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# Alkylphenols in surface sediments of the Yellow Sea and East China Sea inner shelf: Occurrence, distribution and fate

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## HIGHLIGHTS

- Alkylphenols in the Yellow Sea and East China Sea sediments were analyzed.
- Relationships between alkylphenols distributions and sources were illustrated.
- Environment fate of alkylphenols in the Yellow Sea and East China Sea were studied.

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## ABSTRACT

Alkylphenols (APs) have been found as ubiquitous environmental pollutants with reproductive and developmental toxicity. In this study, APs in surface sediments of the Yellow Sea (YS) and East China Sea (ECS) inner shelf were analyzed to assess influences of riverine and atmospheric inputs of pollutants on the marine environment. NP concentrations ranged from 349.5 to 1642.8 ng/g (average 890.1 ng/g) in the YS sediments and from 31.3 to 1423.7 ng/g (average 750.1 ng/g) in the ECS inner shelf sediments. NP distribution pattern was mainly controlled by the sedimentary environment. OP concentration was 0.8–9.3 ng/g (average 4.7 ng/g) in the YS sediments and 0.7–11.1 ng/g (average 5.1 ng/g) in the ECS sediments. Assessment of the influence of distances from land on OP concentrations provided evidence for the predominance of coastal riverine and/or atmospheric inputs rather than long-range transport. And the biological pump may play an important role for sequestration of OP in the nearshore area.

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## 1. Introduction

Nonylphenol (NP) and octylphenol (OP) have been extensively used in the manufacture of nonionic surfactants (alkylphenol ethoxylates, APEOs) since 1940s (White et al., 1994). Nonylphenol polyethoxylates (NPEOs) and octylphenol polyethoxylates (OPEOs) respectively account for about 80% and 20% of total APEOs (Ying et al., 2002). Annual global production of APEOs was over 500,000 tons in 1997 (Ying et al., 2002), and production continues to rise in recent years. Along with a great deal of sewage and garbage being increasingly drained into the sea (Hawrelak et al., 1999; Céspedes et al., 2008), a large portion of APEOs is released into the environment and finally ends up in the aquatic environment (Renner, 1997; Solé et al., 2000). APEOs are unstable in aquatic environments with a half-life of several days and are subject to degradation to alkylphenols (APs) through bio- and photo-degradation (Li et al., 2013a). However, the degradation products, NP

and OP, are much more stable in the environment with a half-life of several decades in sediments (Isobe et al., 2001). Therefore, NP and OP are ubiquitous in the general environment, especially rich in the sphere around city and factory (Ying et al., 2002; Ying, 2006; Soares et al., 2008).

Due to the harmful effects of NP and OP in the environment, the use and production of such compounds have been banned or strictly monitored in many countries (Soares et al., 2008). But up to now, APs are still widely used in China and the Korean peninsula. And with the development of economy, pollution caused by APs becomes clinically evident. As reported by Peng et al. (2007) and Hong et al. (2010), the levels of NP have increased sharply in recent decades in sediments of China's Pearl River estuary (Peng et al., 2007) and Korea's Lake Shihwa (Hong et al., 2010). A large proportion of released pollutants from man-made sources will ultimately sink to continental shelf sediments (Jönsson et al., 2003; Huang et al., 2007). And the Yellow Sea (YS) and the East China Sea (ECS) inner shelf are considered as important sinks of pollutants originated from land-based pollution sources (Duan et al., 2013a,b; Li and Dag, 2004).

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Thus, in order to assess the impacts of anthropogenic activities on the YS and ECS inner shelf, it is necessary to determine the levels of current sediment contaminants. Despite a few studies (Li et al., 2005; Fu et al., 2007; Hong et al., 2010; Wang et al., 2010) regarding AP levels in coast of the YS, our understanding on the occurrence and fate of AP in the YS and ECS is very limited. In this work, 66 surface sediment samples were collected from the YS and ECS inner shelf to demonstrate the spatial distribution of NP and OP and to study their fate in marine sediments in this region.

## 2. Materials and methods

### 2.1. Standards and reagents

4-Nonylphenol (NP, technical mixture) was purchased from Tokyo Chemical Industry. 4-*tert*-octylphenol (OP), internal standard hexa-methyl benzene (HMB) and surrogate standard 4-*tert*-butylphenol (BP) were purchased from Dr. Ehrenstorfer GmbH. NP consists of 11 isomer peaks due to various branched structures in the standard which was quantified by using the sum of all peak areas.

### 2.2. Sampling area and sample collection

The YS, a typical semi-enclosed epicontinental sea, is an important storage sink of terrestrial matter from mainland China and the Korean peninsula. Many rivers (exclude the Yellow River and Yangtze River) drain directly into the YS. While most of the mud deposits in the central YS are considered to be derived primarily from the Yellow River and old Yellow River subaqueous delta based on the circulation pattern in the central YS. (Lee and Chough, 1989; Yang et al., 2003; Yang and Youn, 2007). And under the control of cyclonic circulation and cold water gyre, the sedimentary environment is relatively stable in the YS. The muddy sediments in southwestern Cheju Island were derived from diverse sources (Including the Yangtze River and Yellow River, Yang et al., 2004; Yang and Youn, 2007). The oceanographic conditions (especially oceanic circulation patterns) greatly constrain sediments distributions in this unique epicontinental sea (Hu et al., 2011). The ECS is a typical Western Pacific marginal sea, with the world's broadest continental shelf. Most of the suspended particulate matters discharged from the Yangtze River (YR) are ultimately deposited in the YR estuary; 20–30% of them move to the south with the coastal current and are finally buried in the inner shelf of ECS, forming a ribbon of mud areas (Liu et al., 2007). Thus the YS and ECS inner shelf are considered as important sink of pollutants originated from land-based pollution sources (Duan et al., 2013a,b; Li and Dag, 2004).

We collected 66 surface sediment samples (0–2 cm) from the YS and ECS inner shelf with a stainless steel box-corer during 2010 and 2011. A description of the sampling stations was shown in Fig. 1. Efforts were made to minimize disturbance of the surface sediment layers. All the samples were wrapped in aluminum foil after collection and immediately stored at  $-20^{\circ}\text{C}$  until analysis.

### 2.3. Sample preparation and GC/GC–MS analysis

The sediments were freeze-dried and homogenized. Each sample (10.0 g) was spiked with BP as a surrogate standard. The samples were then ultrasonic extracted with *n*-hexane and acetone (1:1, v/v). Activated copper powder was added into the extracted samples to remove sulfur. The extract was rotary-evaporated to about 2 mL and then cleaned and fractionated on a multilayer silica–alumina composite column, which consisted of 7.0 g of 5% deactivated silica gel, 7.0 g of 5% deactivated aluminum oxide,

and 2.0 g of anhydrous sodium sulfate from bottom to top. The column was pre-cleaned with 50 mL of *n*-hexane and the extract was eluted in sequence with 20 mL of hexane (first fraction), 40 mL of dichloromethane/hexane (3:7, v/v) (second fraction), and 50 mL *n*-hexane/acetone (2:8, v/v) (third fraction). The third fraction was collected and concentrated to near dryness under a gentle  $\text{N}_2$  stream and then reconstituted in 100  $\mu\text{L}$  of isooctane. Prior to analysis, a certain amount of HMB was added as internal standard.

NP and OP were quantified with a Shimadzu 2010 plus GC equipped with an AOC-20i auto injector, a flame ionization detector (FID) and a DB-5MS (Ultra Inert) fused silica column (30 m  $\times$  0.25 mm i.d.  $\times$  0.25  $\mu\text{m}$  film thickness). Operating conditions of GC were as described by Li et al. (2013a). A group of the extracted samples were also detected on a HP6890 gas chromatography (GC) equipped with a HP 5973 mass selective detector and a DB-5MS fused silica capillary column (30 m  $\times$  0.25 mm i.d.  $\times$  0.25  $\mu\text{m}$  film thickness). And there is very little interference from impurities in most of the extracted samples. Therefore, quantification of NP and OP was performed using the internal calibration method based on the data obtained by GC. The five-point calibration curves for NP and OP showed high linearity ( $r^2 > 0.999$ ). NP and OP concentrations were reported on a dry weight basis.

### 2.4. TOC and Total Nitrogen (TN) analysis

As reported by Zhao et al. (2013), prior to analysis, the homogenized dry sediment samples were decalcified with 4 M HCl at room temperature for 24 h, and then rinsed with deionized water and dried in an oven at  $55^{\circ}\text{C}$ . The TOC and TN analysis were performed using a Thermal Flash 2000 Elemental Analyzer, with standard deviations of  $\pm 0.02$  wt% ( $n = 6$ ) and  $\pm 0.002$  wt% ( $n = 6$ ), respectively.

### 2.5. Quality assurance/quality control

Glassware and sodium sulfate were solvent-rinsed and heated 4 h at  $450^{\circ}\text{C}$  prior to use. Reproducibility and efficiency of the analytical procedure was determined by six replicate analyses of pre-extracted sediments spiked with APs standards prior to ultrasonic extraction. The average recovery of NP and OP were 104.7% and 92.4%, respectively, and their RSD were 5.4% and 8.9%, respectively. For each batch of 8 samples, a procedural blank (no sediment), a spiked blank (AP directly dissolved into solvent), a matrix-spiked sample (a pre-extracted sediments spiked with AP) and a sample duplicate were processed in the same way as the sample. The surrogate recoveries for all the samples were 76.3–109.1% for BP.

## 3. Results

### 3.1. Sediments grain size and TOC

#### 3.1.1. YS and southwestern Cheju Island

TOC in surface sediments of the YS and southwestern Cheju Island mud areas ranged from 0.29% to 1.56% (dry weight) of the sediments and the mean was 0.81% (Table S1). The higher values were detected in the samples collected from the central YS mud area. The TOC distribution showed an evident increasing trend from the edge to the central zone (Fig. 2). TOC/TN ranged from 5.4 to 7.71 with a mean of 6.60 (Table S1). The sediments in the YS consisted largely of silt (4–63  $\mu\text{m}$ , 27.5–78.4%) and clay (<4  $\mu\text{m}$ , 11.7–33.4%). The average mud (sum of the clay and silt) content was 89.2%. There was a positive correlation between TOC and the median grain size ( $r^2 = 0.34$ ,  $p < 0.05$ ) or mud constituents

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