Environmental Pollution 237 (2018) 298–307

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

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

Norma I. Torres [a], Xue Yu [b], Ingrid Y. Padilla [a, *], Raul E. Macchiavelli [c], Reza Ghasemizadeh [b], David Kaeli [d], Jose F. Cordero [e], John D. Meeker [f], Akram N. Alshawabkeh [b]

[a] Department of Civil Engineering and Surveying, University of Puerto Rico, Mayagüez, PR 00681, USA
[b] Department of Civil and Environmental Engineering, Northeastern University, Boston, MA 02115, USA
[c] Department of Agroenvironmental Sciences, University of Puerto Rico, Mayagüez, PR 00681, USA
[d] Department of Electrical and Computer Engineering, Northeastern University, Boston, MA 02115, USA
[e] Department of Epidemiology and Biostatistics, University of Georgia, Athens, GA 30602, USA
[f] Department of Environmental Health Sciences, University of Michigan School of Public Health, Ann Arbor, MI 48109, USA

ARTICLE INFO

Article history:
Received 14 July 2017
Received in revised form
30 January 2018
Accepted 30 January 2018

Keywords:
Groundwater contamination
Phthalates
Karst aquifers
Logistic regression model

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 $5.08 \pm 1.37\ \mu g\ L^{-1}$, and range from 0.093 to $58.4\ \mu g\ L^{-1}$. 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 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.

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

☆ This paper has been recommended for acceptance by Dr. Harmon Sarah Michele.

* Corresponding author. Department of Civil Engineering and Surveying, University of Puerto Rico at Mayagüez, PO Box 9000, Mayagüez, PR 00681, USA.
E-mail address: ingrid.padilla@upr.edu (I.Y. Padilla).

https://doi.org/10.1016/j.envpol.2018.01.106
0269-7491/© 2018 Published by Elsevier Ltd.

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 $\mu g\ L^{-1}$ and 6.35 $\mu g\ L^{-1}$, respectively, in wells impacted by landfill leachate in Wuhan, China. Sorensen et al. (2015) reported DEHP (dry season: 22 $\mu g\ L^{-1}$; wet season: 5 $\mu g\ L^{-1}$) and total phthalate (dry: 45 $\mu g\ L^{-1}$; wet: 5.1 $\mu g\ L^{-1}$) 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 $\mu g\ L^{-1}$. 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,