

# Temporal trends of nonylphenol and bisphenol A contamination in the Pearl River Estuary and the adjacent South China Sea recorded by dated sedimentary cores

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## Abstract

Three dated sedimentary cores were collected for the investigation of temporal trends and the environmental loadings of nonylphenol (NP) and bisphenol A (BPA) in recent decades in the Pearl River Estuary (PRE), South China and the adjacent South China Sea (SCS). The peak fluxes of NP and BPA occurred in the mid-1980s in the PRE, coincident with the rapid economic growth in China. The decline of NP and BPA fluxes is attributable to the implementation of sewage treatment in the late 1980s in the Pearl River Delta (PRD). Multi-model distributions were observed for the fluxes of NP and BPA in the SCS with the peak fluxes occurring in the late 1950s and the mid-1970s respectively. The fluxes of NP and BPA have increased since the 1990s due to the lack of adequate wastewater treatment facilities and the constant economic growth. Nonylphenol was quantifiably detected in sediments predating its widespread application (1940s), suggesting the downward penetration of NP in the sediment columns. The characterization results revealed that NP and BPA were preserved well and the isomer-selective degradation of NP did not occur significantly in the sediment cores. The environmental loadings of NP and BPA in the PRE sediments were roughly estimated to be 124 t and 1.7 t respectively over the past 30 years.

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## 1. Introduction

Nonylphenol (NP) and bisphenol A (BPA) have been categorized as endocrine disrupting contaminants

(EDCs) due to their potentially adverse effects on the hormone system of animals, leading to development delay and/or sexual abnormalities (Kawahata et al., 2004; Madsen et al., 2004; Lee and Choi, in press). The US Environmental Protection Agency (USEPA) developed criteria for NP of the acute and chronic toxicity of tens and several micrograms per liter to freshwater and marine organisms respectively (<http://www.epa.gov/waterscience/criteria/nonylphenol/>). Nonylphenol is also listed as one of 27 persistent toxic substances by

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the United Nations Environment Programme (UNEP, 2002). The acute and chronic toxicity of BPA were reported to be in the range of 1–10 µg and sub-micrograms per liter to freshwater and marine species respectively (Kang et al., 2006). Both compounds are bioaccumulating (Keith et al., 2001), posing threats to the health of ecological system and even the human's sustainable development (Rogers-Gray et al., 2000; Kawahata et al., 2004).

Nonylphenol is the degradation product of nonylphenol polyethoxylates (NPnEOs) which are widely used as non-ionic surfactants in domestic and industrial detergents, antistatic agents, emulsifiers for agrochemicals, antioxidants for rubber manufacture, and lubricant oil additives. As the major application (~80% of the demand), industrial and household liquid detergents are responsible for the anticipated steady growth for NP consumption. NP is more persistent and toxic than its ethoxylated precursors (Isobe et al., 2001). BPA is an intermediate in the production of polycarbonate plastics and epoxyresins which are used in a wide variety of products, such as surface coatings and adhesives of food containers and PVC pipes, automobile parts, electronic products, and paints. Commercial production of BPA began in the 1950s when large-scale uses of polycarbonate plastic and epoxy resins were developed and has grown worldwide along with the continued growth of the uses of these materials (<http://www.bisphenol-a.org/>).

Nonylphenol and BPA enter the environment mainly through municipal and industrial wastewater discharge (Shang et al., 1999; Suzuki et al., 2004). The occurrence and environmental behavior of NP and BPA have been well documented in a variety of environmental matrices in North America, Europe, Japan and Korea (Khim et al., 1999; Lye et al., 1999; Shang et al., 1999; Yamashita et al., 2000; Bolz et al., 2001; Isobe et al., 2001; Kannan et al., 2001, 2003; Rice et al., 2003; Stachel et al., 2003; Kawahata et al., 2004; Li et al., 2004). The consumption of NP and BPA in China was about 20,000–25,000 t/yr and 206,000 t/yr respectively in recent years (<http://www.chinainfo.gov.cn/data>, in Chinese). In spite of the heavy use, the information about their occurrence and fate in environment of China is very limited (Chen et al., 2006; Hu et al., 2005). In this work, three sedimentary cores were collected from the Pearl River Estuary (PRE) and the adjacent South China Sea (SCS) to demonstrate the temporal distribution, fluxes, and mass inventories of NP and BPA in recent decades and to study their fate in estuarine and marine sediments in this region.

## 2. Materials and methods

### 2.1. Chemicals and reagents

Nonylphenol (technical mixture), bisphenol A (>99%), surrogate standard bisphenol A-d16 (98% atom D), derivatizing reagent pentafluoropropionic anhydride (PFPA) were purchased from Sigma-Aldrich Canada Ltd. (Oakville, Ont., Canada). Instrumental internal standard (terphenyl-d14) is a product from Supelco (Bellefonte, PA, USA). Distilled chromatographic-grade acetone, dichloromethane (DCM), hexane (HEX), and methanol (MeOH) were from Caledon Laboratories Ltd. (Georgetown, Ont., Canada). Silica gel (100–200 mesh, pore size 150 Å, >99%, Aldrich), anhydrous sodium sulfate, sodium chloride (NaCl), glass wool, and all glassware were sequentially rinsed with MeOH, DCM, and HEX prior to use.

Stock standard solution was prepared at 1 mg ml<sup>-1</sup> with MeOH for each compound except terphenyl-d14 that was prepared with HEX. Working solutions were achieved by dilution of stock solutions with MeOH and HEX respectively. The standard solutions were stored in amber vials at -20 °C.

### 2.2. Studied area

The Pearl River Estuary (PRE) is one of the largest estuaries in the world. It is located in the South China, covering an area of about 2100 km<sup>2</sup> and connecting the continent with the SCS (Fig. 1). The surrounding Pearl River Delta (PRD) is one of the most developed and densely populated areas in China. Around 70% of municipal sewage in the PRD are treated in sewage treatment plants (STPs) prior to discharge into the Pearl River and its tributaries. The remaining municipal wastewater is generally directly discharged into the Pearl River. Industrial wastewaters are basically treated in the plants and then in STPs before they are discharged to the Pearl River. The annual discharge of raw wastewater and STP effluents to the PRE through the Pearl River and its tributaries totalized to >2.0 billion tons in recent years. Therefore, wastewater has become an important contributor to the environmental deterioration in the PRE (Peoples Daily, Jun 15, 2005, in Chinese). Estuarine sediments have been regarded as a significant destination for many anthropogenic pollutants in the PRE, such as PAHs, PCBs, PBDEs, and fecal sterols (Mai et al., 2003, 2005a,b; Peng et al., 2005).

Three sedimentary cores were collected using a four-column static gravity corer (10 cm i.d.) at the PRE and

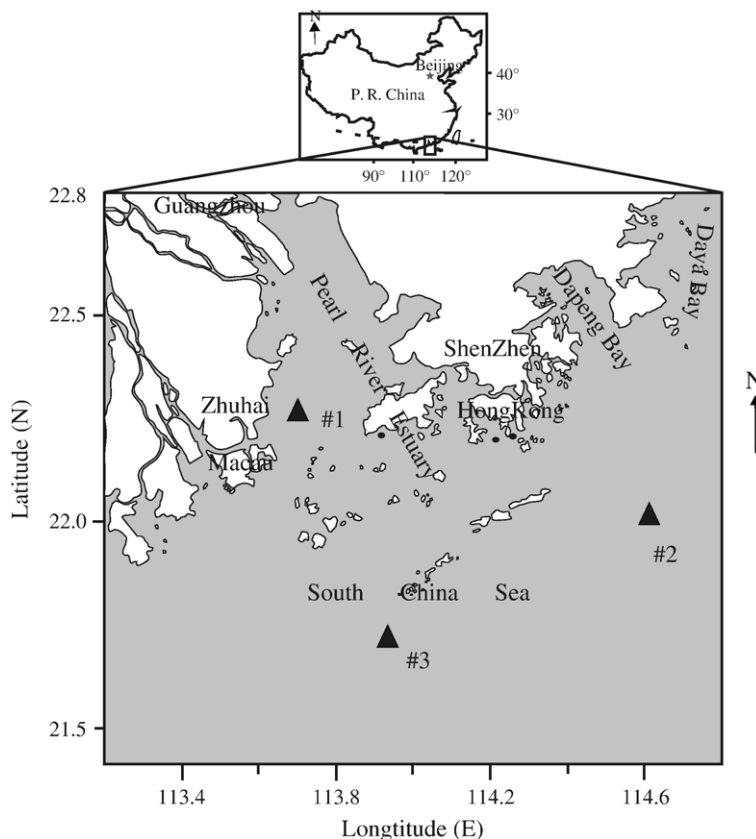


Fig. 1. The sketch map of the studied area and coring stations. ▲ Coring stations; ● submarine outfalls of Hong Kong.

the adjacent SCS (Fig. 1). Care was taken to minimize disturbance of surface sediments. The detailed descriptions of the cores were shown in Table 1. The cores were sectioned at 2-cm interval for core #1, and 1-cm intervals for cores #2 and #3 onboard immediately after collection using a stainless steel blade. The sectioned sediment samples were wrapped with aluminum foil (baked at 450 °C) prior to being packed into polyethylene bags and stored at -20 °C till analysis.

### 2.3. Sample preparation and GC-MS analysis

The extraction and determination of NP and BPA in sediment were described in detail elsewhere (Peng et al., 2006). Briefly, about 10 g of each sedimentary core segment was freeze-dried and homogenized. Appropriate amount of BPA-d16 was added before the sample was sonicated with 5 ml of mixture of acetone and DCM (1:1, v/v), and 3 ml of Milli-Q water for 3 times. The supernatants were combined and were transferred to a separatory funnel that contained saturated NaCl solution. The organic phase was then back-extracted with 15 ml of DCM. The extraction was repeated 3 times. The trace

amount of water in the organic phase was further removed by anhydrous sodium sulfate. The extract was evaporated to about 1 ml and then fractionated on a silica gel column. The column was successively eluted with HEX, DCM and MeOH. The MeOH eluent that contained NP and BPA was blown down to just dryness under a gentle stream of high purity nitrogen and then derivatized with PFPA. The PFPA derivative was finally analyzed by an HP5890 gas chromatograph (GC) coupled with a 5972 mass selective detector (MS) in the selected ion monitoring mode (SIM) after adding terphenyl-d14 as the internal standard. Nonylphenol and BPA were separated on an HP-5 MS column (30 m length × 0.25 mm i.d. × 0.25 μm film). Quantification of NP and BPA was achieved using Enhanced HP ChemStation based on the average relative response factors obtained from the derivatized working standard solutions during GC-MS calibrations (Peng et al., 2006).

### 2.4. Measurement of TOC of the sediment and dating of the sedimentary cores

Content of total organic carbon (TOC) of sediment was measured by an Elementar Vavio EL III elemental

Table 1  
Concentrations, fluxes and inventories of NP and BPA in sediments cores from the Pearl River Estuary and the South China Sea, China

Station	Longitude/latitude	Core length (cm)	Sedimentation rate (cm yr <sup>-1</sup> ) <sup>a</sup>	Time period <sup>b</sup>	Concentration (ng g <sup>-1</sup> dw) <sup>c</sup>		Flux (ng cm <sup>-2</sup> yr <sup>-1</sup> ) <sup>3</sup>		Inventory (ng cm <sup>-2</sup> )		TOC (%)
					NP	BPA	NP	BPA	NP	BPA	
#1	113°42'E/22°16'N	32	0.97	1974–2003	144.0–293.0 (197.5)	2.0–4.3 (3.1)	140–284 (192)	1.9–4.0 (3.0)	5925	92	0.9182–1.0690
#2	114°37'E/22°06'N	37	0.58	1942–1997	76.9–664.7 (246.9)	1.0–12.0 (3.7)	37–262 (108)	<0.3–5.4 (1.7)	6312	97	0.4890–0.6097
#3	113°56'E/21°43'N	31	0.34	1931–1993	134.9–702.7 (322.8)	NA	33–191 (76)	NA	3139	NA	0.3838–0.4855

<sup>a</sup> Mean sedimentation rate.

<sup>b</sup> <sup>210</sup>Pb time.

<sup>c</sup> The numbers in parentheses are mean values.

analyzer (Hanau, Germany) after acidification with HCl (1 N) to remove carbonate. Another aliquot of carbonate-removed sediment was further oxidized thermally at 400 °C for 24 h to eliminate organic carbon prior to elemental carbon (EC) measurement. The sediment cores were dated using <sup>210</sup>Pb dating method which has been described in detail by Zhang et al. (2002) and Mai et al. (2005a). A constant initial <sup>210</sup>Pb concentration model was used to give average sedimentation rates for the sedimentary cores.

## 2.5. Data analysis

The concentrations of NP and BPA in sediments were reported in nanograms per gram of sediment in dry weight (ng g<sup>-1</sup> dw). The flux was estimated using the following equation:

$$\text{Flux} = C_i \rho_i \gamma_i. \quad (1)$$

The inventory was defined as the sum of mass of the contaminant per unit area, and was calculated using the following equation:

$$\text{Inventory} = \sum (C_i - C_b) \rho_i d_i \quad (2)$$

where  $C_i$  (ng g<sup>-1</sup> dw) and  $C_b$  are the measured and background concentrations of NP or BPA in the sediment layer  $i$  respectively ( $C_b$  was assumed to be 0 for both NP and BPA in this work).  $\rho_i$  (g cm<sup>-3</sup>),  $d_i$  (cm) and  $\gamma_i$  (cm yr<sup>-1</sup>) are the dry mass, thickness, and sedimentation rate of the sediment layer  $i$  respectively.

## 2.6. Quality assurance/quality control

A procedural blank (solvent) and a spiked matrix sample (a known amount of NP and BPA spiked into pre-extracted sediment) were set for each batch of 10 field samples. Only trace amount of NP was found in the procedural blanks. Recoveries were 86±17% and 79±13% for NP and BPA respectively in the spiked matrix samples. The surrogate recovery (BPA-d16) averaged 86% with relative standard deviation of 20% in the sediment samples. The presented concentrations were not surrogate recovery corrected.

## 3. Results and discussions

### 3.1. Concentrations, flux and inventories of NP and BPA in the PRE and the SCS

The concentrations, fluxes, and inventories of NP and BPA in sedimentary cores in the PRE and the

adjacent SCS are summarized in Table 1 and Fig. 2. The concentrations of NP and BPA in sedimentary core #1 from the PRE were 144.0–293.0 ng g<sup>-1</sup> and 2.0–4.3 ng g<sup>-1</sup> dw, with the mean values of 197.5 and 3.1 ng g<sup>-1</sup> dw respectively. In sedimentary cores from the SCS (#2 and #3), the concentrations of NP were 76.9–664.7 and 134.9–702.7 ng g<sup>-1</sup> dw, with the mean values of 246.9 and 322.8 ng g<sup>-1</sup> dw respectively. Nonylphenol concentration of the surface sediment in the proximity of core #3 was reported to be 90 ng g<sup>-1</sup> dw (Chen et al., 2006). Levels of BPA varied from 1.0 to 12.0 ng g<sup>-1</sup> dw, with an average of 3.7 ng g<sup>-1</sup> dw in core #2. The levels of NP in the PRE and the adjacent SCS appeared slightly higher than those reported for the Bohai Bay in China with maximum concentration of 203 ng g<sup>-1</sup> dw (Hu et al., 2005) and Yeongil Bay, South Korea with concentrations of 12.3–38.6 ng g<sup>-1</sup> (Koh et al., 2006). Our results for NP were comparable to those of Tokyo Bay (70–530 ng g<sup>-1</sup> dw) in Japan (Isobe et al., 2001), but lower than those in the sediments from the Detroit and

Rouge Rivers (10–60,000 ng g<sup>-1</sup>) in Michigan of USA (Kannan et al., 2001), the Masan Bay (113–3390 ng g<sup>-1</sup>) in South Korea (Khim et al., 1999) and the Tokyo Bay (<10 to 5540 ng g<sup>-1</sup>) in Japan (Yamashita et al., 2000). Lye et al. (1999) reported NP concentrations of 1600–9050 ng g<sup>-1</sup> and 30–80 ng g<sup>-1</sup> in sediments from highly industrialized Tees Estuary and the industrialized/urbanised Tyne estuary respectively in the north-east England. They suggested that effluents from sewage treatment plants and surfactant manufactures were significant contributors to the high levels of NP in the Tees Estuary. The concentrations of BPA in the PRE and the adjacent SCS were similar with those reports for sediments in rivers (<0.5–15 ng g<sup>-1</sup>) of Germany (Bolz et al., 2001) and river mouths in Okinawa and Ishigaki Island (nondetectable – 13 µg kg<sup>-1</sup>) in Japan (Kawahata et al., 2004) but slightly lower than that of sediment in the Masan Bay (2.7–50.3 ng g<sup>-1</sup>) in South Korea (Khim et al., 1999). BPA was found to be <1 ng g<sup>-1</sup> in sediments in the Yeongil Bay in South Korea (Koh et al., 2006).

Nonylphenol fluxes were 140–284, 37–262, 33–191 ng cm<sup>-2</sup> yr<sup>-1</sup>, with mean values of 192, 108, and 76 ng cm<sup>-2</sup> yr<sup>-1</sup> in the sedimentary cores #1, #2, and #3 respectively, lower than the estimated NP fluxes in the Tokyo Bay (170 to 2770 ng cm<sup>-2</sup> yr<sup>-1</sup>) in Japan (Yamashita et al., 2000). The average fluxes of BPA in core #1 and #2 were 3.0 and 1.7 ng cm<sup>-2</sup> yr<sup>-1</sup> respectively. The inventory of NP in core #1 was 5925 ng cm<sup>-2</sup> in the past 30 years, which was comparable to the sum of NP and its NPnEOs (6 µg cm<sup>-2</sup>) in the sediment basin of the Strait of Georgia, Canada (Shang et al., 1999). The high fluxes and inventories in core #1 suggested that PRE is also the major destination of the phenolic EDCs of this region as wastewater and sewage treatment plant effluents pass the Pearl River and its tributaries. The gradually seaward decreasing trend of fluxes in the three cores may indicate the transport of the two phenolic EDCs from the PRE to the offshore SCS. The seaward decreases of NP concentrations were documented for the surface sediments in the Tees Estuary, England (Lye et al., 1999) and Tokyo Bay, Japan (Isobe et al., 2001).

The total organic carbon (TOC) contents were 0.8425–1.0690%, 0.4897–0.6097%, and 0.3150–0.6774% for cores #1, #2, and #3 respectively (Table 1). The concentrations and fluxes of NP and BPA showed no significant relationship with TOC ( $R^2 \leq 0.296$ ), indicating that the environmental loadings of the two phenolic EDCs to the PRE and the SCS were not significantly associated with organic carbon. This is reasonable since NP and BPA gain entry to environment mainly through wastewater

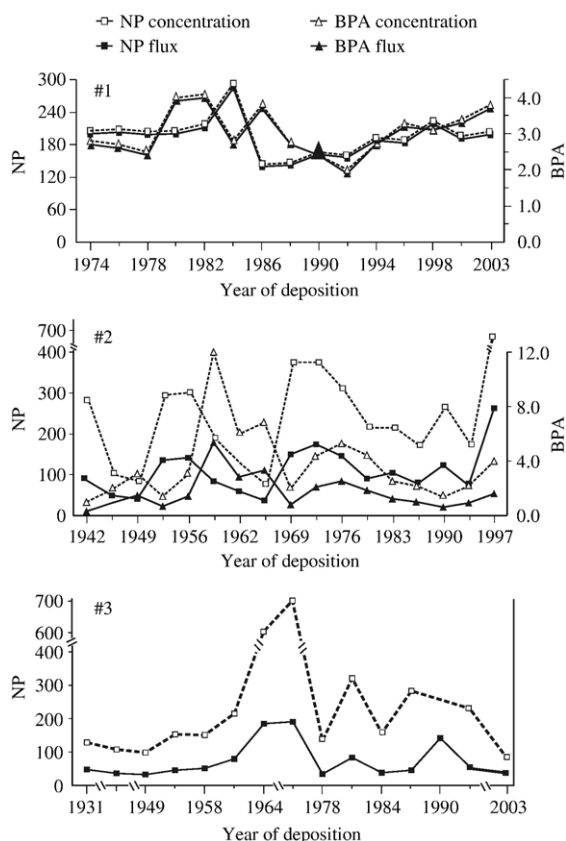


Fig. 2. Temporal variation of the concentrations (ng g<sup>-1</sup> dw) and fluxes (ng cm<sup>-2</sup> yr<sup>-1</sup>) of NP and BPA in the Pearl River Estuary and the South China Sea. NP concentration of the surface sediment in the core #3 (2003) was from Chen et al. (2006).

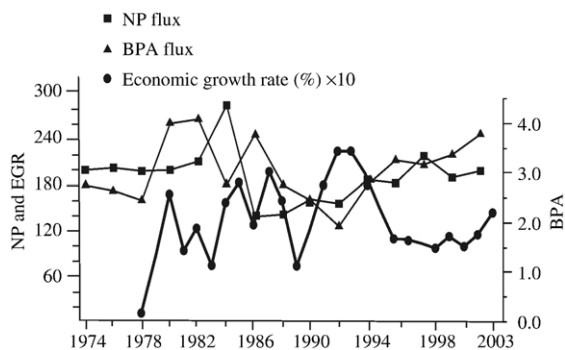


Fig. 3. The flux ( $\text{ng cm}^{-2} \text{yr}^{-1}$ ) of NP and BPA to PRE (core #1) compared to the economic growth rate of the Pearl River Delta in the past three decades (data from <http://www.gdstats.gov.cn/tjtb/gdp/>).

discharge. Little correlation between concentrations of NP and TOC was also reported for the sediment cores in the Bohai Bay in China (Hu et al., 2005).

### 3.2. Temporal trends of fluxes of NP and BPA in sediment in recent decades

The downcore variations of the fluxes of NP and BPA showed difference in the sedimentary cores from the PRE and the SCS. For core #1 located in the PRE, the flux of NP remained constant prior to the early 1980s. The peak flux occurred in the mid-1980s, basically coincident with the rapid economic growth in the PRD (Fig. 3). The NP flux declined at the end of 1980s. This decrease might be attributed to the implementation of wastewater treatment in major cities in the PRD from the late 1980s to the early 1990s. The flux has continued to increase slightly since the mid-1990s, which is possibly related with the constant economic growth in the PRD and inefficient wastewater treatment due to the inadequacy facilities. The temporal trend of BPA flux was similar to that of NP. Multi-model distributions were observed for fluxes of NP and BPA in the core #2 from the SCS. The peak fluxes occurred from the mid- to the late 1950s and the mid-1970s respectively. For core #3, the peak flux of NP also appeared to be from the early to the mid-1970s, which was roughly consistent with the result of Isobe et al. (2001) for the Tokyo Bay, Japan. The fluxes in the cores from the SCS (#2 and #3) declined from 1980s, but showed increasing trends since 1990s, which were consistent with the results for core #1 from the PRE. Upcore decreasing trends of NP were reported for sediment in the Tokyo Bay, Japan (Isobe et al., 2001) and in Shiwa Lake, Korea (Li et al., 2004) due to possible decrease of input resulted from implementation of some legal regulations on industrial wastes and

sewage treatment. The reason for the increasing fluxes of the two phenolic EDCs in PRE and the adjacent SCS is more likely that the wastewater is not efficiently treated ( $\sim 70\%$ ) prior to discharge due to the lack of adequate wastewater treatment facilities in this region (<http://www.gzsewage.com/>, in Chinese). A certain amount of wastewater containing NP and BPA is directly discharged into the Pearl River and its tributaries, and finally reaches PRE and the adjacent SCS, leading to steadily increasing input and accumulation of these phenolic EDCs in recent years. The coincidence of the increasing fluxes between the sedimentary cores after 1990s further confirms the seaward transport of the two anthropogenic phenolic EDCs from the PRE to the SCS.

### 3.3. Persistence and mobility of NP and BPA in sedimentary cores

Nonylphenol was detected in cores #2 and #3 from the South China Sea in the layers corresponding to early 1940s and 1930s (Fig. 2). Alkylphenols were widely used since 1940s (Li et al., 2004). The presence of NP in sediments predating its widespread use may be attributable to downcore penetration of NP in the sediment column and/or physical mixing of sediments. The downward mobilization of NP was also reported in a sedimentary core in the Tokyo Bay, Japan (Isobe et al., 2001).

The peak pattern of NP was fairly uniform throughout the sediment cores and was quite similar to that of the technical mixture standard (Fig. 4), suggesting that isomer-selective degradation of NP after

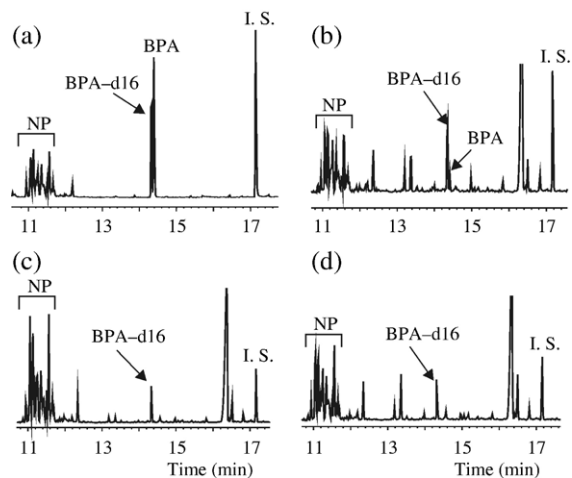


Fig. 4. Gas chromatograms of standard and extracts of the core #2. (a) standard solution; (b) depth of 3 to 4 cm (1997); (c) depth of 25 to 26 cm (1959); and (d) depth of 35 to 36 cm (1942).

deposition did not significantly occur, and that NP composition in technical mixture is relatively constant during the past decades. This is consistent with the results of the previous studies that investigated the post-depositional behavior of NP and NPnEOs ( $n=1-19$ ) in dated sedimentary cores in the Strait of Georgia, Canada (Shang et al., 1999) and in the Tokyo Bay, Japan (Isobe et al., 2001). The vertical profiles of fluxes and isomer pattern of NP in the sedimentary cores in PRE and the adjacent SCS also suggested that NP is quite persistent once it deposits into sediment.

Bisphenol A was quantifiable throughout the sedimentary cores although its concentrations were basically at several nanograms per gram dry weight, generally two orders of magnitude lower than those of NP (Fig. 2). The maximum level of BPA (and therefore the highest flux) was detected at sediment layers deposited in the 1960s, and trace amount of BPA was detected at layer corresponding to early 1940s in core #2, suggesting that BPA is also fairly persistent like NP in sediments. Ying and Kookana (2003) also reported the persistence of BPA in marine sediments.

#### 3.4. Estimates of environmental loadings of NP and BPA in the PRE

Taking the inventories of NP and BPA in the core #1 (5925.2 and 92.4 ng cm<sup>-2</sup> respectively) as the background inventories of PRE, the total stock of NP and BPA in PRE (2100 km<sup>2</sup>) in the past 30 years (1974 to 2003) was around 124 t and 1.7 t respectively. Our recent studies revealed that the mean NP concentrations in aqueous raw municipal sewage (RMS) and sewage treatment plant effluents (STPEs) in Guangzhou (the biggest city in PRD) were 23.898 and 5.260 µg/l respectively. The levels of BPA in RMS and STPEs averaged to 882 and 44 ng/l (data not published). In other words, at least 21.7 t/yr and 0.6 t/yr of NP and BPA were possibly discharged into the Pearl River and its tributaries. Some would transport to PRE and the SCS. Both NP and BPA tend to incorporate into solids as indicated by their Kow values (4.48 and 3.32 respectively, Ying and Kookana, 2003). Therefore, the figures would be bigger if considering the portion adsorbed on suspended particulates in RMS and STPEs. Shang et al. (1999) reported an inventory of 140 t in the past 40 years (1950s to 1990s) and about 4 t/yr supply of total NP and NPnEOs ( $n=1-19$ ) from STPEs in the Strait of Georgia (2700 km<sup>2</sup>), Canada. The large amount of stock and annual input of the two phenolic EDCs constitutes an environmental burden of the PRE and the adjacent South China Sea.

#### 4. Conclusion

The temporal variations and environmental behavior of nonylphenol (NP) and bisphenol A (BPA) were investigated in three sedimentary cores from the Pearl River Estuary (PRE) and the adjacent South China Sea (SCS). Peak fluxes of NP and BPA occurred in the mid-1980s in the PRE, coincident with the rapid economic growth in the Pearl River Delta (PRD). The fluxes declined at the end of 1980s, which might be attributable to the implementation of wastewater treatment in PRD from the late 1980s to the early 1990s. In the SCS, peak fluxes of NP and BPA occurred from mid- to late 1950s and mid-1970s respectively. The constant economic growth and lack of adequate wastewater facilities might have caused the steadily increasing fluxes of NP and BPA since 1990s in the PRE and the adjacent SCS. Both NP and BPA were preserved well in sedimentary cores. NP composition in technical mixture applied in China appeared relatively constant during the past decades. The environmental loadings of NP and BPA were estimated to be roughly 124 t and 1.7 t, respectively, in the PRE over the past 30 years (1974–2003).

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