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Evaluating the impacts of some environmentally relevant factors on the availability of bisphenol A with negligible-depletion SPME

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Abstract

The effect of some environmentally relevant factors including salinity, pH, and humic acids on the availability of bisphenol A (BPA) was evaluated by using the negligible-depletion solid-phase microextraction (nd-SPME) biomimetic method. With the variation of salinity (0–500 mM NaCl) and pH (5.0–8.5) of aqueous solutions, the partition coefficients of BPA between the nd-SPME fiber and the aqueous solution varied in the range of $\log D = 3.55$–3.86, which indicates that the salinity and pH can influence the availability of BPA. By using Acros humic acid as model dissolved organic matter (DOM), it was also demonstrated that the environmental factors such as salinity and pH could affect the partitioning of BPA between DOM and aqueous solutions. The determined partition coefficients of BPA between dissolved organic carbon (DOC) and aqueous solutions were in the range of $\log D_{\mathrm{DOC}} = 4.03$–$5.60$ for Acros humic acid solutions with 1–50 mg l^{-1} DOC. The influence of salinity and pH on $\log D_{\mathrm{DOC}}$ was more significant at low concentration (0–5 mg l^{-1}) of DOC.

Keywords: Negligible-depletion solid-phase microextraction; Partitioning; Availability; Bisphenol A; Dissolved organic matter; Humic acids

1. Introduction

Various environmentally relevant factors such as dissolved organic matter (DOM), salinity and pH might influence the availability of a contaminant in aquatic environments. For example, binding and adsorption by particles and DOM can alter the bioavailability of a contaminant. The freely dissolved concentration (C_{free}) is believed to be the driving force for the transportation, distribution, and bioaccumulation of a contaminant (Mackay and Paterson, 1991), and thus a key parameter controlling its bioavailability and the toxic effect (Suffet et al., 1994). Therefore, study on the effects of environmental factors on the C_{free} or the partitioning between DOM and aqueous solutions can elucidate their influence on the bioavailability of a contaminant. The partitioning between DOM and an aqueous solution of a contaminant is usually normalized to dissolved organic carbon (DOC) and expressed as D_{DOC}.

Many studies about the effect of environmentally relevant factors on the bioavailability of hydrophobic compounds have been reported, and the effect of DOM was the mostly concerned (Carter and Suffet, 1982; Kukkonen and Oikari, 1987; Day, 1991; Chin et al., 1997). Haitzer et al. (1998) reviewed the effects of DOM on the bioconcentration of organic chemicals in aquatic organisms. It was concluded that the presence of DOM in most cases caused decrease of bioconcentration while in a few cases lead to enhance of bioconcentration, and the effect of DOM depends on its sources. The environmental pH can affect the ionization of DOM (Jota and Hassett, 1991) and thus influence the binding of neutral hydrophobic compounds to DOM (Paolis and Kukkonen, 1997). Depending on the

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ions used to control the ionic strength and the properties of DOM, the ionic strength or salinity can increase (Gauthier et al., 1986; Jota and Hassett, 1991; Brunk et al., 1997) or decrease (Schlautman and Morgan, 1993; Jones and Tiller, 1999) the association of DOM with polychlorinated biphenyls (PCBs) or polycyclic aromatic hydrocarbons (PAHs). By using negligible-depletion solid-phase microextraction (nd-SPME), a biomimetic tool, the combined effects of humic acids and salinity on the availability of 4,4′-dichlorodiphenyltrichloroethane (DDT) and chlorpyrifos pesticides were investigated, and it was reported that the binding of DDT and chlorpyrifos by humic acids was greatly reduced with the presence of salt (Mezin and Hale, 2004).

For ionizable compounds, however, studies on their bioavailability and their association with DOM were limited. Schwarzenbach and co-workers investigated the partition in liposome–water system of a series of substituted phenols and anilines with pH dependent results (Escher and Schwarzenbach, 1996; Escher et al., 2002) and Arnold et al. also found that the association of triorganotin compounds with dissolved humic acids was strongly pH dependent (Arnold et al., 1998). A few studies on the association of chlorophenols with various DOM were reported. Depending on the source of DOM, the sorption coefficients ($\log K_{oc}$) of pentachlorophenol ranged from 0 to 3.9 at pH 5.0, and the $\log K_{oc}$ value decreased radically with the increase of pH and reached 0 for almost all kinds of DOM at pH 8.0 (Paolis and Kukkonen, 1997). Aldrich humic acid and chlorophenols have strong and pH dependent association (Ohlenbusch et al., 2000; Liu et al., 2005). The measured $\log K_{oc}$ value for pentachlorophenol was 3.0 at pH 7.3, and the $\log K_{oc}$ values for 2,5-dicholophenol were 2.76 at pH 6.5, 2.60 at pH 7.3, and 1.66 at pH 8.3, respectively (Ohlenbusch et al., 2000). For ionogenic compounds with $K_{ow} < 2$, the association of atrazine with DOM was very low (Akkanen and Kukkonen, 2001) while 4-quinolone antimicrobials (Flumequine, oxolinicacid, and sarafloxacin) showed very large distribution coefficients ($\log D_{DOC} = 3.4$–5.2) with Aldrich humic acid (Lutzhoft et al., 2000).

Bisphenol A (BPA), a relatively polar compound ($\log K_{ow} = 3.40$, $pK_a = 9.6$–10.2) with known endocrine potential, is one of the most produced chemical intermediate used to make polycarbonate plastic, expoxy resins, flame retardants, and other special products (Staples et al., 1998). However, studies on the binding of BPA to DOM and the effect of DOM on the bioavailability of BPA are scarce. Although the distribution coefficient between DOM and water of BPA has been measured ($K_{DOM} = 860\,\mathrm{l\,kg^{-1}}$) (Hollrigl-Rosta et al., 2003), the effect of other environmental relevant factors such as pH and salinity on the bioavailability of BPA is not clear. A few studies on the determination of BPA by SPME were reported (Salafranca et al., 1999; Braun et al., 2003; Cai et al., 2004; Basheer et al., 2005; Chang et al., 2005), but there is no report on the effect of environmental relevant conditions on the availability studied with the nd-SPME technique.

In this present study, the effect of humic acids pH and salinity on the availability of BPA was evaluated by using the nd-SPME biomimetic method. The direct effects of pH and salinity on the availability were studied by measuring their influence on the partitioning of BPA to the fiber (D), while the combined effects of these factors with humic acids were investigated based on their influence on the partitioning of BPA to humic acids (D_{DOC}).

2. Experimental section

2.1. Reagents and materials

All reagents were of analytical-reagent grade and deionized water was used throughout the experiments. BPA (Acros Organics, NJ, USA) standard stock solution ($1000\,\mu\mathrm{g\,ml^{-1}}$) was prepared in methanol, and working solutions were prepared daily by appropriate dilution of the stock solution with water. Humic acid sodium salt made from terrestrial origin (lignite, technical, 50–60% as humic acid; Acros Organics, Morris Plains, NJ) was used as obtained. The DOC of this humic acid sodium salt (measured in a solution prepared by dissolving 20 mg in 200 ml of water and filtrated through 0.45 μm membrane, with a Phoenix 8000 UV-persulfate TOC Analyzer, Tekmar Dohrmann, USA) was 45.0%.

LC-grade methanol and acetonitrile were purchased from Scharlau Chemie SA, Barcelona, Spain. Other chemicals such as sodium dihydrogen phosphate, sodium hydroxide, sodium chloride, and hydrochloric acid were obtained from Beijing Chemicals Corporation (Beijing, China).

2.2. Instrument

The HPLC system was equipped with an Agilent 1100 Series isocratic pump (IsoPump) and an Agilent 1100 Series fluorescence detector (FLD). The fluorescence detector was set at 220 nm excitation and 315 nm emission wavelength, respectively. A personal computer equipped with an Agilent ChemStation program for LC system was used to process chromatographic data. A manual SPME fiber holder (type 57331) and a SPME–HPLC interface from Supelco Inc (Bellefonte, PA) were used to conduct the extraction and introduce the analyte extracted on the fiber into the HPLC system. The SPME–HPLC interface consisted of a six-port Rheodyne valve and a 60-μl desorption chamber.

A pH 211 microprocessor pH meter (Hanna Instruments) was used to adjust the sample pH.

2.3. HPLC separation

The separation of BPA was performed on an Agilent Zorbax Eclipse XDB-C_8 column (150×4.6 mm, particle size 5 μm, pore size 8 nm, polymeric, double endcapped) by using a mixture (75:25, v/v) of acetonitrile and phosphate buffer (0.01 mM, pH 7.0) as mobile phase at $1.0\,\mathrm{ml\,min^{-1}}$.