

Sequestration of Nonylphenol in Sediment from Bohai Bay, North China

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The ubiquity of nonylphenol (NP) in aquatic environments has been well documented, and the long-term fate of NP in sediments is a concern from the viewpoint of risk assessment due to its endocrine-disrupting effects. This paper reports on the assessment of long-term fate of NP in marine sediments by determining extractable and nonextractable fractions of NP in surface sediments and a sediment core from Bohai Bay, North China. The extractable fraction was operationally defined as the fraction of NP that was extracted with a solvent mixture of methanol/methylene chloride, and the nonextractable fraction was the portion of NP that can be released from the sediments by alkaline hydrolyzing after the initial solvent extraction. The total concentrations (extractable and nonextractable) of NP were 3.4–34.3 ng/g dw in the surface sediments and 2.2–17.7 ng/g dw in the sediment core. Depending on the sedimentation time, the percentage of nonextractable NP relative to the total NP in the core ranged from 38 to 99%. Based on the relationship between the percentage of nonextractable NP in sediments and sedimentation time, the sequestration rate of NP in the sediment core from Bohai Bay was estimated to be $0.94\% \cdot a^{-1}$. These results have important implications in understanding the geochemical fate of NP in sediments.

Introduction

Sequestration is the process which includes intraorganic matter and intraparticle diffusion in sediment/soil, which are believed to render contaminants less available for interactions with biological systems (1), as exemplified by laboratory studies of several insecticides (1), 4-nitrophenol (2), and polycyclic aromatic hydrocarbons (PAHs) such as phenanthrene and pyrene (3, 4). The extent of sequestration for chemicals was expressed as the extractability by mild extraction (3), which was affected by time, i.e., aging. Under laboratory conditions, the time-dependent decline in the extractable quantity of ¹⁴C-labeled organic chemicals from soil by a mild extraction has been demonstrated to be a useful

approach to provide evidence for sequestration of chemicals in soil (2–5). In field investigations, however, the chemical degradation procedures such as alkaline hydrolysis and boron tribromide (BBr₃) treatment were generally applied to extract the nonextractable proportion of chemicals which could not be extracted by a mild extraction as exemplified by hexachlorophene (6, 7), 2,2-bis(chlorophenyl)–1,1,1-trichloroethane (DDT) (8), and benzotriazoles (9).

Nonylphenol (NP) is the anaerobic biodegradation product of nonylphenol polyethoxylates (NPEOs) surfactants in aquatic environments, and it is of particular concern because of its endocrine-disrupting effects in aquatic organisms, mammals, and birds. Over the past few decades, thousands of marine and freshwater sediments have been analyzed, which demonstrated that the sediment was a major sink for NP (10). Therefore, it is important to elucidate the sequestration processes of NP in sediments because the long-term fate of NP is a vital criterion for assessing its ecological risks (11–17). Many studies have focused on the fate of NP in the environment such as the spatial and temporal distributions, and clarified both concentration levels at a regional scale and the temporal variation by historic record in field assessments (15, 18, 19). The studies on the characterized temporal distribution of NP have especially emphasized the recent increased (19, 20) or decreased input (15) due to the changes in usage and legal regulation in different countries. However, these results are all induced based on the extractable fraction of NP in sediments, i.e., the amounts that can be extracted with mild organic solvents. In fact, part of NP in sediments could be nonextractable by covalently binding to organic matter as exemplified by several other phenolic compounds such as 4-nitrophenol (2) and hexachlorophene (6, 7).

In this paper, nonextractable NP (NP_{nonextractable}) and extractable NP (NP_{extractable}) were first differentiated by a mild extraction using a mixture of organic solvents (methanol and methylene chloride) followed by alkaline hydrolysis of surface sedimentary samples and a well-dated sedimentary core from Bohai Bay, North China. The sequestration rate, which was expressed as the variation of NP_{nonextractable} percentage in total NP with sedimentation time, was estimated, and the contents of total organic carbon (TOC) and black carbon (BC) in the sediments were also determined to better understand potential sequestration mechanisms. The results obtained in this study have important implications in understanding the long-term fates of NP in sediments.

Materials and Methods

Materials. NP (technical grade), a mixture of compounds with branched side chains, was purchased from Kanto Chemicals (Tokyo, Japan). And 4-*n*-nonylphenol (4-*n*-NP), used as the internal standard for analyzing NP, was obtained from Kanto Chemicals (Tokyo, Japan). Standard stocking solutions were prepared in acetonitrile. N,O-bis-(trimethylsilyl) trifluoroacetamide (BSTFA) reagent was obtained from Supelco (Bellefonte, PA).

Methylene chloride, acetonitrile, acetone, hexane, 2-propanol, and methanol were all HPLC grade obtained from Fisher Chemical Co. (Shanghai, China). Ultra pure water was made by the Easypure UV compact ultrapure system at a resistivity of 18.2 MΩ/cm. All the glassware was rinsed with *n*-hexane and acetone of pesticide residue grade and then baked in a muffle furnace at 400 °C for 4 h before use to avoid contamination.

Sediment Sampling. Figure S1 in the Supporting Information (SI) shows the sampling map for sedimentary samples.

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TABLE 1. Concentrations (ng/g dw) of Extractable and Nonextractable NP in Surface Sediments from Bohai Bay, North China

sites	concentration (ng/g dw)	
	NP _{extractable}	NP _{nonextractable}
I	7.0	27.3
J	2.2	9.7
K	1.4	8.6
L	0.7	5.0
M	1.1	10.3
N	1.8	7.6
O	1.6	7.5
P	2.0	9.0
Q	1.3	6.5
R	1.6	13.0
S	2.3	18.8
T	1.3	17.9
U	2.2	26.8
V	1.5	5.0
W	0.4	3.0

Fifteen surface sediments (0–30 cm beneath the surface) were collected from the Bohai Bay in September of 2002. The sedimentary core was collected from Bohai Bay (Station A: N 38°17902', E 117°48005') using a 6-cm diameter box corer in the summer of 2000. A stainless steel static gravity corer was employed to minimize the disturbance of the surface sediment layer. The core was sectioned at 2.5 cm intervals to the depth of 55 cm and at 5 cm intervals thereafter, and all samples were stored at –20 °C until extraction was carried out.

Extractable Fraction. Prior to chemical degradation, all sedimentary samples of 10–20 g air-dried and homogenized sediments were mixed with 20 g Na₂SO₄ and spiked with recovery surrogate (4-*n*-NP). Then the spiked samples were Soxhlet extracted first with a solvent mixture of methanol/methylene chloride (3:7) for 24 h. The extracts were rot-evaporated and reconstituted with 3 mL hexane. The 3 mL extract was passed through aminopropyl silica cartridges (500 mg, 6 mL, Supelco) conditioned with 9 mL acetone, 3 mL methylene chloride, and 9 mL hexane. After the extract of the sedimentary sample was passed through the cartridge, a 1 mL rinse of hexane was added. The cartridge was eluted with 8 mL hexane/2-propanol (90:10 v/v). The eluent was nitrogen-evaporated to dryness and reconstituted by 0.4 mL hexane, and was derivatized by adding 100 μL BSTFA reagent to analyze NP. This fraction was operationally defined as the extractable fraction in this paper.

The procedure described above was validated by recovery (90% for NP), and the surrogate recovery of 4-*n*-NP in the sedimentary samples was 95%. The concentrations reported here have not been corrected for recovery. Precision was estimated at better than 20% based on analysis of three replicate samples.

Nonextractable Fraction. The chemical degradation procedures were sequentially carried out basically according to the alkaline hydrolysis and BBr₃ treatment described in previous papers (8, 9). Briefly, the pre-extracted sediment samples (5.0 g) were placed in 22 mL vials, and 180 mg KOH dissolved in a mixture of 0.3 mL water and 12 mL methanol was added. Then the closed vials were heated at 105 °C for 24 h. After cooling, the supernatant liquid was decanted, and the solid residue was washed twice with 3 mL methanol. And then, 8 mL water was added, and the mixed solution was acidified to pH 3–5 by addition of 300 μL hydrochloric acid. Subsequently the solution was extracted with 5 mL hexane five times. The combined hexane layers were rot-evaporated to dryness, and reconstituted by 0.5 mL hexane. The final extract was derivatized by adding 100 μL BSTFA

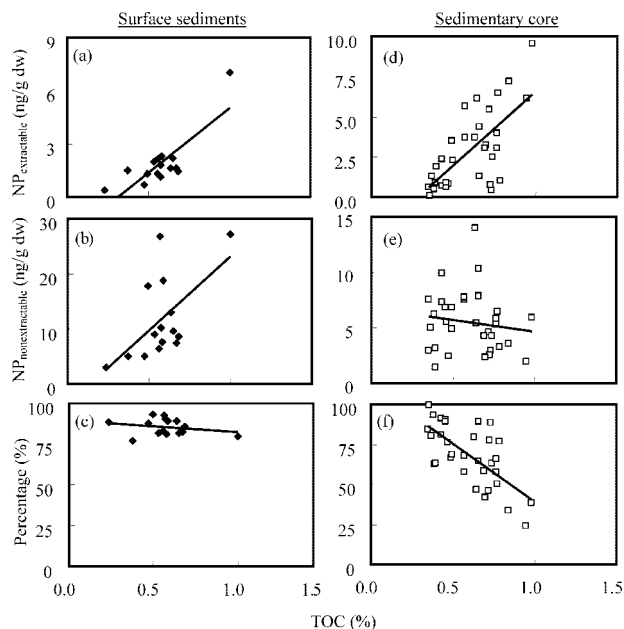


FIGURE 1. Relationships between concentrations of NP_{extractable}, NP_{nonextractable}, and percentage of NP_{nonextractable} and total organic carbon (TOC) content in sediments. The lines represent linear regression in surface sediments (♦) and sedimentary core (□). (a) NP_{extractable}, $p < 0.0001$, $r^2 = 0.662$; (b) NP_{nonextractable}, $p = 0.018$, $r^2 = 0.347$; (c) the percentage of NP_{nonextractable} relative to total NP, $p = 0.432$, $r^2 = 0.058$; (d) NP_{extractable}, $p < 0.0001$, $r^2 = 0.466$; (e) NP_{nonextractable}, $p = 0.403$, $r^2 = 0.020$; (f) the percentage of NP_{nonextractable} relative to total NP, $p < 0.0001$, $r^2 = 0.461$.

reagent (21) to analyze NP by GC-MS analysis. For BBr₃ treatment, sediment samples (2.0 g) were extracted for 2 h using 8 mL 1.0 mol/L BBr₃ solution in a water bath. The process of cleanup and concentrating was same as mentioned-above.

To validate whether chemical degradation procedures degraded NP itself, we applied the two processes to the reference material of NP. It was found that no alteration of NP was observed in the extracts after alkaline hydrolysis as illustrated in SI Figure S2(b), whereas BBr₃ treatment degraded NP as shown in SI Figure S2(c). Thus, only alkaline hydrolysis procedure was applied to all sedimentary samples in this study, and the nonextractable NP was designated to the fraction of NP that was released by alkaline hydrolysis from sediments. This part of NP reflects the covalently bound NP (via ester bonds), and NP noncovalently incorporated into organic matter.

Analysis. The instrumental conditions for analyzing NP and 4-*n*-NP, and the quantitation and quality assurance/quality control (QA/QC) are all provided in the Supporting Information.

Dating of the Core Sediment. Data of dating in this study were quoted from Wang et al. (23) and Li et al. (24). Briefly, the specific activities of the isotopes ¹³⁷Cs and ²¹⁰Pb in different slices of the core were measured in the different slices by direct gamma assay. And the sediment chronologies for the core were inferred based on a correlation of Pb isotopes profiles, depending on the apparent sedimentation rate in the core. The depth of the surface mixed layer (7 cm) was chosen by direct observation, and the constant initial concentration (CIC) model was fitted between ²¹⁰Pb flux and depth excluding the surface mixed layer. The average sedimentation rate in the core (A) was 3 cm·a⁻¹ according to the profile of Pb isotope.

TOC. TOC was measured by the high temperature combustion method. Dry sediments (about 5 mg) were put

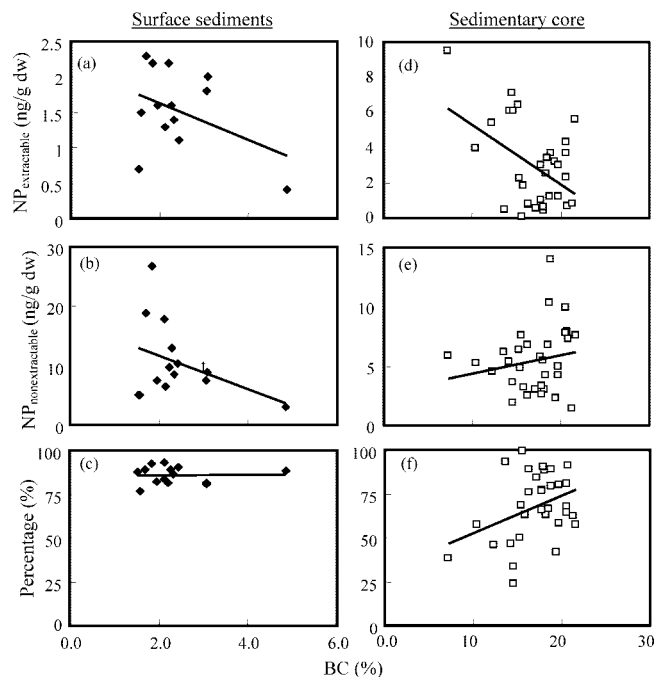


FIGURE 2. Relationships between concentrations of $\text{NP}_{\text{extractable}}$, $\text{NP}_{\text{nonextractable}}$, and percentage of $\text{NP}_{\text{nonextractable}}$ and black carbon (BC) content in sediments. The lines represent linear regression in surface sediments (\blacklozenge) and sedimentary core (\square). (a) $\text{NP}_{\text{extractable}}$, $p = 0.177$, $r^2 = 0.134$; (b) $\text{NP}_{\text{nonextractable}}$, $p = 0.198$, $r^2 = 0.134$; (c) the percentage of $\text{NP}_{\text{nonextractable}}$ relative to total NP, $p = 0.809$, $r^2 = 0.005$; (d) $\text{NP}_{\text{extractable}}$, $p = 0.007$, $r^2 = 0.211$; (e) $\text{NP}_{\text{nonextractable}}$, $p = 0.334$, $r^2 = 0.034$; (f) the percentage of $\text{NP}_{\text{nonextractable}}$ relative to total NP, $p = 0.038$, $r^2 = 0.135$.

into small precombusted (600 °C, 4 h) quartz sample boats. Phosphoric acid (44%) was added to remove inorganic carbon from the samples. Finally, the samples were analyzed using a total organic carbon (TOC) analyzer (Apollo 9000, Tekmar-Dohrmann, Mason, OH).

BC. BC was referred to as a particulate phase, including soot and charcoal, formed during incomplete combustion of fossil fuels and biomass (25), which has a high degree of aromatic structure and contains reactive oxygenated surface functional groups (26). The analysis procedure was based on Lim's chemical oxidation method (27). 3.0000 g of dried sediments were weighed into precleaned Teflon test tubes and carefully treated with 15 mL of 3 mol·L⁻¹ HCl over 24 h to remove carbonate from the sediment matrix. Following repeated centrifuge and rinsing (3–6 times) with filtered ultra pure water, about 15 mL of 10 mol·L⁻¹ HF/ 1 mol·L⁻¹ HCl were added to the residue and the reaction allowed to continue at room temperature for a further 24 h. Sediment samples were then subjected to a final 24 h treatment of 10 mol·L⁻¹ HCl after centrifuge and rinsing (3–6 times) until the pH of rinsing water was 4–5. The washed acid-treated sediment samples were allowed to dry at 60 °C until constant weight was obtained. Then the sediment acid-treated was weighed in glass test tubes and treated with 10 mL of 0.1 mol·L⁻¹ K₂Cr₂O₇/ 2 mol·L⁻¹ H₂SO₄. For the oxidation step, samples were kept in test tubes and transferred to a water bath at 55 °C over 60 h to remove kerogen from the sediment matrix. Following repeated centrifuge and rinsing (3–6 times) with filtered ultra pure water, the residue was transferred to porcelain crucible and dry at 60 °C until constant weight (M_{BC}) was obtained. Finally, the carbon content (TOC_{BC}) was measured using Element Analysis instrument (Elementar, Germany). Black carbon in sediment can be calculated using the relationship as follows:

$$\text{BC} (\%) = [(\text{TOC}_{\text{BC}} \times M_{\text{BC}}) / (\text{TOC}_0 \times 3.0000)] \times 100 \quad (1)$$

where TOC_0 was the TOC of original sediment.

Statistical Analysis. The statistical program SPSS (Ver 11.0; Chicago, IL) was used to analyze the collected data. Correlations were examined by Pearson's rank correlation test.

Results and Discussion

Extractable and Nonextractable NP in Surface Sediments.

$\text{NP}_{\text{extractable}}$ was detected in all 15 surface sediments (Table 1), and the chromatogram of the extract from site J was shown in SI Figure S2(d). The highest concentration (7 ng/g dw) was found at site I (SI Figure S1), near to the Nanpawu River which receives industrial and municipal wastewaters from Tianjin City. The lowest concentration (0.4 ng/g dw) was found at site W (SI Figure S1) which is far from Tianjin. These concentration levels were comparable to those (<1–6.37 ng/g dw) reported for Ulsan Bay, Korea (28), but were much lower than those in Tokyo Bay (120–640 ng/g dw) (15), in marine sediments in Spain (<10–1050 ng/g dw) (29), and in the Dutch coastal zone of the North Sea (30) which were close to outfall points of sewage effluent or estuaries.

$\text{NP}_{\text{nonextractable}}$ was also detected in all 15 surface sediments ranging from 3.0 ng/g dw at site W to 27.3 ng/g dw at site I, which was several times higher than those of the extractable fractions. SI Figure S2 (d, e) shows the GC-MS chromatogram of the extract from site J, and the peak composition of $\text{NP}_{\text{nonextractable}}$ (SI Figure S2 (e)) was found to be similar to that of $\text{NP}_{\text{extractable}}$ (SI Figure S2 (d)), suggesting that no obvious isomer selective bound reaction to sediment occurred in Bohai Bay. The total concentrations (extractable and nonextractable) of NP (NP_{total}) were 3.4–34.3 ng/g dw in the surface sediments. The percentage of $\text{NP}_{\text{nonextractable}}$ relative to NP_{total} ranged from 79.6% at site I to 93.3% at site T, indicating that NP is prone to convert to the more stable nonextractable form in sediments.

In addition, the concentration of $\text{NP}_{\text{extractable}}$ at site J was 2.2 ng/g dw, similar to that at site U, while the concentration of $\text{NP}_{\text{nonextractable}}$ at site J was 9.7 ng/g dw, much lower than that at site U (26.8 ng/g dw) suggesting that the potential to form a nonextractable portion could be associated with the chemical and physical characteristics of sediments. Figure

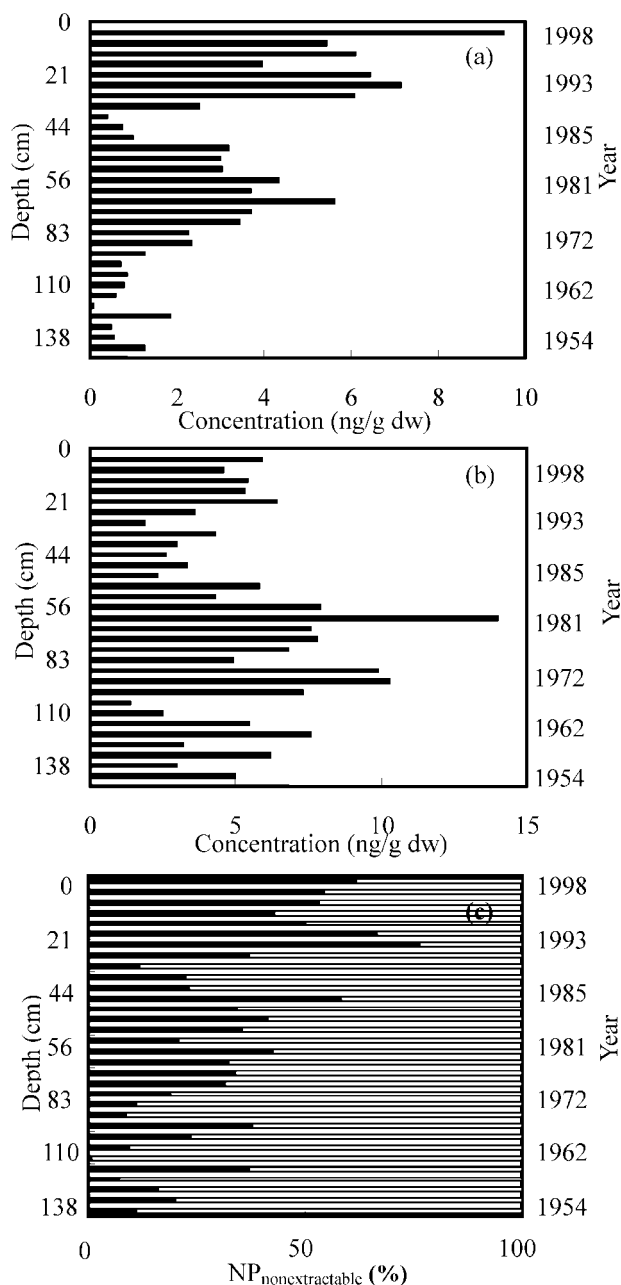


FIGURE 3. Vertical profiles of NP concentrations in the sediment core from Bohai Bay, north China. (a) concentration of NP_{extractable}; (b) concentration of NP_{nonextractable}; (c) percentage of NP_{nonextractable} (%).

1 shows the relationship between the concentrations of NP_{extractable}, NP_{nonextractable} and percentage of NP_{nonextractable} and TOC in sedimentary samples. It was found that NP_{extractable} was significantly correlated to the TOC values in sediments from Bohai Bay ($p < 0.001$, $r^2 = 0.662$). A similar phenomenon was also found for some other compounds such as dioxins, hexachlorocyclohexanes (HCHs) and DDTs in Bohai Bay and its adjacent river (17, 31), suggesting that the spatial distribution of NP_{extractable} in sediments would depend on the TOC contents of sediments. However, no relationship between NP_{nonextractable} or percentage of NP_{nonextractable} and TOC was obtained (Figure 1(b, c)), which was similar to the results of benzotriazoles in a Pawtuxet river sedimentary core (9). Whereas sedimentary BC was reported to affect the sorption of some hydrophobic organic contaminants (HOCs) to a greater extent than sedimentary organic carbon (OC) (32), there was no correlation between NP_{extractable} or NP_{nonextractable}

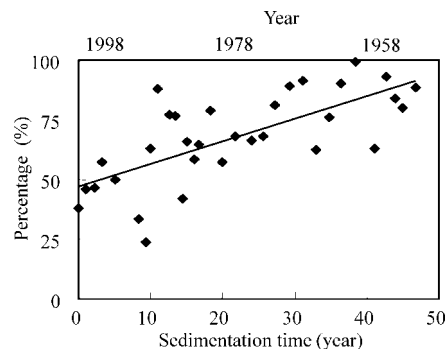


FIGURE 4. Relationship between the percentage of NP_{nonextractable} relative total NP and sedimentation time in the sedimentary core from Bohai Bay, north China ($p < 0.001$, $r^2 = 0.492$).

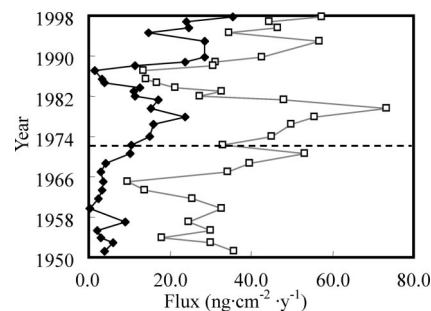


FIGURE 5. Fluxes of NP into Bohai Bay, north China based on total NP concentrations (◆) and extractable NP concentration (□).

and BC content in the surface sediments from Bohai Bay (Figure 2(a–c)).

Sequestration of NP in Sedimentary Core. In the sedimentary core, the concentrations of NP_{extractable} ranged from 0.1 to 9.5 ng/g dw (SI Table S1). The concentration profile of NP_{extractable} shows a bimodal distribution (Figure 3(a)). NP_{extractable} concentration decreased from the 61–66 cm layer corresponding to early 1980s toward the 39–41 cm layer corresponding to late 1980s, which was probably related to the implementation of environmental regulations starting in 1979. The obvious increasing trend observed from late 1980s might be related to the increase of its production in 1990s (SI Table S2) due to the rapid economic growth of China (33). In the deeper sections of the sediment core (>66 cm), the concentrations of NP_{extractable} showed a decreasing trend toward the bottom layer deposited in 1950s.

The concentrations of NP_{nonextractable} in the core ranged from 1.4 to 14 ng/g dw (SI Table S1). Figure 3(b) shows the vertical profile of NP_{nonextractable} in this core. It was found that, the highest concentration of NP_{nonextractable} was 14 ng/g dw at a depth of 61–66 cm deposited around 1980 followed by 10.3 ng/g dw at a depth of 94–99 cm corresponding to late 1960s, which was different from that of extractable fraction. The percentage of NP_{nonextractable} relative to NP_{total} along the core was calculated to be in the range from 23.8 to 99%. It is clear that while the percentages of NP_{nonextractable} relative to NP_{total} (23.8–57.3%) in the surface sediments (7–36 cm) corresponding with the most recent decade were lower than those in deeper sediments (57.5–99%), except for the depth 49–51 cm (41.8%) (Figure 3(c)). This increasing trend of the percentage of NP_{nonextractable} relative to NP_{total} with sedimentation time (or depth in sediment core) was similar with that of C1-benzotriazole in the Pawtuxet River Core (9) as shown in SI Figure S3. The relationships between the percentage of NP_{nonextractable} and TOC or BC content were shown in Figure 1(f) and Figure 2(f), respectively. The percentage of NP_{nonextractable} decreased with increasing TOC, and vice versa

for the relationship with BC content ($p < 0.05$). However, considering no correlation between the percentage of NP_{nonextractable} and TOC or BC content in surface sediments (Figure 1(c) and Figure 2(c)), it is difficult to explain the role of TOC or BC on the sequestration of NP in sediments.

Aging and biodegradation can be expected to be two main factors influencing the percentage of NP_{nonextractable} relative to NP_{total} in the sediment core. Since NP is not biodegradable in anaerobic environments (34, 35), the effects of biodegradation on the percentage of NP_{nonextractable} relative to NP_{total} could be neglected. Therefore, the sequestration rate of NP in the sedimentary core was defined as the following relationship between the percentage of NP_{nonextractable} relative to NP_{total} and sedimentation time (years aging) using a simple linear regression (eq 2).

$$\text{percentage (\%)} = a + b \times T \quad (2)$$

where percentage (%) is the concentration percentage of NP_{nonextractable} relative to NP_{total}; T is the sedimentation time, and b is defined as the sequestration rate of NP in sediment. Figure 4 shows the relationship between the concentration percentage of NP_{nonextractable} relative to NP_{total} and sedimentation time in the sedimentary core. The percentage of NP_{nonextractable} relative to NP_{total} appears to increase with increasing sedimentation time in the sedimentary core (eq 3).

$$\text{percentage (\%)} = 47.286 + 0.9415 \times T (r^2 = 0.492, n = 32, p < 0.05) \quad (3)$$

From eq 3, the sequestration rate of NP in the core was determined to be $0.94\% \cdot a^{-1}$, which is the first time that a quantitative estimate of the sequestration rate of NP in sediment was obtained from a field investigation.

Fluxes. In previous studies, fluxes were estimated only using the concentration of extractable fraction of chemicals, neglecting the nonextractable fraction. As shown in Figure 5, without regard to the presence of NP_{nonextractable}, the flux was relatively low ($0.2\text{--}9.1 \text{ ng}/(\text{cm}^2 \cdot \text{a})$) in the sedimentary layer deposited in the 1950s, and subsequently increased to $23.7 \text{ ng}/(\text{cm}^2 \cdot \text{a})$ in the $100\text{--}105 \text{ cm}$ layer corresponding to the late 1970s. It was found that the maximum value of flux was $57.5 \text{ ng}/(\text{cm}^2 \cdot \text{a})$, and occurred in recent years.

On the other hand, when considering NP_{nonextractable} in sediments, the fluxes of NP were estimated in the sediments by eq 4:

$$\text{flux} = (C_E + C_N) \times R \times FF \quad (4)$$

where C_E and C_N are the concentrations of NP_{extractable} and NP_{nonextractable} in sediment segment ($\text{ng}/\text{g dw}$), respectively; R is the sedimentation rate in sediment segment (cm/a), and FF is the density of the location (g/cm^3). As a result, estimated fluxes were about $1.3\text{--}8.5$ times higher than those in the extractable fraction in layers ($<83 \text{ cm}$) deposited after the 1970s, and its vertical profile was similar to that estimated by the extractable fraction after the 1970s. In addition, the maximum value of flux was $73.2 \text{ ng}/(\text{cm}^2 \cdot \text{a})$ occurred around 1980, and the flux in the layer ($\geq 83 \text{ cm}$) deposited before the 1970s fluctuated, which is obviously different from that of the extractable fraction in the same layers.

Thus, this paper first clarified the sequestration of NP in a sedimentary core from Bohai Bay, which could not be neglected, for the studies of the long-term fate, bioavailability and risk assessment of NP in sediment. The sequestration of NP in sediments based on its total bound fraction should be further investigated, considering that only alkaline hydrolysis procedure was applied to release the bound NP in this study.

Acknowledgments

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Supporting Information Available

Additional information as noted in text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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