Environmental Pollution 198 (2015) 61–69

Contents lists available at ScienceDirect

Environmental Pollution

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

Biosorption of nonylphenol by pure algae, field-collected planktons and their fractions

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ARTICLE INFO

Article history:
Received 28 September 2014
Received in revised form
7 December 2014
Accepted 9 December 2014
Available online

Keywords:
Nonylphenol (NP)
Biosorption
Algae
Lipid (LP)
Acid nonhydrolyzable carbon (NHC)

ABSTRACT

Algal samples were fractionated into lipid (LP), lipid free (LF), alkaline nonhydrolyzable carbon (ANHC), and acid nonhydrolyzable carbon (NHC) fractions, and were characterized by the quantitative ^{13}C multiCP NMR technique. The biosorption isotherms for nonylphenol (NP) were established and compared with previously published data for phenanthrene (Phen). The log K_{OC} values are significantly higher for the field-collected plankton samples than for the commercial algae and cultured algae samples, correlating with their lipid contents and aliphatic carbon structure. As the NHC fraction contains more poly(methylene) carbon, it exhibits a higher biosorption capacity. The sorption capacities are negatively related to the polarity index, COO/N–C=O, polar C and O-alkyl C concentrations, but are positively related to the H/O atomic ratios and poly(methylene) carbon. The higher sorption capacities observed for NP than for Phen on the investigated samples are explained by specific interactions such as hydrogen bonding and π–π interaction.

1. Introduction

Nonylphenol (NP) is one of endocrine disrupting chemicals (EDCs) since it is able to mimic natural estrogens and disrupts the endocrine systems of higher organisms by interacting with the estrogen receptor (Soares et al., 2008; Vazquez-Duhalt et al., 2005). NP can also affect plankton community structure when released into an aquatic environment (Gao et al., 2011a). Traditional techniques for NP removal such as adsorption on activated carbon, photo-oxidation, and ozone treatments have been studied and found to be effective, but cost-effectiveness is relatively low and limits widespread practical use (Nakada et al., 2006; Kawasaki et al., 2001). Biosorption is a physicochemical process that utilizes inexpensive live or dead biomass to remove contaminants and deals with the sorption of a chemical substance in/on a biological matrix/surface (Kratochvil and Volesky, 1998; Chen et al., 2010). Biosorbents are prepared from the naturally abundant and/or waste biomass of algae, moss, fungi or bacteria that has been sterilized by washing with acids and/or bases before final drying and granulation (Kratochvil and Volesky, 1998). Moreover, algae are found to be highly effective, reliable, and economic in the removal of contaminants from aqueous solutions (Kratochvil and Volesky, 1998; Navarro et al., 2008).

The coupling between primary producer biomass dynamics and the distribution and fate of persistent organic pollutants in a lake pelagic ecosystem has been reported (Nizzetto et al., 2012). Algae are the important primary producers in aquatic ecosystems, and play an important role in determining the transport and fate of NP in aquatic systems. Due to their substantial biomass and extensive range of habitat and diversity, algae constitute the largest and most widely distributed group of photosynthetic organisms in aquatic ecosystems. Algae act as precursors of natural organic matter (NOM) in sediment organic matter through selective preservation, which is based on the presence of highly aliphatic biomacromolecules, termed algaenans (Gelin et al., 1999).

Investigation on biosorption of toxic organic compounds with biomass showed that better removal was obtained with dead biomass than with live biomass (Aksu, 2005). Most studies reported that structural components of biomass affect the biosorption of

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http://dx.doi.org/10.1016/j.envpol.2014.12.020
0269-7491/

hydrophobic organic compounds (Chen et al., 2005; Chen and Schnoor, 2009; Kwon et al., 2007; Li et al., 2010; Wang et al., 2007; Wang and Xing, 2007). In recent studies, the sorption mechanisms of EDCs by activated sludge biomass, stream biofilms, synthetic membrane vesicles and condensed SOM of soils and sediments have been investigated (Kwon et al., 2007; Sun et al., 2010; Writer et al., 2011; Xu et al., 2008). Other investigation reported that the molecular interactions such as hydrogen bonding and hydrophobic interaction could play an important role for the NP biosorption on biomass (Lang et al., 2009). However, few investigations are available about biosorption mechanisms of NP by algae (Gao et al., 2011a, 2011b).

This study investigates the biosorption of NP on three field-collected plankton samples, two cultured algal species, and three commercial algal species and their algal fractions. In our previous study (Zhang et al., 2013a), acid nonhydrolyzable carbon (NHC) is considered to be organic carbon in algae not soluble in acid, base, and organic solvents. We hypothesize that some of the algal fractions such as NHC and lipid (LP) are very important to the biosorption of NP. We examine the biosorption behaviors of NP on the bulk algal samples (OS) and their isolated organic matter fractions, relate the biosorption behaviors of NP to the compositions of the algal samples determined by elemental analysis and quantitative solid-state NMR, and compare biosorption behaviors of NP with those of phenanthrene (Phen) to infer the possible biosorption mechanism.

2. Material and methods

2.1. Algal samples and isolation of algal fractions

The sample set included the following algae: two cultured algal species (*Chlorella, Sphaerellopsis*) cultured in lab conditions, three commercial algal species (*Spirulina, Seaweed, Porphyra*) purchased in a supermarket, and three field-collected plankton samples from two eutrophication lakes. The LHH25 sample was collected by using 25 size plankton net in August 2011 from the Liuhuahu park in Guangzhou city, China. The LHHPOM sample was separated from the large volume of water sample collected in the Liuhuahu park by using a continuous flow centrifuge at 8000 rpm. The YTDQ algal sample was collected by using 25 size plankton net in September 2011 from the Yanta Bridge reservoir in Zengcheng city, China. The sample details were described elsewhere (Zhang et al., 2013a).

The three commercial algae were fractionated into the lipid (LP), lipid free (LF), alkaline nonhydrolyzable carbon (ANHC), and acid nonhydrolyzable carbon (NHC). The flow chart in Fig. S1 in Supplemental data summarizes the major steps for isolation of the algal fractions, as described elsewhere (Zhang et al., 2013a). Briefly, the OS samples were extracted to separate lipids by using Soxhlet extraction with 2:1 $CHCl_3/CH_3OH$ (v/v) for 24 h. The lipid fractions (LP) were dried at 100 °C. Subsamples of the lipid-free fractions (LF) were saponified for 1 h in 1 M KOH in 85:15 methanol/H_2O (v/v). The alkaline nonhydrolyzable carbon (ANHC) fractions were hydrolyzed twice with 2 M trifluoroacetic acid (TFA, Acros) at 100 °C for 3 h. Subsequently subsamples of ANHC fractions were hydrolyzed in 4 and 6 M TFA at 100 °C for 18 h. Finally, the residual hydrolyzable organic matter was removed with 6 M HCl at 110 °C for 24 h.

2.2. Characterization of algae and algal fractions

The algal and zooplankton samples were then analyzed for C, H, N, and O using an Elementar Vario ELIII or a Heraeus CHN-O-RAPID elemental analyzer. The elemental compositions of the investigated samples are summarized in Table 1 and Table S1 in Supplemental data.

Solid-state NMR experiments were performed on a Bruker DSX400 spectrometer operating at 400-MHz ^1H and 100-MHz ^{13}C frequencies. The ^{13}C chemical shifts were referenced to tetramethylsilane, using the COO resonance of glycine in the α-modification at 176.46 ppm as a secondary reference. The high-spinning speed multi-ramped amplitude cross polarization/magic angle spinning technique was applied for acquiring quantitative ^{13}C NMR spectra (Johnson and Schmidt-Rohr, 2014). This multiple-cross polarization (multiCP) technique provides a simple, robust way to obtain quantitative solid-state ^{13}C NMR spectra of organic materials, with

Table 1
Elemental compositions of the original algal samples and their fractions.

Sample	N %	C %	H %	O %	CHNO %	C/N	H/C	H/O	O/C	(O + N)/C
OS										
Spirulina	3.72	33.9	4.97	38.0	80.6	10.6	1.76	2.09	0.84	0.93
Seaweed	2.17	28.8	4.29	33.3	68.6	15.5	1.79	2.06	0.87	0.93
Porphyra	5.43	42.7	6.45	42.7	97.3	9.17	1.81	2.42	0.75	0.86
Chlorella	4.32	25.5	4.85	30.9	65.5	6.89	2.28	2.51	0.91	1.05
Sphaerellopsis	4.06	26.0	4.91	31.2	66.2	7.47	2.27	2.52	0.9	1.03
LHH25	3.07	20.2	3.59	18.4	45.3	7.68	2.13	3.12	0.68	0.81
LHHPOM	5.87	31.9	5.11	26.9	69.8	6.34	1.92	3.04	0.63	0.79
YTDQ	7.42	41.8	6.56	34.9	90.7	6.57	1.88	3.01	0.63	0.78
LP										
Spirulina	0.83	66.1	9.09	21.6	97.6	92.9	1.65	6.73	0.25	0.26
Seaweed	0.92	68.2	8.84	21.4	99.4	86.5	1.56	6.61	0.24	0.25
Porphyra	1.59	62.4	8.86	29.7	102	45.8	1.7	4.77	0.36	0.38
LF										
Spirulina	4.59	28.6	4.26	31.5	69	7.27	1.79	2.16	0.83	0.96
Seaweed	2.74	25.4	4.05	29.9	62.1	10.8	1.91	2.17	0.88	0.97
Porphyra	5.73	42.9	6.5	42.3	97.3	8.73	1.82	2.46	0.74	0.85
ANHC										
Spirulina	0.87	30.0	4.21	44.2	79.3	40.2	1.69	1.52	1.11	1.13
Seaweed	1.2	31.4	4.2	40.6	77.4	30.5	1.61	1.66	0.97	1.00
Porphyra	0.61	40.5	6.18	51.0	98.3	77.5	1.83	1.94	0.94	0.96
NHC										
Spirulina	0.71	36.1	3.40	34.2	74.4	59.32	1.13	1.59	0.71	0.73
Seaweed	0.81	38.4	3.21	32.7	75.1	55.31	1.00	1.57	0.64	0.66
Porphyra	0.92	43.1	4.19	32.9	81.1	54.66	1.17	2.04	0.57	0.59

good signal-to-noise ratio. The spectra were measured at a spinning speed of 14 kHz, where spinning sidebands are fairly small (<3%) and have little overlap with center bands. The 90° pulse lengths were 4.3 μs for ^{1}H and 4 μs for ^{13}C. To achieve dead-time-free detection, which is indispensable for spectra with broad lines, all spectra were recorded with a Hahn echo generated by an EXORCYCLED 180° pulse applied one rotation period (t_r) after the end of cross polarization. The ^{1}H decoupling field strength was $|\gamma B_1|/2\pi = 65$ kHz during the period of 2 $t_r = 0.14$ ms duration before the Hahn echo, and ca. 55 kHz during signal detection. The ramp for each CP period was implemented with 11 steps of 0.1 ms duration and a 1% amplitude increment (90–100%). The recycle delays were 2 s. The duration of the repolarization period (t_z) in multiCP was 0.7 s. Corresponding multiCP spectra of nonprotonated C and mobile segments were selected by recoupled dipolar dephasing (multiCP/DD) with a dipolar dephasing time of 68 μs. The number of transients averaged was between 768 and 3072.

2.3. Biosorption experiments

The equilibrium biosorption isotherms were conducted for NP, a technical mixture, which was obtained from Sigma–Aldrich (purity >94%). The physicochemical properties of NP are presented in Table S2. Its log K_{ow} is 4.48 and water solubility is 5.43 mg L^{-1}. Concentrated stock solutions (100 mg L^{-1} and 2000 mg L^{-1}) in methanol were prepared and spiked to distilled water as needed. Methanol concentrations in the aqueous biosorption solutions were less than 0.2% and have no measurable effect on the biosorption (Wauchope and Koskinen, 1983). All the biosorption isotherms were obtained using a batch equilibration technique in 20 mL glass ampules at 25 ± 1 °C. Background solution (pH = 7) contained 5 mg L^{-1} $NaHCO_3$, 0.005 mol L^{-1} $CaCl_2$ and 100 mg L^{-1} NaN_3 as a biocide. Preliminary tests showed that the apparent biosorption equilibrium for the algal samples was reached during 14 d. The vials were sealed with fire to prevent any NP vapor loss and then placed on a shaker set at 125 rpm for 14 d. After the equilibrium, the vials were put upright for 2 d to allow suspended solids to settle. 2 mL of the supernatant was mixed with 1 mL of methanol in 4 mL glass vials in order to prevent NP uptake to the vial wall. NP concentrations were measured by using high performance liquid chromatograph (HPLC) fitted with fluorescence detector and Inertsil ODS-SP reverse-phase column (150 cm × 4.6 mm × 5 μm). Injection volume was 10 μL. 70% acetonitrile/30% water was used as a mobile phase at a flow rate of 1.0 mL min^{-1}, and an excitation and emission wavelength for the detector was 277 nm and 300 nm, respectively.

2.4. Biosorption model

The Freundlich isotherm model has the following form:

$$\log q_e = \log K_F + n \log C_e \quad (1)$$

and the modified Freundlich equation

$$\log q_e = \log K_f' + n \log C_r \quad (2)$$

where q_e is the solid-phase concentration (μg g^{-1}) and C_e is the liquid-phase equilibrium concentration (μg L^{-1}). K_F is the biosorption capacity-related parameter ((μg g^{-1})/(μg L^{-1})^n) and n is the isotherm nonlinearity index.

K_f' is the modified Freundlich isotherm capacity coefficient, and C_r is the dimensionless aqueous phase concentration. For less polar and sparely soluble compounds, C_r is related to solute activity (a) in water phase referenced to their respective pure liquid or supercooled liquid state at a given temperature condition (Carmo et al., 2000). The values of K_f' and K_F are correlated in the following equation:

$$K_f' = K_F(S_W)^n \text{or} \quad K_F(Sscl)^n \quad (3)$$

where S_w and C_e are the solubility and the equilibrium concentration of the solute at temperature T (K), respectively. The supercooled liquid-state solubility (S_{scl}) was used instead of S_w for crystalline organic compounds.

3. Results and discussion

3.1. Composition and elemental ratios of bulk algae and isolated algal fractions

These samples had been used in a study of Phen sorption (Zhang et al., 2013a), and will be introduced briefly. The percentages of the organic fractions for the commercial algae are presented in Table S1. LP, LF, ANHC, and NHC account for 3.27–14.24%, 65.15–93.98%, 9.81–27.31%, and 4.07–5.93% of total organic carbon (TOC), respectively. It is noted that these NHC contents are much lower than those observed in estuary sediments and soils (25.6–73.8% of TOC) (Ran et al., 2007a).

The H/O atomic ratio can be used as an index of the degree of oxidation of the organic matter. The H/O atomic ratios range from 2.06 to 2.42, from 2.51 to 2.52, and from 3.01 to 3.12 in the bulk commercial algal species, cultured algal species, and field-collected plankton samples, respectively. The H/O atomic ratios were highest for LP, with an order of ANHC, NHC < OS < LF < LP. The field-collected plankton samples have higher H/O ratios than the commercial algal species and cultured algal species. A high H/O ratio indicates relatively low amounts of oxygen-containing functional groups and may result in an increase in the sorption capacity.

The (O + N)/C atomic ratio can be used as a polarity index of the organic matter. The O/C ratios are significantly related to the (O + N)/C ratios, therefore the O/C atomic ratio can be replaced by (O + N)/C ratio as a polarity index of the organic matter. The (O + N)/C atomic ratios range from 0.74 to 1.05, from 0.25 to 0.38, from 0.85 to 0.97, from 0.96 to 1.13, and from 0.59 to 0.73 in the OS, LP, LF, ANHC, and NHC fractions of the commercial algae, respectively. These values are lower than those of plant biomass (Chen et al., 2005; Wang et al., 2007). Moreover, the polarity index ((O + N)/C) is lowest for LP, and may be arranged in an order: LP < NHC < OS, LF < ANHC. These ratios indicate that the bulk algae and algal fractions have different polarities.

3.2. Structure of bulk algae and isolated algal fractions

The ^{13}C NMR experiments were performed for all the OS, the LF and NHC fractions, except for the LHH25 field-collected plankton sample due to its limited amount. The spectra in thin lines and thick lines represent quantitative ^{13}C NMR spectra of all C (multiCP) and of nonprotonated or mobile C (multiCP with recoupled dipolar dephasing), respectively (Fig. 1). The assignments are as follows: 0–45 ppm, alkyl C; 45–61 ppm, O–CH_3/NCH; 61–92 ppm, O-alkyl C; 92–115 ppm, O–C–O anomeric C; 115–146 ppm, aromatic C (including aromatic C–C and aromatic C–H); 146–165 ppm, aromatic C–O; 165–190 ppm, COO/N–C=O; and 190–220 ppm, ketone/aldehyde (Mao et al., 2012). The relative percentages of different C functional groups are listed in Table 2.

After dipolar dephasing, all spectra (thick lines) contain signals derived from C–CH_3 at 0–24 ppm and from mobile $(CH_2)_n$ around 30 ppm. The poly(methylene) C fraction is estimated by integrating

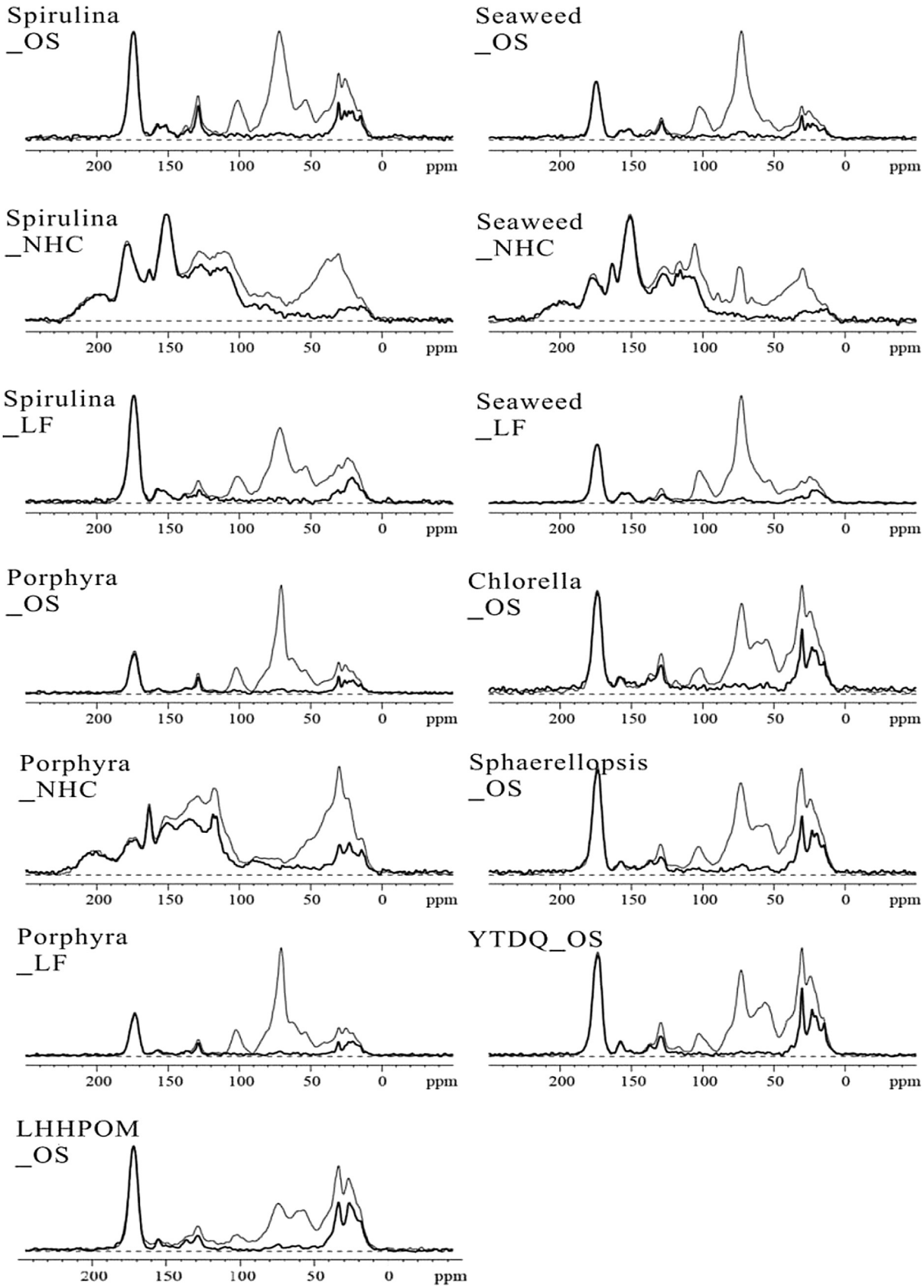

Fig. 1. MultiCP ^{13}C spectra (thin lines) and multiCP ^{13}C spectra after recoupled dipolar dephasing (thick lines) of the original algal samples (OS) as well as LF and NHC fractions.

Table 2
Functional groups from the quantitative multiCP ^{13}C NMR spectra.

Samples	0 −45 ppm alkyl(%)	45–61 ppm O −CH_3/NCH(%)	61–92 ppm O-alkyl(%)	92–115 ppm anomeric(%)	115–146 ppm		146–165 ppm arom C–O(%)	165–190 ppm COO/N–C=O(%)	190–220 ppm ketone/ aldehyde(%)	Aliphaticity(%)[a]	Polar C (%)[b]	27.5 −31.8 ppm $(CH_2)_n$
					arom C −C(%)	arom C −H(%)						
OS												
Spirulina	24.7	8.9	30.7	7.8	4.5	3.1	2.6	17.6	0.1	81.2	59.9	5.0
Seaweed	17.7	7.1	41.2	10.7	3.8	2.5	2.7	13.9	0.5	79.3	65.3	5.8
Porphyra	20.7	10.6	42.0	8.1	4.0	1.6	1.0	11.9	0.0	84.8	65.6	5.8
Chlorella	34.6	11.5	23.3	5.1	4.5	3.4	2.3	15.3	0.0	85.3	52.5	7.4
Sphaerellopsis	33.3	10.9	25.0	5.8	3.6	2.7	1.9	16.2	0.7	86.0	54.6	7.1
LHHPOM	19.1	9.6	42.9	11.0	2	1.9	1.9	11.6	0.1	82.8	66.1	2.7
YTDQ	35.8	12.1	22.4	4.6	3.6	3.1	1.8	16.5	0.1	87.5	53.0	7.9
LF												
Spirulina	23.3	10.4	27.5	7.4	3.6	2.7	3.5	21.3	0.4	80.8	63.0	3.4
Seaweed	17.1	9.0	40.2	10.7	2.8	2.0	3.2	14.8	0.2	79.9	67.4	2.7
Porphyra	20.6	10.9	41.8	8.4	2.9	2.2	1.2	11.9	0.0	85.4	65.8	3.9
NHC												
Spirulina	17.7	5.4	7.7	13.1	17.2	3.2	15.7	13.7	6.3	40.1	48.8	3.0
Seaweed	14.9	4.3	11.4	15.5	17.0	2.7	18.7	10.4	5.2	37.4	49.9	2.9
Porphyra	27.0	6.0	5.6	8.1	20.5	6.7	12.3	8.2	5.8	48.5	37.8	5.4

[a] Aliphaticity = 100 × aliphatic C(0–115 ppm)/[aromatic C (115–165 ppm) + aliphatic C(0–115 ppm)] and Aromaticiy = 100 × aromatic C(115–165 ppm)/[aromatic C (115–165 ppm) + aliphatic C(0–115 ppm)].
[b] Polar C = polar aliphatic (45–92 ppm) + polar aromatic and C = O (146–220 ppm) (%).

the chemical shift region 27.5–31.8 ppm (Mao et al., 2002; Hu et al., 2000). Because the signals in the 45–61 ppm region are just above the baseline in almost all dipolar-dephased spectra (thick lines), this indicates that mobile OCH_3 groups are not present in these samples, and NCH groups instead account for most of the signals in the 45–61 ppm region in the multiCP spectra (thin lines). While the dipolar-dephased spectra of NHC samples show signals from nonprotonated O-alkyl C (61–92 ppm) and nonprotonated anomeric C (92–115 ppm), these intensities are insignificant in the spectra of most OS and LF samples.

In general, the OS samples contain high O-alkyl C (22.4–42.9% of all C) and alkyl C (17.7–35.8%), but low aromatic C (5.80–10.2%) (Table 2). The OS samples also have high polar C (52.5–66.1%) and high aliphaticity (79.3–87.5%). Compared with other algal samples, the OS samples of Chlorella and Sphaerellopsis algal species, and the YTDQ field collected plankton samples contain more alkyl C and poly(methylene) C (i.e., $(CH_2)_n$), but less O-alkyl C and anomeric C.

After organic solvent extraction, the mobile $(CH_2)_n$ percentages decrease in the LF fractions relative to the corresponding OS samples for *Spirulina* and *Seaweed* (Table 2). This is consistent with the less prominent $(CH_2)_n$ signals in their dipolar dephased spectra (Fig. 1), and suggests that the removed lipid fraction contains higher mobile $(CH_2)_n$. This finding also agrees with previous results (Mao et al., 2007). But for *Porphyra,* the mobile $(CH_2)_n$ signal varies slightly and is quite similar to that of the OS, likely due to the lower content of lipid in *Porphyra*.

More prominent differences in C functional group compositions are noted between the NHC fractions and their corresponding OS and LF samples (Fig. 1 and Table 2). The NHC fractions generally contain much lower O-alkyl C (5.6–11.4% of all C) than their corresponding OS (30.7–42.0%) and LF samples (27.5–41.8%), indicating that the majority of polysaccharides and carbohydrates were removed during alkaline and acid hydrolysis. In addition, the aromatic C including aromatic C–C, aromatic C–H and aromatic C–O, and ketone/aldehyde C are much more abundant in the NHC fractions than in corresponding OS and LF samples. The signal at 27.5–31.8 ppm is the most intense in the NHC fraction of *Porphyra*, suggesting that its NHC fraction contains the highest polymethylene carbon among the three commercial algae.

3.3. Biosorption isotherms

The data presented in Table 3 indicate that all of the biosorption isotherms for NP on the 20 samples are well fitted to the Freundlich equation. The Freundlich biosorption isotherms of NP by the OS samples and their LP, LF, ANHC and NHC fractions are presented in Fig. S2. The biosorption isotherms for OS are linear, indicating that the primary mechanism of sorption is partitioning into algae biomass. However, there are few data available for the biosorption of NP. Previous studies reported similar linear sorption parameters for NP on humic acids (Li et al., 2011) and terrestrial soils (Düring et al., 2002). In addition, the biosorption isotherms for LP and LF are linear, but slightly nonlinear for the ANHC fractions (n = 0.867–0.975), and essentially nonlinear for the NHC fractions (n = 0.450–0.525). This phenomenon is in agreement with our previous study on Phen (data presented in Table S3). Moreover, the nonlinearity factor n in this study for NP sorption by each of the NHC fractions is lower than that for Phen (n = 0.707–0.727).

The Freundlich isotherm is the most commonly used model to describe retention of HOCs by heterogeneous sorbents. Because of inconsistent units of constants calculated from the Freundlich model, it is difficult to strictly compare the sorption of organic molecules by different sorbents. The modified Freundlich coefficient (K_f') has units that are independent of the values of n, thus allowing direct comparison of sorption data for different sorbents (Carmo et al., 2000). The log K'_{foc} values range from 2.24 to 2.59, from 1.94 to 2.90, from 2.34 to 2.75, from 1.87 to 2.20, and from 2.69 to 3.59 (μg g^{-1} OC^{-1}) for the OS, LP, LF, ANHC, and NHC fractions, respectively (Table S4). The biosorption capacity values for the commercial algal fractions, except for the *Porphyra* sample, increase in the order: ANHC < OS, LF < LP, NHC. It is obvious that the LP and NHC fractions have higher biosorption capacities for NP than other fractions do for the three commercial algae.

The K_{OC} values range from 31,916 to 71,044 mL g^{-1} for the bulk algae in this study, which are similar to those of river sediments (Navarro et al., 2009), but higher than those of humic acids (Li et al., 2011) and aquifer materials (Ying et al., 2003). The biosorption capacity parameters log K_{Foc} for the bulk field-collected plankton samples and bulk *Spirulina* sample are significantly higher than for the other bulk commercial algae and cultured algae, potentially relating to their lipid contents.

Table 3
Freundlich isotherm parameters and partitioning coefficients (K_{OC}) for the samples.

Sample	K_F[a]	n	N[b]	R^2	f_{oc}(%)	K_{FOC}[c]	log K_{FOC}	K_{OC}, ml/g		
								$C_e = 0.005S_w$	$C_e = 0.05S_w$	$C_e = 0.5S_w$
OS										
Spirulina	20.9 ± 0.06	1	18	0.9957	33.89	61.76	1.79	61,759		
Seaweed	9.22 ± 0.02	1	17	0.9928	28.82	31.98	1.50	31,978		
Porphyra	14.5 ± 0.06	1	16	0.9915	42.67	33.91	1.53	33,911		
Chlorella	10.5 ± 0.01	1	13	0.9035	25.49	41.15	1.61	41,153		
Sphaerellopsis	8.31 ± 0.02	1	16	0.9181	26.04	31.92	1.50	31,916		
LHH25	13.6 ± 0.02	1	16	0.9917	20.21	67.34	1.83	67,343		
LHHPOM	22.7 ± 0.09	1	15	0.9798	31.91	71.04	1.85	71,044		
YTDQ	23.8 ± 0.08	1	16	0.9458	41.82	57.04	1.76	57,037		
LP										
Spirulina	96.2 ± 0.01	1	12	0.9916	66.09	145.5	2.16	145,544		
Seaweed	79.6 ± 0.09	1	8	0.9905	68.16	116.7	2.07	116,725		
Porphyra	9.96 ± 0.01	1	14	0.9415	62.38	15.96	1.20	15,959		
LF										
Spirulina	15.4 ± 0.01	1	12	0.9834	28.62	53.88	1.73	53,878		
Seaweed	10.2 ± 0.06	1	11	0.9867	25.42	40.20	1.60	40,205		
Porphyra	44.6 ± 0.05	1	10	0.9877	42.85	104.2	2.02	104,154		
ANHC										
Spirulina	5.42 ± 0.03	0.899 ± 0.003	11	0.9958	29.96	18.091	1.26	12,968	10,278	8145
Seaweed	4.50 ± 0.01	0.975 ± 0.001	12	0.9941	31.38	14.34	1.16	13,209	12,470	11,773
Porphyra	15.0 ± 0.06	0.867 ± 0.002	14	0.9981	40.50	36.91	1.57	23,813	17,531	12,907
NHC										
Spirulina	81.3 ± 0.04	0.460 ± 0.015	20	0.9467	36.09	225.4	2.35	38,017	10,964	3162
Seaweed	170 ± 0.08	0.450 ± 0.002	19	0.9440	38.36	443.7	2.65	72,415	20,409	5752
Porphyra	691 ± 0.09	0.525 ± 0.002	17	0.9654	43.09	1603	3.21	335,074	112,238	37,596

[a] K_F is the sorption capacity coefficient with units of $(g/g)/(ug/l)^n$.
[b] Number of data.
[c] K_{FOC} is the OC-normalized sorption capacity coefficient with units of $(ug/g)/(ug/l)^n$.

LP accounts for 14.24%, 18.50% and 23.58% of the total organic carbon for the bulk *Spirulina* and field-collected plankton samples (LHHPOM and YTDQ), respectively (Table S1), exhibiting the highest biosorption capacities among all of the bulk algal samples. As a result, the biosorption coefficients of the LF fractions decrease after removal of the LP fractions for the *Spirulina* sample. But for the *Seaweed* and *Porphyra* samples, the removal of the LP components increases the sorption capacity, which may suggest that the presence of LP in *Seaweed* and *Porphyra* samples should block the accessibility of sorption sites for NP. This phenomenon is likely related to a strong competition between lipids and Phen as previously observed (Zhang et al., 2013a). It also suggests that the sites occupied by the LP component are partially associated with high energy sorption.

The highly elevated ratios of (N + O)/C after saponification suggest an obvious increase in the polarity for the ANHC samples, which is responsible for their significantly decreasing biosorption capacity. Other studies have indicated that after saponification, the increase of hydrophilic groups (e.g., carboxyl and hydroxyl) may block the access of hydrophobic Phen to adsorption sites and partitioning domains in the biomass (Chen et al., 2005; Chen and Schnoor, 2009).

For the NHC fractions, the K_{OC} value for NP decreases as a function of C_e due to the isotherm nonlinearity. The average K_{OC} value for Phen at $C_e = 0.005S_w$ is 42,549 ± 12,806 mL g^{-1} and 148,503 ± 124,381 mL g^{-1} for the bulk commercial algae and their NHC isolates, respectively. The biosorption capacities of the NHC fractions increase in the order: *Spirulina* < *Seaweed* < *Porphyra*. Previous studies revealed that NHC including kerogen carbon, black carbon (BC), and aged organic matter in soils and sediments is very important to the sorption and fate of PAHs (Ran et al., 2007b) and EDCs (Sun et al., 2010). Moreover, recent investigations (Chen et al., 2005; Chen and Schnoor, 2009; Li et al., 2010) found that the n values ranged from 0.790 to 0.836, and the K_{OC} values at $C_e = 0.005$ S_w ranged from 56,593 to 127,637 mL g^{-1} for the biosorption of Phen on the NHC fractions isolated from plant cuticlar materials and root tissue of switchgrass seedlings. These data indicate that both properties of the investigated organic matter, and the physical and chemical properties of the pollutants are crucial to the sorption behavior.

3.4. Correlation between biosorption isotherm parameters and properties of algae

Negative correlations between log K'_{foc}(μg g^{-1} OC^{-1}) and polarity index (O/C and (O + N)/C) on the OS samples and their fractions excluding the LP fractions are highly significant ($p < 0.0001$, Fig. S3a and b). The log K'_{foc} values are negatively related to O–CH_3/NCH, O-alkyl C, COO/N–C=O and polar C groups obtained from MultiCP ^{13}C NMR spectra for the OS, LF, and NHC fractions (Fig. S4a–d). These correlations strongly suggest that polarity affects the biosorption capacity of NP, which is consistent with previous investigations. A strong negative linear relationship between K_{OC} and polarity for NP was observed when three samples consisting of lignin, chitin, and cellulose were used (Burgess et al., 2005). The same trend was also observed for the biosorption of Phen (Chen et al., 2005; Wang et al., 2007).

In addition, the log K'_{foc} values are positively related to the H/O atomic ratios for the OS, LF, and ANHC fractions ($p < 0.01$, Fig. S3). This significant correlation is consistent with previous observation (Grathwohl, 1990), which found a positive linear relationship between the log K_{OC} and atomic H/O ratio for TCE on a wide variety of SOM.

In this investigation, the log K_{OC} (mL g^{-1} OC^{-1}) values are moderately related to the weight percentages of LP for the OS samples (Fig. 2a), consistent with our previous results (Zhang et al., 2013a). The log K_{OC} (mL g^{-1} OC^{-1}) values are positively related to the immobile $(CH_2)_n$ for the OS, LF, and NHC fractions of three commercial algae (Fig. 2b). As the NHC fraction isolated in this study for the *Porphyra* samples contain higher immobile

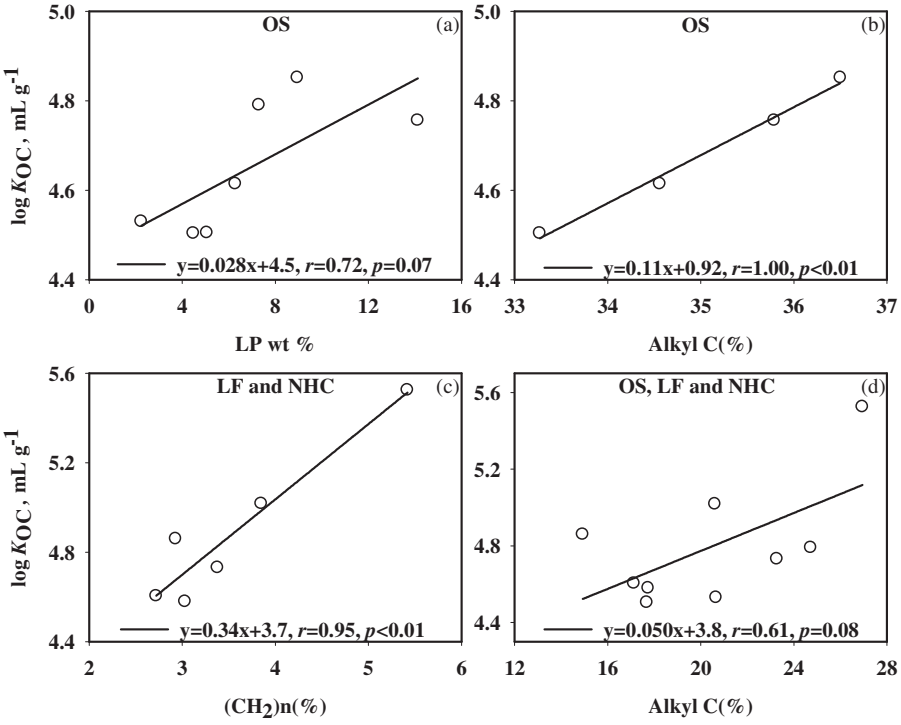

Fig. 2. Correlation between log K_{OC} (mL g^{-1} OC^{-1}) values of nonylphenol (NP) and the weight percentages of LP for the original algal samples (OS) (a). Correlation between log K_{OC} (mL g^{-1} OC^{-1}) values of NP and alkyl C groups for the two cultured algae and two field-collected plankton bulk samples (b). Correlation between log K_{OC} (mL g^{-1} OC^{-1}) values of NP and $(CH_2)_n$ for the LF and NHC fractions of three commercial algae (c). Correlation between log K_{OC} (mL g^{-1} OC^{-1}) values of NP and alkyl C groups for the OS, LF and NHC fractions of three commercial algae (d).

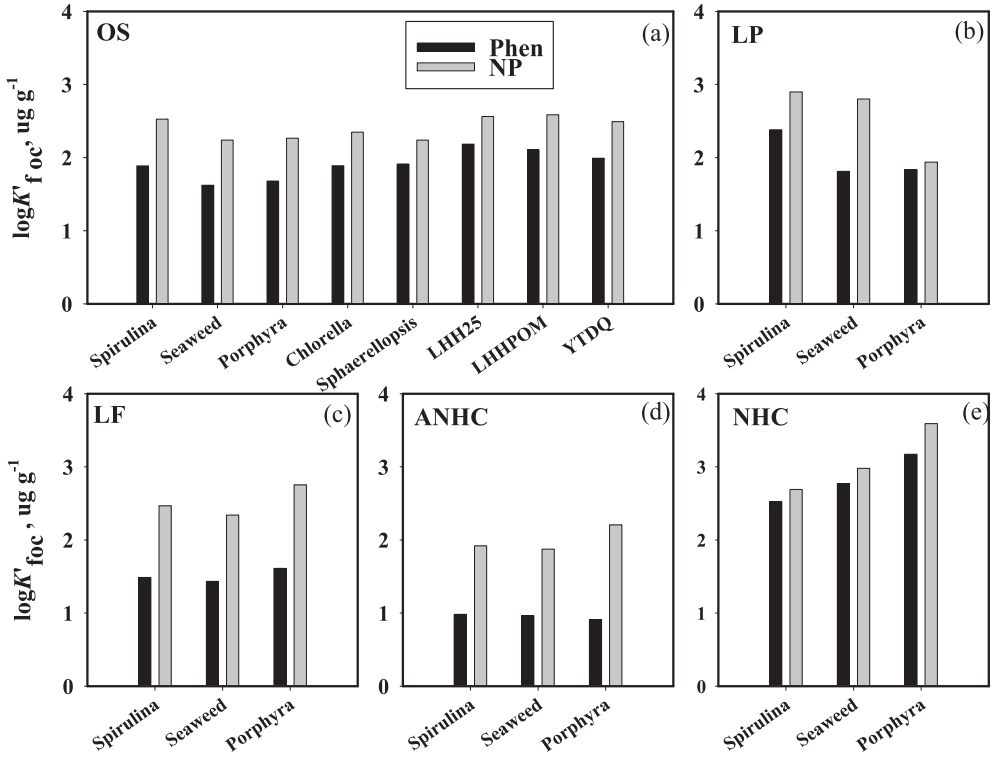

Fig. 3. Comparison of OC-normalized biosorption capacity coefficients (log K'_{foc}) of NP and Phen on OS (a), LP (b), LF (c), ANHC (d) and NHC (e) based on the modified Freundlich model.

polymethylene carbon than that for the *Seaweed* or *Spirulina*, it exhibits higher biosorption capacity. Structurally condensed polymethylene NHC exhibits greater isotherm nonlinearity, consistent with previous investigations (Ran et al., 2007a; Sun et al., 2010). Moreover, significant correlations between log K_{OC} (mL g^{-1} OC^{-1}) values and alkyl C groups for the OS samples of two cultured algae and two field-collected plankton samples are observed (Fig. 2b). The log K_{OC} (mL g^{-1} OC^{-1}) values are moderately correlated with alkyl C groups for the OS, the LF and NHC fractions of three commercial algae (Fig. 2d), demonstrating the importance of aliphatic structures. A previous study found that the K_{OC} values were positively related to alkyl contents, indicating that the aliphaticity of humic acids was important to the sorption of NP (Li et al., 2011). Other studies reported a significant positive correlation between Phen sorption capacity and content of nonpolar aliphatic poly(-methylene)-rich domains (Chefetz et al., 2000; Mao et al., 2002; Salloum et al., 2002). Hence, aliphatic compositions and structures of the algal samples are very important to the biosorption of NP in the investigated biosorption system.

3.5. Biosorption mechanism for NP

The Freundlich isotherm parameters and partitioning distribution coefficients (K_{OC}) for Phen by all the algal samples in our previous study are presented in Table S3 (Zhang et al., 2013a). Comparison between OC-normalized biosorption capacity coefficients (log K'_{foc}(μg g^{-1} OC^{-1})) of NP and Phen on the OS, LP, LF, ANHC, and NHC samples based on the modified Freundlich model is shown in Table S4 and Fig. 3.

The log K'_{foc}(μg g^{-1} OC^{-1}) values for the biosorption of NP by the OS samples, LP, LF, ANHC, and NHC fractions are greater than those for Phen, respectively. However, the log K_{ow} value of NP (4.48) is close to that of Phen (4.57). In Fig. S5, log $[K'_{foc(NP)}/K'_{foc(Phen)}]$ values show strong positive correlations with O/C, (N + O)/C ratios, O-alkyl C, and polar C groups, suggesting the significance of hydrogen bonding. Besides, the multivariate correlation equation among the log $[K'_{foc(NP)}/K'_{foc(Phen)}]$ and aromatic C–H and polar C for the bulk algal samples (OS), LF and NHC fractions has the form: log $[K'_{foc(NP)}/K'_{foc(Phen)}]$ = 0.22 x_1 + 0.050 x_2 − 2.9 (r = 0.88, p = 0.001; x_1 is aromatic C–H, x_2 is polar C), indicating that π electron interaction and hydrogen bonding may be the reason for the higher biosorption capacity of NP. This finding is similar to the previous observation that the sorption coefficients of selected endocrine disruptors were positively correlated with the aromaticity and phenolic groups for a wide variety of dissolved organic matter (DOM) (Yamamoto et al., 2003). The above facts indicate that nonspecific hydrophobic partitioning and other specific chemical interactions occur for the sorption of NP on the investigated samples.

A previous investigation (Gong et al., 2012) found that hydrophobic partitioning is the main mechanism for sorption of phenolic xenoestrogen on particulate organic carbon (POC) in the Pearl River. Other investigators (Ran et al., 2007b) also reported significant correlation between log K_{OC} and log K_{ow} for polycyclic aromatic hydrocarbons (PAHs) in the soils and sediments of the Pearl River Delta. Gong et al. (2012) and Yamamoto et al. (2003) suggested that the contribution of different specific binding mechanisms could cause such a deviation from the log K_{OC}–log K_{ow} relationship. The specific interaction mechanisms may include polar interaction (Chen et al., 2005), π–π electron donor–acceptor interaction (Zhu et al., 2004), and hydrogen bonding (Yamamoto et al., 2003) and so forth. The interaction between phenolic groups of endocrine disruptors and DOM increases the importance of H-donor, H-acceptor, and polarizability contributions relative to the simple hydrophobic interactions in the sorption mechanisms (Yamamoto et al., 2003). The above facts indicate that besides nonspecific hydrophobic partitioning, other specific chemical interactions such as hydrogen bonding and π–π electron donor–acceptor interaction occur for the sorption of NP on the investigated samples.

4. Conclusions

The biosorption isotherms of NP on the bulk algae and the algal organic fractions have been investigated. Negative correlations between log K'_{foc} and polarity index are significant. The log K'_{foc} values are positively related to the H/O atomic ratios. These data indicate that polarity and aliphatic carbon affects the biosorption capacity of NP. Based on quantitative multiCP ^{13}C NMR data, we have further shown that the log K'_{foc} values are negatively related to COO/N–C=O groups, polar C and O-alkyl C. Moreover, positive correlation between the log K'_{foc} and $(CH_2)_n$ indicates the importance of poly(methylene) carbon for NP sorption. The K'_{foc} values for NP are greater than for Phen for all of the samples. The log $[K'_{foc(NP)}/K'_{foc(Phen)}]$ values show strong positive correlations with O/C, (N + O)/C ratios, O-alkyl C, polar C groups, and aromatic carbon, suggesting that π electron interaction and hydrogen bonding may be the reason for the higher biosorption capacity of NP. These findings help to further understand the important role of algae in determining the distribution, transport and fate of NP in the environment.

Acknowledgments

This study was supported by GIGCAS 135 project (Y234081001), a key joint project of the National Natural Science Foundation of China and Guangdong Province (U1201235), a “Team Project” of the National Natural Science Foundation of China (41121063), and the Earmarked Foundation of the State Key Laboratory (SKLOG2009A04). This is contribution No. IS-1998 from GIGCAS.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.envpol.2014.12.020.

References

Aksu, Z., 2005. Application of biosorption for the removal of organic pollutants: a review. Process Biochem. 40, 997–1026.
Burgess, R.M., Pelletier, M.C., Gundersen, J.L., Perron, M.M., Ryba, S.A., 2005. Effects of different forms of organic carbon on the partitioning and bioavailability of nonylphenol. Environ. Toxicol. Chem. 24, 1609–1617.
Carmo, A.M., Hundal, L.S., Thompson, M.L., 2000. Sorption of hydrophobic organic compounds by soil materials: application of unit equivalent Freundlich coefficients. Environ. Sci. Technol. 34, 4363–4369.
Chefetz, B., Deshmukh, A.P., Hatcher, P.G., Guthrie, E.A., 2000. Pyrene sorption by natural organic matter. Environ. Sci. Technol. 34, 2925–2930.
Chen, B., Johnson, E.J., Chefetz, B., Zhu, L., Xing, B., 2005. Sorption of polar and nonpolar aromatic organic contaminants by plant cuticular materials: role of polarity and accessibility. Environ. Sci. Technol. 39, 6138–6146.
Chen, B., Schnoor, J.L., 2009. Role of suberin, suberan, and hemicellulose in phenanthrene sorption by root tissue fractions of switchgrass (*Panicum virgatum*) seedlings. Environ. Sci. Technol. 43, 4130–4136.
Chen, B., Wang, Y., Hu, D., 2010. Biosorption and biodegradation of polycyclic aromatic hydrocarbons in aqueous solutions by a consortium of white-rot fungi. J. Hazard. Mater. 179, 845–851.
Düring, R.A., Krahe, S., Gäth, S., 2002. Sorption behavior of nonylphenol in terrestrial soils. Environ. Sci. Technol. 36, 4052–4057.
Gao, Q., Wong, Y.S., Tam, N.F.Y., 2011a. Removal and biodegradation of nonylphenol by different Chlorella species. Mar. Pollut. Bull. 63, 445–451.
Gao, Q., Wong, Y.S., Tam, N.F.Y., 2011b. Removal and biodegradation of nonylphenol by immobilized *Chlorella vulgaris*. Bioresour. Technol. 102, 10230–10238.
Gelin, F., Volkman, J.K., Largeau, C., Derenne, S., Sinninghe Damsté, J.S., De Leeuw, J.W., 1999. Distribution of aliphatic, nonhydrolyzable biopolymers in marine microalgae. Org. Geochem. 30, 147–159.
Gong, J., Ran, Y., Chen, D., Yang, Y., Zeng, E.Y., 2012. Association of endocrine-disrupting chemicals with total organic carbon in riverine water and suspended

particulate matter from the Pearl River, China. Environ. Toxicol. Chem. 31, 2456–2464.
Grathwohl, P., 1990. Influence of organic matter from soils and sediments from various origins on the sorption of some chlorinated aliphatic hydrocarbons: implications on K_{OC} correlations. Environ. Sci. Technol. 24, 1687–1693.
Hu, W., Mao, J., Xing, B., Schmidt-Rohr, K., 2000. Poly(methylene) crystallites in humic substances detected by nuclear magnetic resonance. Environ. Sci. Technol. 34, 530–534.
Johnson, R.L., Schmidt-Rohr, K., 2014. Quantitative solid-state ^{13}C NMR with signal enhancement by multiple cross polarization. J. Magn. Reson. 239, 44–49.
Kawasaki, N., Araki, M., Nakamura, T., Tanada, S., 2001. Inclusion behavior of 4-nonylphenol into cyclodextrin derivatives. J. Colloid Interf. Sci. 238, 215–218.
Kratochvil, D., Volesky, B., 1998. Advances in the biosorption of heavy metals. Trends Biotechnol. 16, 291–300.
Kwon, J.H., Liljestrand, H.M., Katz, L.E., Yamamoto, H., 2007. Partitioning thermodynamics of selected endocrine disruptors between water and synthetic membrane vesicles: effects of membrane compositions. Environ. Sci. Technol. 41, 4011–4018.
Lang, W., Dejma, C., Sirisansaneeyakul, S., Sakairi, N., 2009. Biosorption of nonylphenol on dead biomass of Rhizopus arrhizus encapsulated in chitosan beads. Bioresour. Technol. 100, 5616–5623.
Li, C., Berns, A.E., Schäffer, A., Séquaris, J.M., Vereecken, H., Ji, R., Klumpp, E., 2011. Effect of structural composition of humic acids on the sorption of a branched nonylphenol isomer. Chemosphere 84, 409–414.
Li, Y., Chen, B., Zhu, L., 2010. Single-solute and bi-solute sorption of phenanthrene and pyrene onto pine needle cuticular fractions. Environ. Pollut. 158, 2478–2484.
Mao, J., Cory, R.M., McKnight, D.M., Schmidt-Rohr, K., 2007. Characterization of a nitrogen-rich fulvic acid and its precursor algae by solid-state NMR. Org. Geochem. 38, 1277–1292.
Mao, J., Hundal, L.S., Thompson, M.L., Schmidt-Rohr, K., 2002. Correlation of poly(methylene)-rich amorphous aliphatic domains in humic substances with sorption of a nonpolar organic contaminant, phenanthrene. Environ. Sci. Technol. 36, 929–936.
Mao, J., Kong, X., Schmidt-Rohr, K., Pignatello, J.J., Perdue, E.M., 2012. Advanced solid-state NMR characterization of marine dissolved organic matter isolated using the coupled reverse osmosis/electrodialysis method. Environ. Sci. Technol. 46, 5806–5814.
Nakada, N., Tanishima, T., Shinohara, H., Kiri, K., Takada, H., 2006. Pharmaceutical chemicals and endocrine disrupters in municipal wastewater in Tokyo and their removal during activated sludge treatment. Water Res. 40, 3297–3303.
Navarro, A., Endo, S., Gocht, T., Barth, J.A., Lacorte, S., Barceló, D., Grathwohl, P., 2009. Sorption of alkylphenols on Ebro River sediments: comparing isotherms with field observations in river water and sediments. Environ. Pollut. 157, 698–703.
Navarro, A.E., Portales, R.F., Sun-Kou, M.R., Llanos, B.P., 2008. Effect of pH on phenol biosorption by marine seaweeds. J. Hazard. Mater. 156, 405–411.
Nizzetto, L., Gioia, R., Li, J., Borga, K., Pomati, F., Bettinetti, R., Dachs, J., Jones, K.C., 2012. Biological pump control of the fate and distribution of hydrophobic organic pollutants in water and plankton. Environ. Sci. Technol. 46, 3204–3211.
Ran, Y., Sun, K., Yang, Y., Xing, B., Zeng, E., 2007a. Strong sorption of phenanthrene by condensed organic matter in soils and sediments. Environ. Sci. Technol. 41, 3952–3958.
Ran, Y., Sun, K., Ma, X., Wang, G., Grathwohl, P., Zeng, E.Y., 2007b. Effect of condensed organic matter on solvent extraction and aqueous leaching of polycyclic aromatic hydrocarbons in soils and sediments. Environ. Pollut. 148, 529–538.
Salloum, M.J., Chefetz, B., Hatcher, P.G., 2002. Phenanthrene sorption by aliphatic-rich natural organic matter. Environ. Sci. Technol. 36, 1953–1958.
Soares, A., Guieysse, B., Jefferson, B., Cartmell, E., Lester, J.N., 2008. Nonylphenol in the environment: a critical review on occurrence, fate, toxicity and treatment in wastewaters. Environ. Int. 34, 1033–1049.
Sun, K., Gao, B., Zhang, Z., Zhang, G., Liu, X., Zhao, Y., Xing, B., 2010. Sorption of endocrine disrupting chemicals by condensed organic matter in soils and sediments. Chemosphere 80, 709–715.
Vazquez-Duhalt, R., Marquez-Rocha, F., Ponce, E., Licea, A.F., Viana, M.T., 2005. Nonylphenol, an integrated vision of a pollutant. Appl. Ecol. Environ. Res. 4, 1–25.
Wang, X., Cook, R., Tao, S., Xing, B., 2007. Sorption of organic contaminants by biopolymers: role of polarity, structure and domain spatial arrangement. Chemosphere 66, 1476–1484.
Wang, X., Xing, B., 2007. Importance of structural makeup of biopolymers for organic contaminant sorption. Environ. Sci. Technol. 41, 3559–3565.
Wauchope, R.D., Koskinen, W.C., 1983. Adsorption-desorption equilibria of herbicides in soil: naphthalene as a model compound for entropy-enthalpy effects. Weed Sci. 744–751.
Writer, J.H., Ryan, J.N., Barber, L.B., 2011. Role of biofilms in sorptive removal of steroidal hormones and 4-nonylphenol compounds from streams. Environ. Sci. Technol. 45, 7275–7283.
Xu, K., Harper Jr., W.F., Zhao, D., 2008. 17α-Ethinylestradiol sorption to activated sludge biomass: thermodynamic properties and reaction mechanisms. Water Res. 42, 3146–3152.
Yamamoto, H., Liljestrand, H.M., Shimizu, Y., Morita, M., 2003. Effects of physical-chemical characteristics on the sorption of selected endocrine disruptors by dissolved organic matter surrogates. Environ. Sci. Technol. 37, 2646–2657.
Ying, G.G., Kookana, R.S., Dillon, P., 2003. Sorption and degradation of selected five endocrine disrupting chemicals in aquifer material. Water Res. 37, 3785–3791.
Zhang, D., Ran, C., Yang, Y., Ran, Y., 2013a. Biosorption of phenanthrene by pure algae and field-collected planktons and their fractions. Chemosphere 93, 61–68.
Zhang, Y., Ran, Y., Mao, J., 2013b. Role of extractable and residual organic matter fractions on sorption of phenanthrene in sediments. Chemosphere 90, 1973–1979.
Zhu, D., Hyun, S., Pignatello, J.J., Lee, L.S., 2004. Evidence for π-π electron donor-acceptor interactions between π-donor aromatic compounds and π-acceptor sites in soil organic matter through pH effects on sorption. Environ. Sci. Technol. 38, 4361–4368.