



Profiles and inventories of organic pollutants in sediments from the central Beibu Gulf and its coastal mangroves



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HIGHLIGHTS

- First organic pollution history of central Beibu Gulf, South China Sea.
- Local and regional pollution recorded despite tide and storm influence.
- Changing BaA/(BaA + Phe) and Ant/(Ant + Phen) ratios reflect phases in use of energy carriers.
- First conservative estimate of mangrove sediment POP inventory.
- Mangrove are relatively small reservoirs with potential as local sinks.

ARTICLE INFO

Article history:

Received 14 December 2015

Received in revised form

24 February 2016

Accepted 10 March 2016

Available online 21 March 2016

Handling Editor: Keith Maruya

Keywords:

Sediment cores

Pollution trends

Polycyclic aromatic hydrocarbons

Organo-chlorine pesticides

Mass inventory

South China Sea

ABSTRACT

Sediment cores from the central Beibu Gulf and its northern coastal mangroves were analyzed for polycyclic aromatic hydrocarbons (PAH), the organo-chlorine pesticides dichlorodiphenyltrichloroethane (DDT) and hexachlorobenzene (HCB), and polychlorinated biphenyls (PCB), to reconstruct the organic pollution history of developing south-west China. Reflecting regional development, in the gulf \sum PAH (38–74 ng g⁻¹) decreased towards the surface after peak concentrations near 10 cm, while \sum DDT (ND–0.5 ng g⁻¹) increased due to fresh inputs, and HCB (ND–0.04 ng g⁻¹) occurred only in surface sediments. Profiles in mangrove sediments showed a continuing local scale increase in \sum PAH (29–438 ng g⁻¹) as well as \sum DDT (0.2–41.0 ng g⁻¹) and HCB (0.01–1.01 ng g⁻¹) pollution, despite some variability. No trend was evident for \sum PCB (ND–0.22 ng g⁻¹), which was not detected in the central gulf. Calculated loads estimate that 2816 ng cm⁻² PAHs and 7 ng cm⁻² DDTs are stored in depositional areas of the Beibu Gulf. Mangrove sediments, threatened by land-use-change, contain 1400–4600 ng cm⁻² PAHs and 34–39 ng cm⁻² DDTs.

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1. Introduction

Modern human development has increased output of persistent organic pollutants (POPs) from agriculture, industry and urbanization into the natural environment. Soils or coastal and marine sediments act as archives of pollution history (Charles et al., 2005), and allow its reconstruction from vertical profiles in sediment cores (Bigus et al., 2014; Breivik et al., 2002). Distinct features,

particularly the first occurrence of a tracer, in sediment profiles can be linked to input events (Gschwend and Hites, 1981; Hartmann et al., 2005). The reconstruction of China's recent organic pollution history has mainly focused on sediment cores from the rapidly developing eastern and south-eastern regions (e.g. Bigus et al., 2014). The Beibu Gulf, a marginal shallow shelf region in the northwest of the South China Sea, has only recently begun to receive scientific attention. Dated sediment core records have revealed a history of increasing anthropogenic pollution in the central gulf (Xia et al., 2013) as well as its northern coast and estuaries (Gan et al., 2013; Li et al., 2015, 2014; Xia et al., 2011), especially since the beginning of rapid economic development in coastal Guangxi province in the early 1990s (Xia et al., 2011). However, the organic pollution history of the central gulf has not

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been addressed. Likewise, there is scant data on organic pollution in mangroves (Zhang et al., 2014), which accumulate organic substances (Donato et al., 2011; Kaiser et al., 2015a; Ke et al., 2005; Tam et al., 2001; Tian et al., 2008; Vane et al., 2009; Zhang et al., 2014; Zheng et al., 2000), and hold potential as pollution archives (Wu et al., 2014). These reservoirs face high risk of destruction due to land-use-change (see e.g. Murdiyarto et al., 2015).

The aim of this study was to retrieve sediment core profiles of POPs from the central Beibu Gulf and from mangrove forests at its northern coast in order to reconstruct regional and local pollution history, respectively. In addition, first tentative POP inventories in sediments of mangroves shall estimate the potential release during land-use-change, and an inventory of the central Beibu Gulf shall indicate current storage of POPs.

2. Study site and sampling

The Beibu Gulf is a marginal shallow (average 45 m; maximum 100 m) shelf region in the northwest of the South China Sea (Fig. 1). Bordering the northern coast is Guangxi province, home to the largest remaining mangrove area in China (Gan et al., 2013; Li and Lee, 1997). The study region has a macro tidal environment and experiences episodic storm events. The climate, hydrography, and biogeochemistry, as well as organic pollution in surface sediments of the central gulf and the northern coastal and estuarine waters have been described in recent studies (Bauer et al., 2013; Kaiser et al., 2015a, 2014; Li et al., 2015; Wu et al., 2008).

One sediment core from the central Beibu Gulf (SO26: 18°28′25.80″N, 107°33′9.60″E, 45 cm length) was retrieved by

multi-corer from a water depth of 57 m on 13 December 2011 during cruise SO219 of the German research vessel SONNE (Fig. 1). The core was stored at 4 °C in the dark until sectioning and freeze drying for several days at –60 °C and 50 mbar. True mangrove sediment cores were obtained from two intertidal locations inside mangrove forests of the Nanliu River Estuary on 7 October 2010 (Fig. 1; C1: 21°37′28.23″N, 109° 2′35.62″E, 30 cm length; C2: 21°35′56.82″N, 109° 4′18.78″E, 40 cm length), using a handheld corer holding Plexiglas liners. Sample material that had no contact with the plastic liner was transferred to aluminum trays, dried at 40 °C for at least 24 h and ground in a planetary mill.

3. Sample treatment and analyses

Analyses of polycyclic aromatic hydrocarbons (PAHs) and organo-chlorines was performed by gas chromatography – mass spectrometry (GC-MS) with internal standard calibration (e.g. Blanz et al., 1999). Standard solutions for PAHs and organo-chlorines respectively contained PAH-Mix 9 (Dr. Ehrensdorfer, Augsburg, Germany) and a deuterated standard PAH (CIL, USA), and PCB-Mix 3 and Pesticide-Mixture 14 (Dr. Ehrensdorfer, Augsburg, Germany) and a mixture of ¹³C labeled standards (PCB 28/52/101/138/153/180, 4,4′-DDE, 4,4′-DDT and hexachlorobenzene) (CIL, USA). Analyzed compounds include 22 polychlorinated biphenyl (PCB) congeners (28/31, 52, 49, 44, 95, 99, 110, 77, 151, 149, 118, 146, 153, 132, 105, 138, 187, 183, 128, 177, 180, 170) (Schulz et al., 1989), p,p′-DDT, o,p′-DDT, p,p′-DDD, p,p′-DDE, hexachlorobenzene (HCB), and 15 EPA (US environmental protection agency) priority PAHs (Table 1).

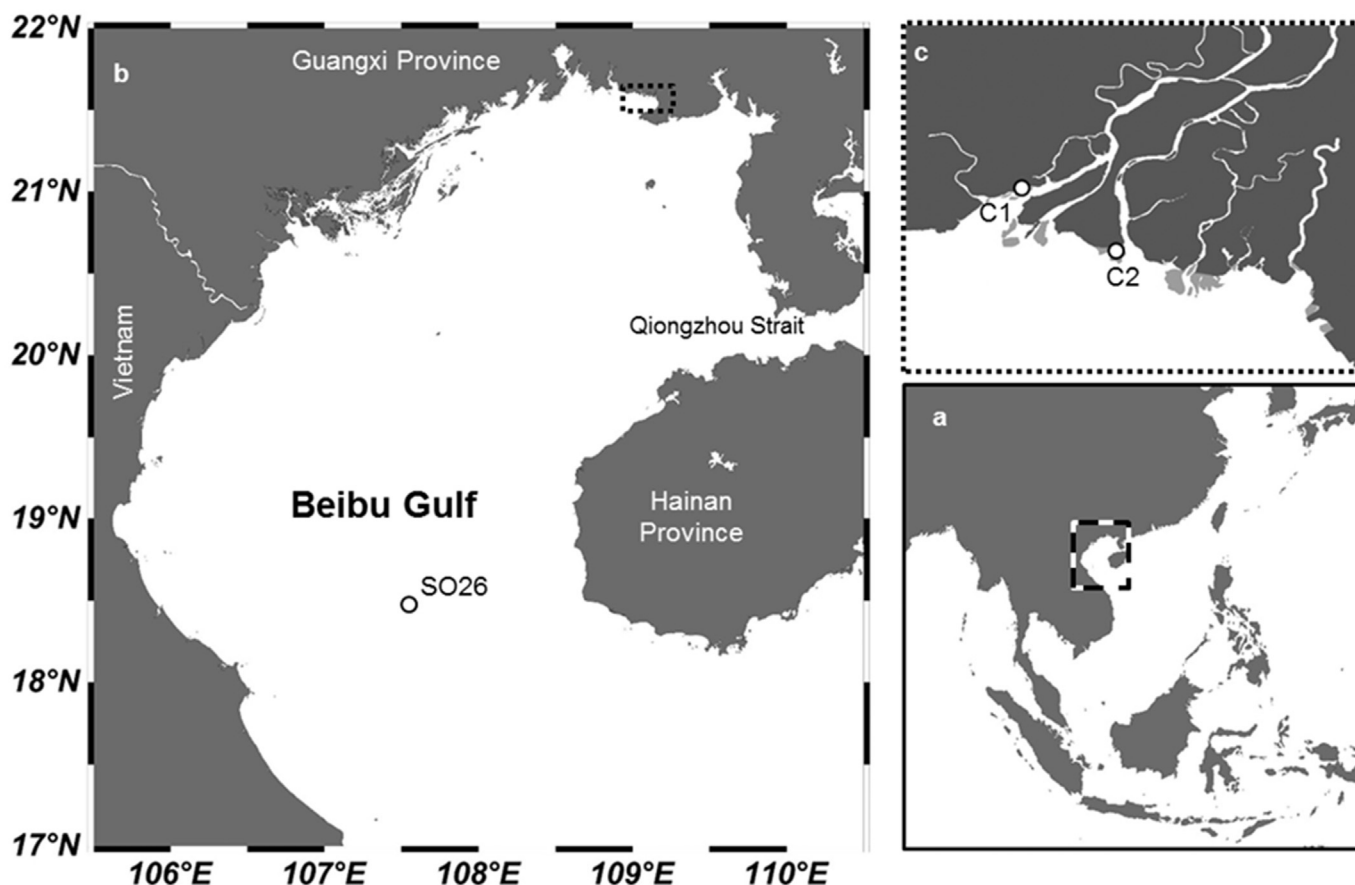


Fig. 1. Location of the study site in the South China Sea (a) and the sediment core sampling positions in the Beibu Gulf (b) and Nanliu Estuary (c).

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