



Research papers

Fate of parabens and 4-hydroxybenzoic acid in aquifer materials columns during step experiments with fresh and sea waters



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ARTICLE INFO

Article history:

Received 1 March 2017

Received in revised form 6 December 2017

Accepted 11 December 2017

Available online 12 December 2017

This manuscript was handled by L. Charlet, Editor-in-Chief, with the assistance of Jiin-Shuh Jean, Associate Editor

Keywords:

Parabens

4-Hydroxybenzoic acid

Laboratory column

Reactive transport

Seawater intrusion

Sorption

ABSTRACT

Coastal areas submitted to seawater intrusion and with discharges from urban and industrial wastewaters, municipal landfill leachates, rivers, recreational waters and other sources are sensitive to be polluted with parabens. Understanding the fate of these compounds in environmental studies, it requires previously the knowledge of the reactive processes in controlled conditions. In this research, laboratory columns experiments were carried out with a group of parabens (methyl-, ethyl-, propyl- and butylparaben) and their main degradation compound (4-hydroxybenzoic acid) to study mainly the dynamic sorption processes in different aquifer materials (100% sand and heterogeneous: 81% sand, 9% silt and 10% clay) and with fresh and sea waters, the end members of seawater intrusions. To the column hydrodynamic characterization, tracer assays with increase and decrease of salinity were performed, to obtain the mean residence time of each column and other transport parameters which allow us to compare parabens' sorption in different conditions. The results of the adsorption and desorption of parabens in the sand column demonstrated be fast and simultaneous, with a short delay and without influence of the water salinity. Very different results were found in the column experiments with heterogeneous material, where the presence of clay and organic matter increase the time of adsorption/desorption as the length of the alkyl chain paraben increased, according with their hydrophobicity. It should be noted that despite the quick desorption of the major quantities of parabens, the elution of their trace concentrations was very slow (for the seawater, the butylparaben required a dimensionless time of 800). Planning the restoration of a coastal aquifer with freshwater, and in the conditions of the studied sand column experiment, it will need a dimensionless time of 160. However, it is necessary to take into account that the studied parabens and 4-hydroxybenzoic acid are biodegradable substances, as can be seen in long term experiments, when bacterial proliferation could occur, despite starting the experiment under sterile conditions.

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1. Introduction

In terms of chemical structure, parabens are esters of 4-hydroxybenzoic acid, which can be esterified with alkyl substituents ranging from methyl to butyl or benzyl groups. Fig. 1 show the structure of the parabens considered in this study: methylparaben (M), ethylparaben (E), propylparaben (P) and butylparaben (B), together 4-hydroxybenzoic acid (H), their main degradation compound.

Błądzka et al. (2014) refers that parabens are widely used as preservatives, mainly in cosmetics (toothpastes, deodorants, skin-care creams, bath gels and shampoos) and pharmaceuticals, but

also in food commodities and industrial products. These compounds are antimicrobial characteristic with a broad spectrum of activity, low cost, heat stable, effective over an extensive pH range, sufficiently soluble in water to achieve effective concentrations in aqueous media, no perceptible odour or taste and do not induce discoloration (Neidig and Burrell, 1944).

Parabens are lipophilic compounds and their physic-chemical properties depend on the carbon number of the alkyl chain. Table 1 summarizes some physical constants and chemical properties of parabens considered in this study (Lide, 2002; NCBI, 2016; Jewell et al., 2007; Figueiredo et al., 2016; Soni et al., 2005). The compounds are solid at room temperature and are expected to be essentially non-volatile from water surfaces, due to the low vapour pressures. As the ester chain length increases, water solubility decreases and the octanol/water partition coefficients (log K_{ow}) increase (Elder, 1984). The 4-hydroxybenzoic acid is dissociated

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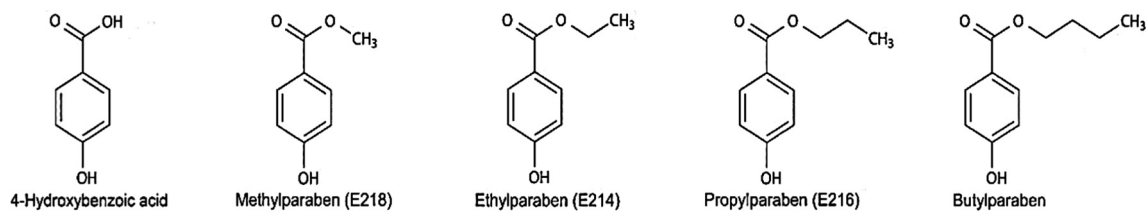


Fig. 1. Structure of the different compounds considered in the present study.

Table 1
Physical constants and chemical properties of 4-hydroxybenzoic acid and parabens considered in this studio from Handbook of Chemistry and Physics (Lide, 2002) and other authors.

Chemical names	4-hydroxybenzoic acid	Methyl p-hydroxybenzoate	Ethyl p-hydroxybenzoate	n-Propyl p-hydroxybenzoate	n-Butyl p-hydroxybenzoate
Short name in this study	H	M	E	P	B
Molecular formula	C ₇ H ₆ O ₃	C ₈ H ₈ O ₃	C ₉ H ₁₀ O ₃	C ₁₀ H ₁₂ O ₃	C ₁₁ H ₁₄ O ₃
CAS Registry Number	99-96-7	99-76-3	120-47-8	94-13-3	94-26-8
Molecular weight (g/mol)	138.12	152.15	166.17	180.20	194.23
Melting point (°C)	214.5	131	117	97	68.5
Boiling point (°C)	336 ^d	275	297.5	294 ^d	309 ^d
Vapor Pressure (mm Hg at 25 °C) ^a	1.9 10 ⁻⁷	2.37 10 ⁻⁴	9.29 10 ⁻⁵	5.55 10 ⁻⁴	1.86 10 ⁻⁴
Density (g/cm ³) at t (°C)	1.46 ²⁵			1.063 ¹⁰²	
Water solubility at 25 °C (g/100 mL) ^b	0.60	0.25	0.17	0.05	0.02
Log Kow ^c	1.33	1.67	2.03	2.55	3.00
pKa ^d	4.57	8.17	8.22	8.35	8.37

^a Data from NCBI (2016).

^b Data from Jewell et al. (2007).

^c Values from Chemspider (Figueiredo et al., 2016).

^d Data from Soni et al. (2005).

at neutral pH, and as a consequence of its acid character, this compound is different to those with basic characteristics. Antimicrobial activity increases according to the length of the chains of the parabens (Han and Washington, 2005), but generally, microbial replication occurs in water and hence, the amount of paraben dissolved in the aqueous phase and the antimicrobial activity determine the preservative ability.

However, these compounds may have harmful consequences for human health (Dagher et al., 2012; Soni et al., 2005; Okubo et al., 2001). Recent reports have indicated that exposure to parabens may modulate or disrupt the endocrine system. Furthermore, due to the high oil/water partition coefficient, if any parabens enter the human body intact, they may be able to accumulate in fatty components of body tissues in a similar manner to that of other lipophilic pollutants that are known to bioaccumulate and they have carcinogenic potential (Darbre et al., 2004). This researcher referred that parabens are quickly absorbed from the gastrointestinal tract and from blood, hydrolyzed to 4-hydroxybenzoic acid and excreted in the urine, and he provides levels of parabens in foods in the 0.5–2.0 mg/g range, while in pharmaceuticals the concentrations were below 10 mg/g (Soni et al., 2002; Sandanger et al., 2011). Parabens have been detected in human fluids i.e., blood (10 µg/L of methyl-, ethyl- and propylparaben from Sandanger et al., 2011), urine (43.9 µg/L of methyl- and 9.05 µg/L of propylparaben in 96% of the samples, from Ye et al., 2006), milk (1–8 µg/L of methyl-, 1–1.5 µg/L of propyl- and 1–2 µg/L of butylparaben, from Schlumpf et al., 2010), and human breast tumours (5.1 µg/g of methyl-, 0.5 µg/g of ethyl-, 2.1 µg/g of propyl- and 0.1 µg/g of butylparaben, from Barr et al., 2012) in different populations. Currently, some manufacturers altered composition of their cosmetic products by replacing parabens with other preservative system and introducing so called “paraben free” formulae. In European Union countries, the allowable content of parabens in cosmetic products is 0.4% (4 mg/g) for single ester and 0.8% (8

mg/g) for mixtures of all parabens (Official Journal of the European Union, 2009).

As regards environmental samples, levels of methyl-, ethyl- and propylparaben below 80 ng/L have been measured in rivers (Benijts et al., 2004; Canosa et al., 2006). Concentrations of these compounds in untreated waste waters are below 2500 ng/L, while levels in the effluents of treatment plants are below 100 ng/L. In these samples, propylparaben is considered the main representative of the parabens group (Lee et al., 2005). A great part of the environment input of these compounds is through wastewaters, although agricultural use of fertilizers can also be an important source of parabens because they can lixiviate and contaminate groundwater and aquifers. In addition, they are compounds found in moisturizing, nourishing and sun creams so another possible pollution route to the environment is by direct bathing, washing or swimming in the waters of rivers, lakes or seas (Núñez, 2010).

Once released into the environment, these compounds will suffer from different processes such as degradation or distribution among the different phases of the system. The role of these processes in the fate of contaminants depends on several variables: (i) compound properties (ii) water characteristics and (iii) system properties. Therefore, it is necessary to understand the behaviour of pollutants in the environment, where they can remain in solution or adsorbed in different types of materials. The sorption process plays a significant role as an attenuation process during subsurface flow as the retention or the release of compounds in the liquid phase, on the solid phase, controls the mobility of the substances in the environment (Limousin et al., 2007). Hence, the investigation of the sorption properties of chemical compounds is mandatory for assessing the environmental behaviour of pollutants in general and, particularly, to assess their potential to leach into the groundwater (Burke et al., 2013). Sorption processes can be driven by diverse mechanisms, including physisorption, chemisorption and mechanical inclusion (Von Oepen et al.,

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