, at least one type of phthalates was present in 92% of the sites, although only 24% showed detection above DL. DEHP was the most commonly found phthalate, with 89% of the sites sampled for DEHP showing detection (4% above the MCL). Approximately 20% of the sites showed concentration above DLs for DEP, DBP, and DEHP. For phthalate concentrations above DL, 19% of sites sampled for DEP, DBP, and DEHP contained mixtures having two or more phthalates species. The most dominant mixture contained DEP, DBP, and DEHP (60% of the mixtures), followed by DEP-DEHP (20%), DBP-DEHP (13%), and DEP-DBP (7%). DEHP was found in 93% of all mixtures.

Of the total 2004 phthalate samples, 1561 and 443 were taken in the shallow and lower aquifers, respectively. Of these, 7% of the samples in the upper aquifer and 6% in the lower aquifer showed phthalate concentrations above DLs. All of the detections in the lower aquifer (100%) were for DEHP, whereas detections in the upper aquifer showed DEHP (49%), DBP (46%), DEP (26%), and DNOP (<1%) as single or multiple phthalate entities.

4.2. Phthalate concentrations

In general, phthalate contamination was frequent at low concentrations, with a high percentage below DLs. Because the uncertainty on concentration levels below DLs (as many records do not report concentrations below DLs), the statistical analysis was conducted on samples and sites with values above DLs. All other values were assumed as no detection.

Analysis of the detected phthalates showed that DEP, DBP and DEHP were the dominant phthalates present in the groundwater of the KRNPR. Mean concentrations for all samples above DL were 5.76 ± 2.6 μg L^{-1} for DEP, 4.16 ± 1.95 μg L^{-1} for DBP, and 4.02 ± 1.54 μg L^{-1} for DEHP (Fig. 3a). Total phthalate concentrations (sum of the three most-detected phthalates above DLs) averaged 5.08 ± 1.37 μg L^{-1} and ranged from 0.093 to 58.4 μg L^{-1}. Concentration means for the most-detected phthalates (DEHP, DEP, DBP) were not found to be statistically different ($p = 0.511$) from each other. Cumulative quantile plots (Fig. 3b) for phthalates with concentrations above DL showed that the majority of the concentrations were in the low range, with DEP and DEHP showing higher concentration ranges. DEHP showed the highest concentration range with a highly skewed distribution toward low concentrations, yielding a median of 1.0 μg L^{-1} and a significant number (15% of all samples above DL) of samples with high-concentrations outliers (Fig. 3a and b). DBP showed the lowest concentration range, with some skewness toward low concentrations, but a higher median (3.5 μg L^{-1}) than DEHP and DEP (Fig. 3a and b).

4.3. Spatial and temporal phthalate occurrences

The sampling frequencies varied significantly over time due to differences in sampling objectives of the various data sources. Driven by regulatory requirements, sampling frequency increased for DEHP in water supply wells after 1995. Sampling frequencies for DEP and DBP were limited before 2010, when we began our sampling campaign, due to lack of monitoring requirements by regulatory stakeholders. Overall, DEHP concentrations and detection above DL have increased through time, although at a variable rate (Fig. 4a). Maximum detected concentrations of phthalates have also shown to increase over time.

Concentration distributions for the most detected phthalates and total phthalates varied spatially, and showed particular hot-spots (areas with higher probability of phthalate detections and concentrations) in the upper aquifer of the Arecibo-Barceloneta and Vega Alta-Dorado areas (Fig. 5). The lower aquifer showed fewer hot-spot areas, mostly in the Arecibo-Barceloneta area. The highest percent detection frequency (df) occurred in the western side of the study area, including the municipalities of Barceloneta (df = 6.0%), Arecibo (df = 5.2%), and Florida (df = 4.9%), followed by Toa Baja (df = 4.5%), Dorado (df = 3.7%), and Vega Alta (df = 2.8%) on the eastern side. Manatí (df = 2.51%) and Vega Baja (df = 0.91%), in the central region of the study area, showed the lowest detection frequencies. The highest DEHP concentrations were found in the municipalities of Manatí (45.9 μg L^{-1}), Arecibo (23.7 μg L^{-1}), and Barceloneta (19.8 μg L^{-1}) on the western side of the study area, although Dorado (17.9 μg L^{-1}) and Toa Baja (15.0 μg L^{-1}) on the eastern side also showed concentrations above MCL.

4.4. Hydrogeology and anthropogenic effects

DEHP detections and concentrations were slightly higher for the upper aquifer (7%, 4.81 ±2 μg L^{-1}, n = 53) than the lower aquifer (6%, 2.45 ± 2.79 μg L^{-1}, n = 27). Detection frequencies were significantly different ($p = 0.0104$), but mean concentrations between the groups were not ($p = 0.176$). The upper aquifer showed a higher number of samples with high concentrations (Fig. 6a) and a wider range of concentrations. DEHP concentrations in springs (16.46 ± 5.9 μg L^{-1}, n = 5) of the upper aquifer were significantly higher than those in wells (3.19 ± 1.52 μg L^{-1}, n = 75, $p < 0.0005$). In general, higher relative percent of DEHP detection was observed in regions with higher hydraulic conductivities (K) (12.3% of detection for K higher than 300 m d^{-1}, compared to 2.8% and 2.7% for K less than 30 and from 30 to 300 m d^{-1}, respectively) and higher sinkhole coverage (6.9% for sinkhole coverage higher than 21% of the area, compared to 2.1%, 4.4% and 5.5% for sinkhole coverage area less than 1%, from 1 to 10% and from 11 to 20%, respectively). Higher concentration distributions were, however, observed for regions of lower hydraulic conductivities and sinkhole coverage (Fig. 6b and c). The detection of DEHP was not significantly different ($p = 0.0663$) for the different groups of sinkhole coverage, but significantly different for the different groups of hydraulic conductivities ($p < 0.0001$). Topographic elevations were initially postulated to affect the number of detections and concentrations of phthalates because of the higher number of potential sources of contamination and greater capture areas of contaminated groundwater at the downstream areas of lower elevations. Results showed higher number of phthalate detections and concentrations at lower elevation ranges (Fig. 4b), but significant difference was only observed for DEHP detection frequencies ($p < 0.0001$), and not for concentration distribution ($p = 0.482$) among the different elevation categories. Although DEHP detection frequency and average concentrations were slightly higher in dry seasons (df = 4.10%; 4.99 ± 2.5 μg L^{-1}, n = 34) than in wet seasons (df = 3.95%; 3.30 ± 2.15 μg L^{-1}, n = 46), they showed no significant difference between wet and dry samples. While this was true even for the lower DEHP concentration range, the lag between quantile curves for wet and dry seasons (Fig. 6d) increased for higher DEHP concentrations, suggesting strong sensitivity of measured concentrations to changes in hydrologic seasonality.

4.4.1. Population and land use—DEHP average concentrations were not statistically correlated with population variables: population (r = 0.082, $p = 0.469$), population density (r = 0.103, $p = 0.360$), nor population categories ($p = 0.396$). Similarly, DEHP detection frequencies showed no correlation with these population variables. No significant differences were observed for DEHP detection frequencies ($p = 0.471$) among land use categories (agricultural df = 4.5%, natural df = 4.4%, industrial df = 2.7%, residential df = 2.4%, and other developed df = 2.2%). Pearson Correlation tests showed no significant correlation between DEHP concentration and industrial (r = −0.017, $p = 0.88$), residential (r = −0.175, $p = 0.121$), agricultural (r = 0.073, $p = 0.522$), or natural (r= −0.092, $p = 0.417$) land use patterns.

4.4.2. Potential source site impacts—Proximity analysis showed that highest DEHP detection frequencies downstream of potential contamination sites occur between 0 and 1.6 km from RCRA-CA sites, superfund with phthalates, and landfills and between 1.6 and 3.2 km from all Superfund sites. DEHP detection frequencies were significantly different for distance intervals from RCRA-CA sites ($p < 0.0005$) and landfills ($p = 0.02$), but not for Superfund ($p = 0.366$). DEHP concentrations showed a tendency to decrease with distance from Superfunds, RCRA-CA sites, and landfills, although they were not significantly different at the different distance intervals.

4.5. Multidimensional factors impact

Among hydrogeological factors, time, elevation, hydraulic conductivities greater than 30 m d^{-1}, and sinkhole density greater than 11% significantly influenced the presence of DEHP in karst groundwater when these factors were tested within each individual category. Rainfall seasonality, low hydraulic conductivities, and low sinkhole densities were not significant predictors of DEHP presence above DL. When tested among all hydrogeological variables, only time ($p = 0.008$) and hydraulic conductivities greater than 300 m d^{-1} ($p < 0.0005$) were significant predictors of detection frequencies. None of the anthropogenic factors evaluated within or among population, land use, and distance to potential contaminated site categories were significant in predicting the presence of DEHP. When evaluating the combination of hydrogeological and anthropogenic factors, the logistic model indicated that time ($p = 0.02$) and high hydraulic conductivities ($p = 0.008$) were the statistically significant variables in predicting the detection frequencies for DEHP.

5. Discussion

Our results show that phthalates are prevalent in karst groundwater of eogenetic character, and indicate high vulnerability of karst to contamination with these types of pollutants. Average phthalate concentrations (e.g. DEHP: 4.02 ± 1.54 µg L^{-1}, total phthalate: 5.08 ± 1.37 µg L^{-1}) and maximum DEHP concentrations (e.g., DEHP = 45.9 µg L^{-1}, total phthalate = 58.4 µg L^{-1}) in the KRNPR are among the highest reported in groundwater, even for sites impacted by landfills and urban development (Liu et al., 2010; Sorensen et al., 2015). This suggest easy entry and transport processes that favor persistence of phthalates in the karst system. A significant number of samples (19%) show the presence of phthalate mixtures, suggesting that the sources of contaminations for the different species of phthalates are similar.

The presence of phthalates in 24% of sampled sites is relatively high and their widespread spatial concentration distribution show extensive contamination throughout the karst system (Fig. 5). The widespread distribution suggests that the sources of phthalates are spatially disperse, from multiple sources and difficult to delineate. High concentration hotspots are located among the most productive groundwater zones of the region (Irizarry, 2014; Padilla et al., 2015; Yu et al., 2015), increasing the potential for contaminant exposure. The locations of these hotspots are associated with potential sources of contamination and influenced by hydrogeological factors.

Hydrogeological factors affect the rate at which phthalate contaminants enter, move, and are attenuated and stored in the system, hence affecting their detection, concentrations and distributions. Higher detection frequencies of DEHP in the upper aquifer than the lower aquifer is attributed to the larger outcrop area of this aquifer for phthalate to enter the aquifer. Similar DEHP concentration in the upper and lower aquifers suggest comparable types of sources. The higher concentrations in springs, which serve as discharge outlets of internal drainage features in karst systems, reflect the capacity of these features to collect and transmit contaminants toward focal discharge points. Similar to the study by Sorensen et al. (2015), higher DEHP detection frequencies and concentrations in dry seasons than in wet seasons (Fig. 6d) indicate that dilution processes from aquifer recharge during the wet season play a greater role than the additional mass load from runoff of non-point phthalate sources (Sun et al., 2013). Higher presence of phthalates in regions of higher hydraulic conductivities is attributed to higher capacity of the system to transport anthropogenic contaminants in the subsurface, whereas the influence of high sinkhole coverage is associated with areas of direct contaminant input and high drainage capabilities. Phthalate concentrations are slightly higher in regions of low hydraulic conductivity and sinkhole coverage, reflecting higher storage capacity and lower diluting flow through these regions. Similar detection frequencies and concentrations at different elevation ranges suggest that the effect of locally distributed phthalate sources may influence phthalate distributions to a greater extent than cumulative transport from higher to lower elevations.

Anthropogenic factors address the influence of potential sources of contamination on the presence of phthalates. Population and land use factors do not significantly influence the detection frequencies and concentrations of DEHP. The relative lack of influence from population and land use is attributed to the higher effect posed by hydrogeological factors. Other studies (Zhang et al., 2009; Huang et al., 2012) have also reported that hydrogeological factor, such as strong hydraulic connection between groundwater and surface water, are more important in predicting the presence and concentrations of phthalates in groundwater than population and land use. Proximity analysis to localized potential sources suggest greater likelihood of finding phthalates more frequently near RCRA-CA and landfill sites and, similar to Liu et al. (2010), a potential significant contribution of landfills to phthalate contamination. Although the presence of phthalates may be associated with some particular superfund sites (Fig. S2), in general there is no significant different in DEHP detection frequencies and concentrations as a function of distance from Superfund sites. It is, therefore, considered that superfund sites contribute to phthalate contamination at about the same level than other widespread sources.

Logistic modeling of multiple explanatory variables indicates that hydrogeological factors are significantly more important in predicting the detection of phthalates in karst aquifers of eogenetic character. Of these, time of detection and high hydraulic conductivities (> 300 m d^{-1}) are the most influential factors. The significance of time as a variable is attributed to high and increasing detection frequencies through time. Significant detection in regions of high hydraulic conductivity denotes the importance of contaminant transport from sources of contamination to potential points of exposure.

6. Conclusions

Analysis of phthalate presence and concentrations in the karst aquifers of northern Puerto Rico indicate that there is extensive spatial and temporal contamination of phthalates as single entities or as mixtures in the area of study. Results show that at least one type of phthalate is present above DLs in 7% of the samples and 24% of the sampling sites during the study period. The most detected contaminant, DEHP, is present in both upper and lower aquifers. Widespread spatial detections indicate that these widely-used contaminants enter the aquifer system as dispersed sources that are difficult to isolate and delineate. Population and land use do not show to influence the distribution of DEHP in karst aquifers, perhaps because of the higher impact of hydrogeological characteristics on their presence. Higher presence of DEHP is observed near landfills and some heavily contaminated sites, but data analysis and logistic regression models suggest that high phthalate distributions in karst groundwater are more strongly associated with hydrogeological factors, particularly time and hydraulic conductivities. While higher detections frequencies are associated with regions of high hydraulic conductivities, higher concentrations are observed in areas of low hydraulic conductivities having lower water flux and high storage capacity. Persistent contamination through time reflects continuous sources of phthalates entering the aquifer system. It also reflects the high capacity of the karst aquifers to store and slowly release contaminants for long periods of time. Our results indicate that the distribution of phthalates contaminants entering karst aquifers over dispersed sources are strongly controlled by the same hydrogeological characteristics that make these aquifers highly productive. As a result, karst aquifers pose high risk of exposure to phthalate contamination.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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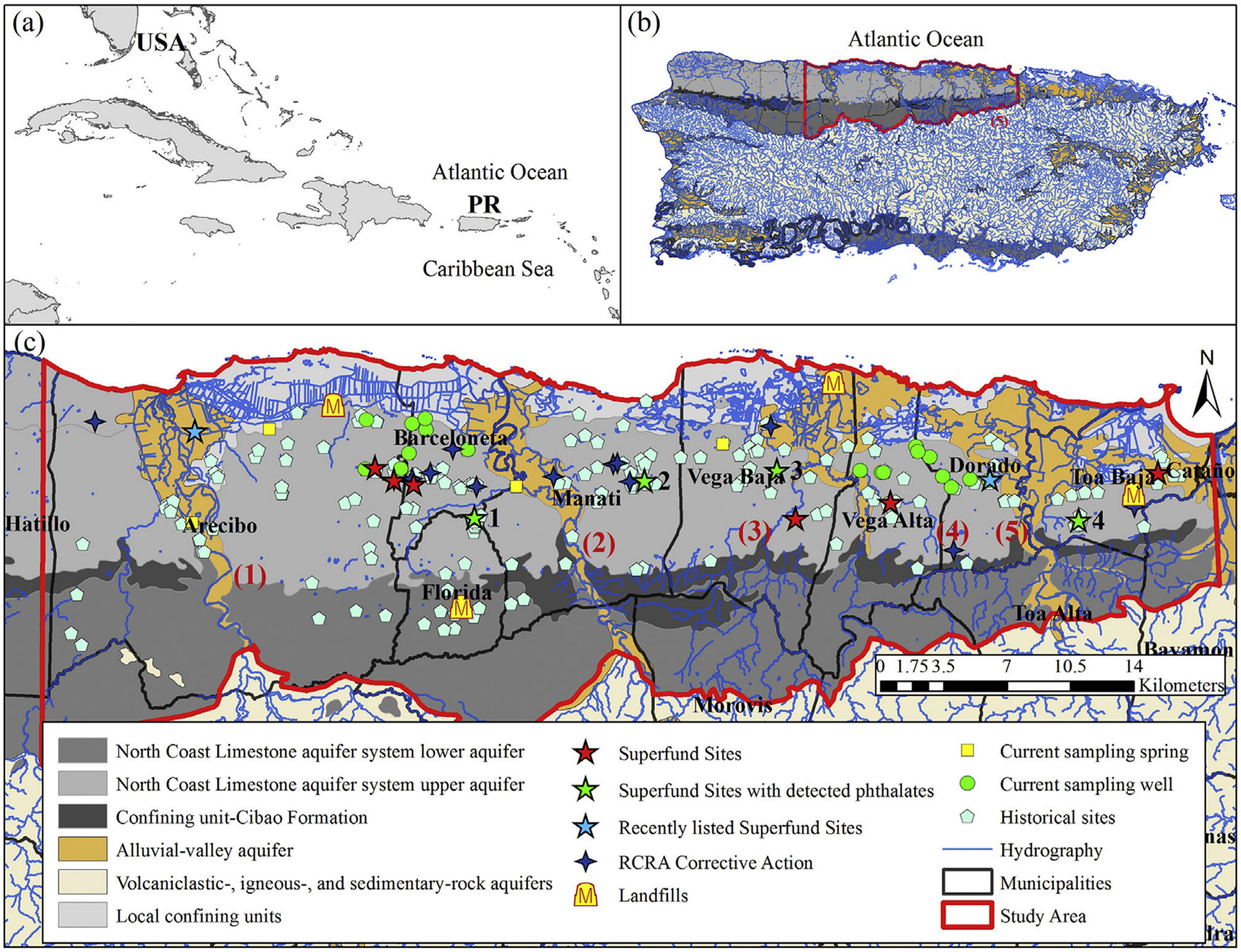

Fig. 1.

(a) Location of Puerto Rico, (b) Principal aquifers in Puerto Rico, (c) Major streams in the KRNPR area include (from west to east, numbers in red): Río Grande de Arecibo (1), Río Grande de Manatí (2), Río Indio (3), Río Cibuco (4), and Río La Plata (5); aquifer hydrogeology of the KRNPR study area; location of contamination sites in the area of study and location of historical and current sampling sites. Superfund sites with detected phthalates are identified with numbers (1–4, in black). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

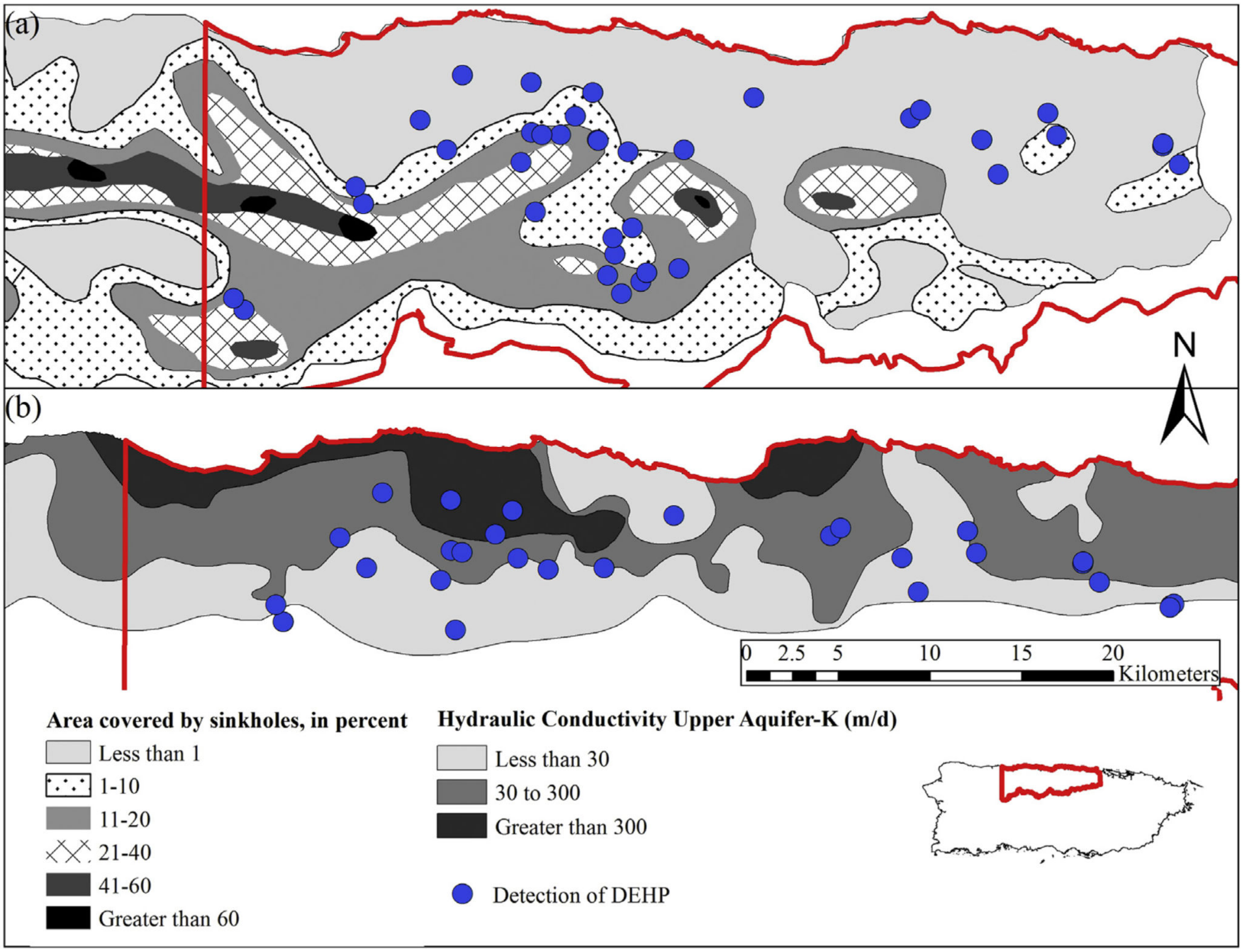

Fig. 2.

Hydrogeological properties of the upper karst aquifer of NPR: (a) Density distribution of sinkholes in the study area (adapted from Giusti, 1978), (b) Hydraulic conductivity distribution in the study area (adapted from Renken et al., 2002).

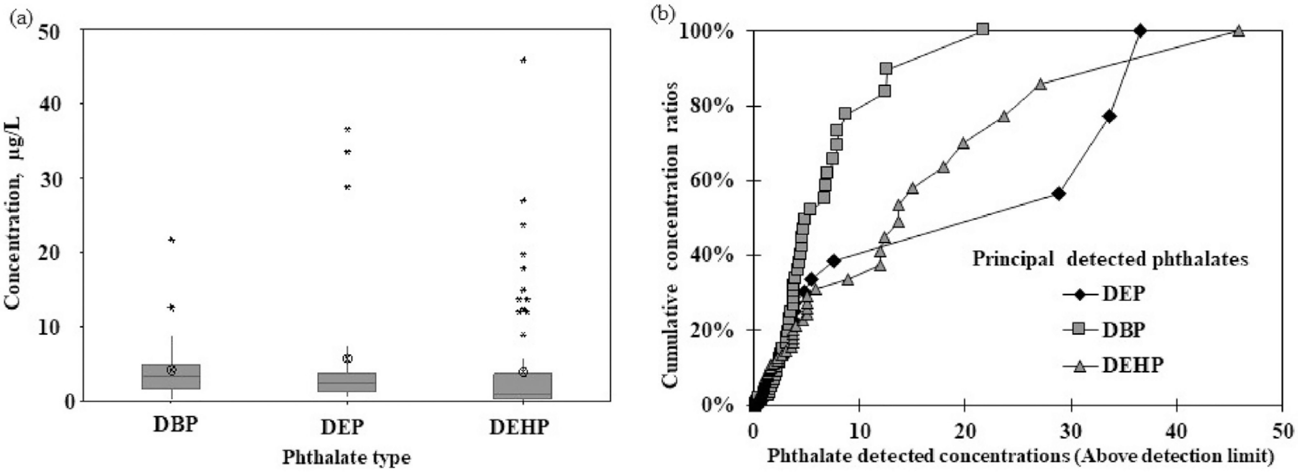

Fig. 3.

(a) Box plots of phthalates concentrations; (b) Quantile plot showing concentrations of phthalate species.

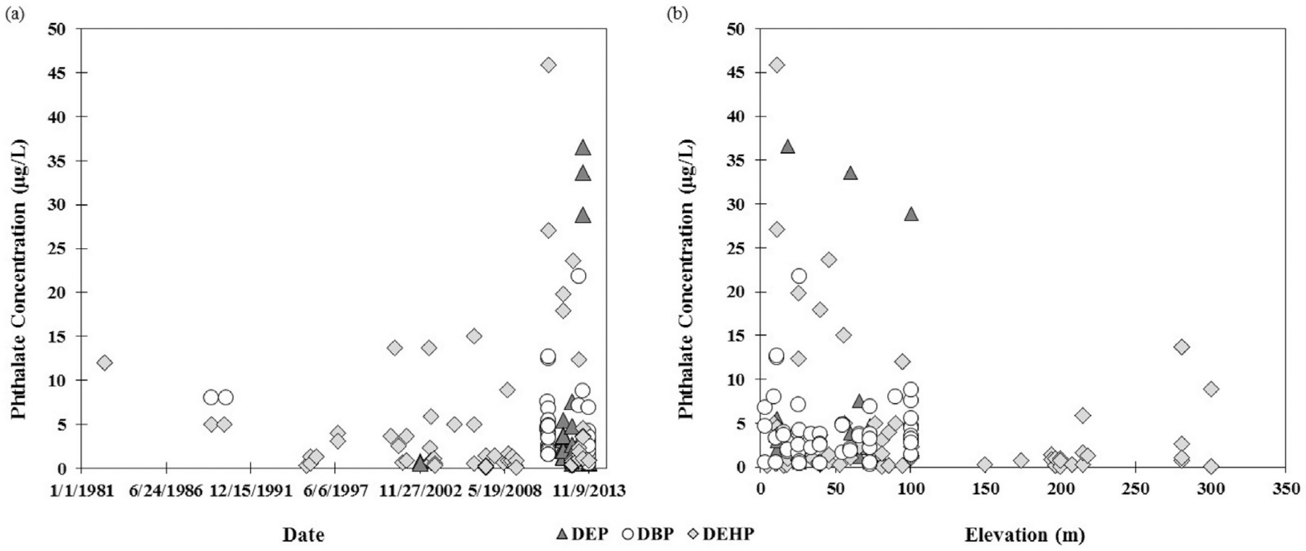

Fig. 4.

(a) Temporal distribution of phthalate concentrations, (b) Plot of phthalate concentrations vs elevation.

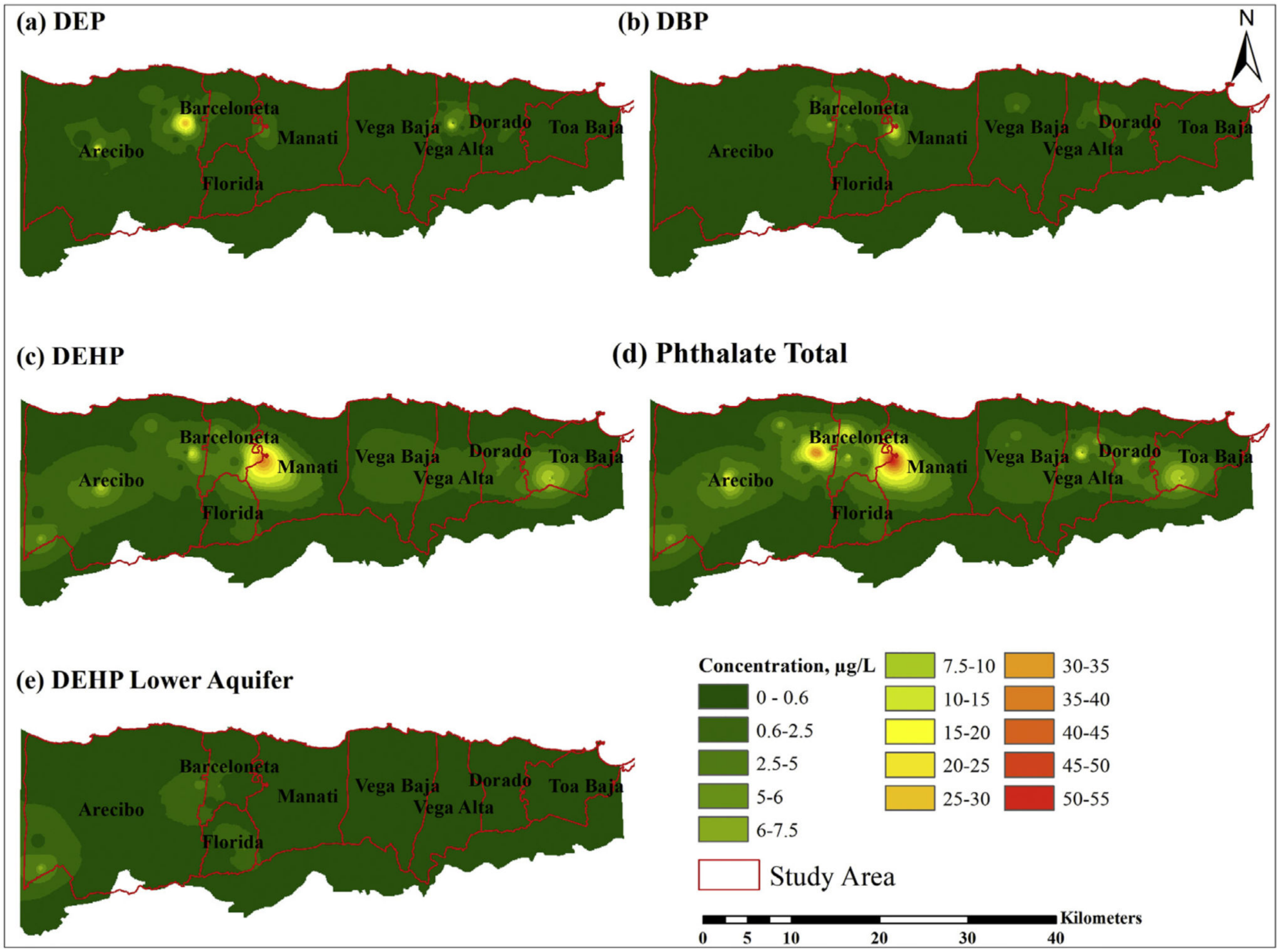

Fig. 5.

Spatial distribution of (a) DEP, (b) DBP, (c) DEHP, and (d) total phthalate (µg L^{-1}) in the upper aquifer and (e) DEHP in the lower aquifer.

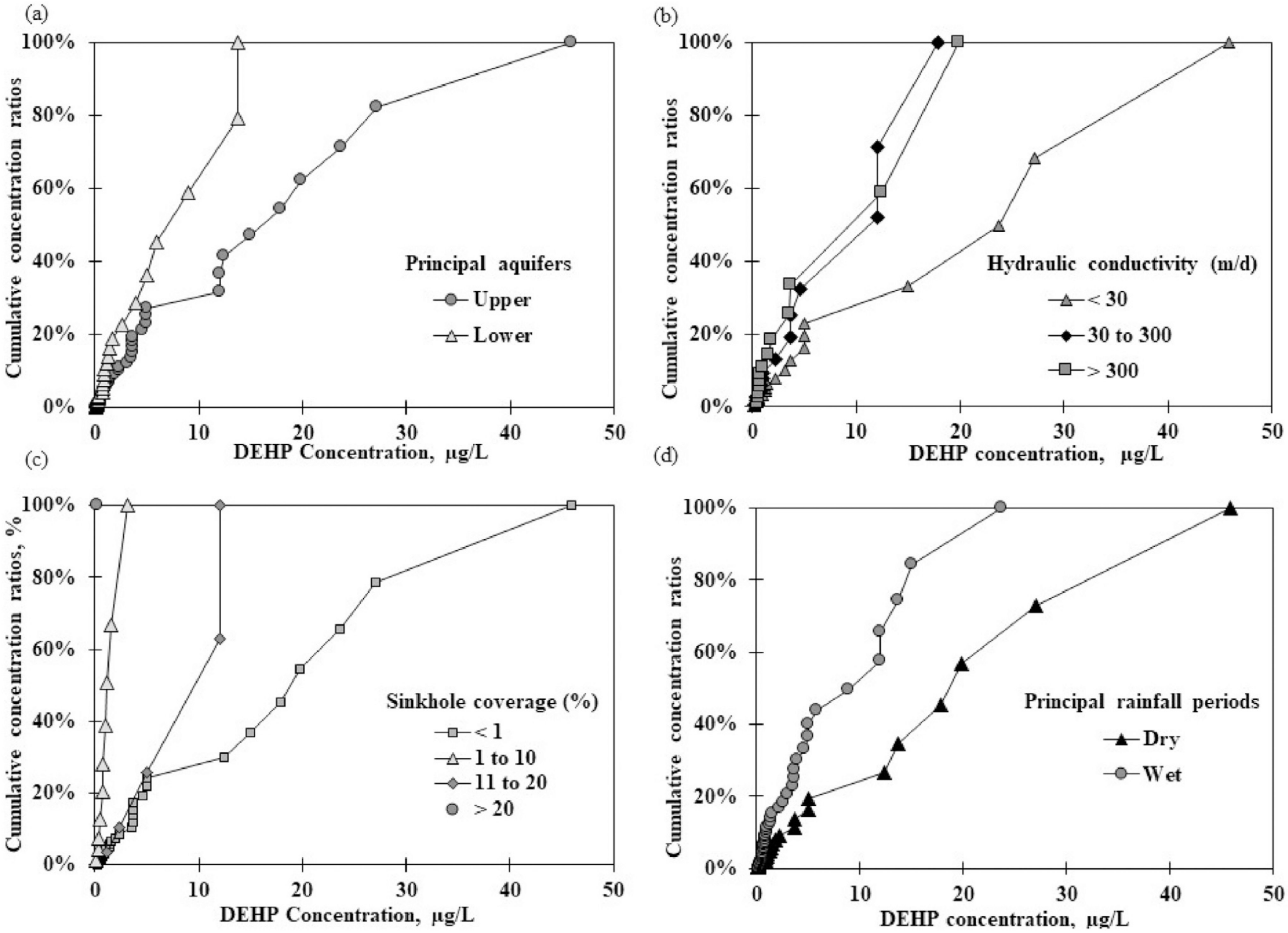

Fig. 6.

(a) DEHP cumulative concentration plot for different aquifer types; (b) DEHP cumulative concentration plot for different hydraulic conductivities; (c) DEHP cumulative concentration plots for different sinkhole area coverage; (d) DEHP seasonal cumulative concentration plot.