



Spatial distribution and historical trends of heavy metals in the sediments of petroleum producing regions of the Beibu Gulf, China



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ABSTRACT

The concentrations of As, Sb, Hg, Pb, Cd, and Ba in the surface and core sediments of the oil and gas producing region of the Beibu Gulf were measured by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES), Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Atomic Fluorescence Spectrometry (AFS), and the spatial distribution and historical trends of these elements are discussed. The results show that the concentrations of these elements are highest near the platforms. The results of Enrichment Factor (EF) and Potential Ecological Risk Index (PERI) also reveal significantly higher enrichment around the platforms, which imply that the offshore petroleum production was the cause of the unusual distribution and severe enrichment of these elements in the study area. The environment around the platforms was highly laden with toxic elements, thereby representing a very high ecological risk to the environment of the study area.

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1. Introduction

Offshore oil and gas output accounted for approximately 30% of the total global oil and gas production in 2009 and will increase to 40% by 2015 (Douglas Westwood, 2009). On the one hand, large-scale petroleum production meets humans' needs for energy, and on the other hand, petroleum production is detrimental to the environment (Davies et al., 1984; Warwick and Clarke, 1991; Denoyelle et al., 2010; Norwegian Oil and Gas, 2013). Oil seepage has been linked to significant increases in oil-sourced organisms in marine sediments and high trace element concentrations in sediments associated with long-term and large-scale oil exploration (Smith, 2001; Cundy et al., 2003). Currently, research on the effects of petroleum exploration on the seafloor environment is primarily performed in developed countries in Europe and the Americas (Davies et al., 1984; Warwick and Clarke, 1991; Dalmazzone et al., 2004; Bakke et al., 2013), whereas few studies have been undertaken in China. This situation will indeed influence key policy formulation, particularly with regard to the marine environment and sustainable development of the marine economy.

China is one of the largest consumers of fossil fuel in the world, and offshore oil production has contributed immensely to China

energy needs and economic growth. The area off the coast of southwestern Weizhou Island in the Beibu Gulf is one of the earliest offshore oil fields, and petroleum exploration first started in this area in 1974 (Zhong and Pan, 1997). With the expansion of exploration, the current annual output of oil and gas fields near Weizhou Island has reached approximately 1.5 million tons (News center of China National Petroleum Corp, 2007). Although no oil spills have been recorded, the long-term and large-scale exploration and production have likely already caused severe impacts on the seafloor environment. To date, no investigation has been performed to ascertain the impact of oil exploration and exploitation activities on the seafloor environment in this area. Therefore, a large gap exists in the availability of vital information regarding the impact of offshore petroleum exploration and exploitation on the seafloor environment. This lack of knowledge may seriously endanger the marine environment and the organisms inhabiting in this area.

Arsenic (As) and heavy metals in bottom sediments have been used to decipher the impact of human activity on the bottom environment (Smith, 2001; Cundy et al., 2003). As and heavy metals, such as Sb, Hg, Pb, Cd, and Ba, are the most deleterious environmental pollutants due to their high toxicity, non-degradability and biological accumulation (Yu et al., 2008; Ennouri et al., 2010; Masiol et al., 2014). Additionally, bottom sediments are the major source of heavy metals and As to the overlying seawater (Dassenakis et al., 1997; Masiol et al., 2014) and will produce

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perpetual damage to the marine environment once these elements exceed safe limits. In addition, heavy metals and As in the marine sediments could also archive various environmental changes caused by human activities because As is widely used in reconstructing the history of anthropogenic influence on the marine environment (Smith, 2001; Cundy et al., 2003).

Thus, this study investigates the spatial distribution of heavy metals and As in the surface sediments and core samples from the offshore oil field off the southwestern coast of Weizhou Island, Beibu Gulf, to ascertain the degree of heavy metals and As enrichment, accumulation and potential ecological risk. Additionally, we also wish to provide fundamental scientific information that can be used as a universal guide for assessing offshore petroleum fields without oil spills, thereby enhancing environmental policy formulation and the development of the marine environment.

2. Materials and methods

The core BBW-1 (108°42.66'E, 20°49.31'N; 176-cm long) and 40 surface samples were obtained from the oil and gas exploration area of southwest Weizhou Island in the Beibu Gulf in 2011 (Fig. 1). Subsequently, detailed examinations of grain size, major and trace elements, and heavy metal concentrations were carried on the surface samples. The grain size tests were conducted on core samples at an interval of 4 cm, whereas the major and trace element and heavy metal analyses were conducted at an interval of 5 cm (above 40 cm) and at every 10 cm (below 40 cm). There are two platforms in the study area; one is a service platform for relaying the oil and gas (#1; Fig. 1), and the other one is a drilling platform for petroleum production (#2; Fig. 1).

The grain size, major and trace elements, and heavy metals analyses were performed at the Key Laboratory of Marine Sedimentology and Environmental Geology of the China State Oceanic Administration. The grain sizes of 84 sediment samples were analyzed using a laser particle size analyzer (Master Sizer 2000) with a measurement range of 0.02–2000 μm and a relative error based on repeated measurements of less than 3%. Fifty milligrams of powdered and homogenized sample were used for the analysis of the major and trace elements. The subsamples were digested with a mixture of $\text{HNO}_3 + \text{HCl} + \text{HF}$ in a ratio of 5:4:1 at 120 °C for 2 h in closed Teflon bombs. These steps were repeated until a negligible amount of the white residue remained. Then, each sample was leached with diluted HNO_3 . Al and Ba were analyzed by Inductively

Coupled Plasma Optical Emission Spectrometry (ICP-OES), and Pb and Cd were analyzed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Results were obtained for 49 group of major and trace elements. The heavy metal samples were digested in a mixture of $\text{HNO}_3 + \text{HCl}$ in a ratio of 1:3, and the elements were transformed to hydride in an acidic medium. Then, As, Sb, and Hg were determined by Atomic Fluorescence Spectrometry (AFS). Additionally, ^{210}Pb radioactivity dating was performed on 13 samples at the Laboratory of Marine Radioactive Technology and Environmental Security Evaluation, Third Institute of Oceanography, China State Oceanic Administration. The total radioactivity of ^{210}Pb was obtained by testing the α radioactivity of ^{210}Po , which is the second-generation daughter product of ^{210}Pb (Wang, 1997). The sedimentation rate of core BBW-1 was calculated by constant initial concentration mode (CIC; Wang, 1997; Fan et al., 2000).

3. Results

3.1. Content and distribution of the heavy metals in surface sediments

The spatial distribution of the grain size in surface sediments from the study area revealed two obvious areas with coarse particles, each separately located near the platform and in the west of the study area (Fig. 2h). Fine particles were distributed in the northeast and southwest of the study area (Fig. 2h). The spatial distribution pattern of Al corresponded with the grain size (Fig. 2g); Al concentration increased with decreasing grain size.

The analyzed heavy metals and As were categorized into three groups (Zhao and Yan, 1994): the chalcophile elements (As, Sb, Hg and Pb), dispersed elements (Cd), and alkali elements (Ba). Ideally, the spatial distribution of elements in marine sediments should conform to the grain-size standards, and the pattern of these elements in scatter plots should correlate with Al. However, the heavy metal and As concentrations in the surface sediments of the study area exhibited an abnormal spatial distribution pattern.

The average concentration of As, Sb, Hg, Pb, and Cd in sediments in the study area was 7.44, 0.85, 0.08, 36.22, and 0.12 $\mu\text{g/g}$, respectively (Table 1), which agree with the values from a previous study (Dou et al., 2013). In contrast, Ba was 1416.29 $\mu\text{g/g}$ (Table 1). The spatial distribution pattern of these elements displayed two high-concentration areas around the two drilling platforms (Fig. 2). However, the sediment samples around the #2 platform

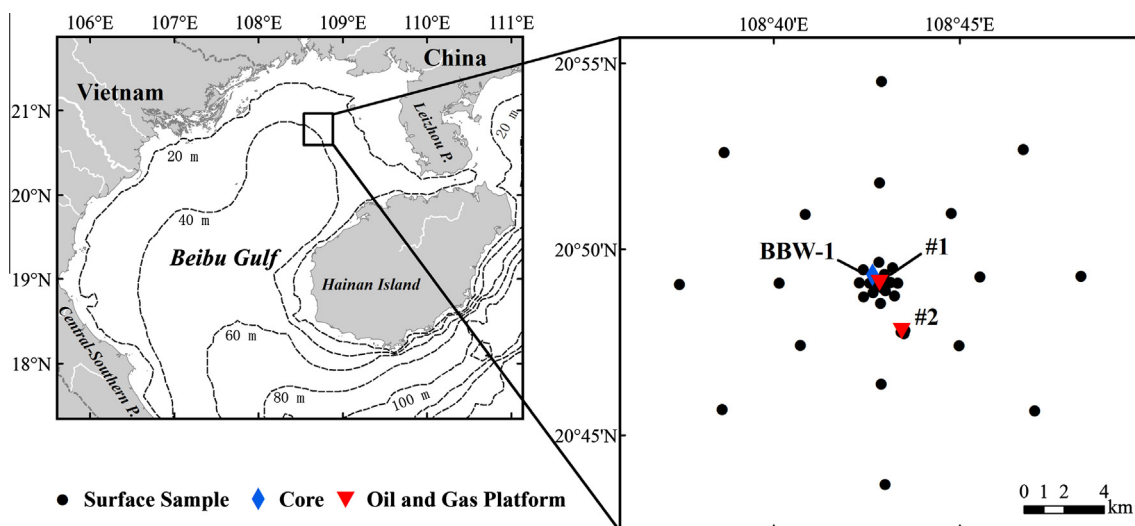


Fig. 1. Location of the study area, core BBW-1, surface samples, and platforms. Platform #1 is a service platform for relaying oil and gas, and #2 is a drilling platform for petroleum production.

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