Marine Pollution Bulletin 135 (2018) 1007–1015

Contents lists available at ScienceDirect

Marine Pollution Bulletin

journal homepage: www.elsevier.com/locate/marpolbul

# The distribution of and biodegradation impact on spilled oil in sediments from Dalian Bay, NE China

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ARTICLE INFO

*Keywords:*
Oil spill
Extractable organic matter
Source-specific biomarkers
Hierarchical cluster
Dalian Bay

ABSTRACT

Three cores collected in the area of 16th July 2010 oil spill by box crab in May 2013 and July 2014 at the Dalian Bay have been geochemically characterized to investigate the fate of chemical components in sediments. The total organic carbon, extractable organic matter contents and biomarker compositions have been applied for the differentiation of alien organic matters from in situ ones and evaluation of the biodegradation impact. Multivariate statistical analysis suggests four groups of sediments. Except a few samples at deepest part of BQ050, majority samples have certain affinity with the spilled oil. The most contaminated sediments occur at site BQ050 and the spilled oil has migrated to 8–12 cm depth. The degree of contamination can be ranked by the similarity of molecular compositions with spilled oil. Variable biomarker components in sediment extracts were also altered by ongoing biodegradation.

## 1. Introduction

Oil spills have become a global problem. From 1907 to 2014, > 7 million tonnes of oil has been released to the environment from over 140 large spills (Li et al., 2016). More than 1.3 million tonnes of oil was released to sea due to the natural seeps, petroleum extraction, transportation and consumption. In four main categories of oil sources in sea, natural seep accounts for 46%; oil and gas exploration or production introduces about 5%; the transportation (including refining and distribution activities) results in the release of about 9%; and roughly 37% is triggered by consumption of petroleum (National Research Council (US). Steering Committee for the Petroleum in the Marine Environment Update, 2003). Although dwarfed by some other sources of oil to the marine environment, petroleum extraction and transportation inputs are not trivial, as they can occur as large spills, example for the Exxon Valdez oil spill in 1989, the Deepwater Horizon oil spill in 2010, and the Penglai 19-3 oil spill (Bohai Gulf, China) in 2012.

Dalian, located in the NE China, is a port city. On 16th July 2010, an estimated 1500 t of crude oil spilled into the sea caused by a rupture and subsequent explosion of two crude oil pipelines that run to an oil storage depot of the China National Petroleum Corporation in Xingang Harbor. The spilled oil driven by the westward wind and coastal current had spread from the source of the spill to northwest and accumulated in the northern part (head of bay) of the Dalian Bay. The oil slick area is over 430 $km^2$. During the accident treatment, oil spill recovery vessels and workers were hired to salvage oil on the surface of water, meanwhile the biological and chemical dispersant were put into the heavy and light pollution area, respectively.

The field surveying and monitoring data showed that the content of total petroleum hydrocarbon (TPHs, measured by ultraviolet spectrophotometry) was > 0.5 mL/L (up to 1.04 mL/L) in the surface water, and > 3000 mg/kg in the subsurface sediment (Liu et al., 2013; Wang et al., 2013; Guo et al., 2017) in the heavily polluted area (the head of the bay) during August to October of 2010. Although the mouth of the bay is closer to the spill source, its pollution damage is less significant than the head of the bay due to the hydrodynamic and wind direction (Gao et al., 2014; Guo et al., 2017). The results of subsequent surveying and monitoring showed that the TPHs in the environment gradually decreased over time. The TPHs decreased to 0.05 mL/L in May 2012 in the surface water. The temporal and spatial distribution of TPHs in subsurface sediments varies greatly. The TPHs concentration decreases from > 2500 mg/kg in May 2012 to < 1000 mg/kg in July 2014 at the head of the bay, and is < 500 mg/kg at the middle and mouth of the bay (Gao et al., 2014; Guo et al., 2017).

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https://doi.org/10.1016/j.marpolbul.2018.08.032
Received 20 March 2018; Received in revised form 27 July 2018; Accepted 16 August 2018


**Fig. 1.** Map showing the location of sediment samples in Dalian Bay
S: sediment site; RP: the point of ruptured line; SS: source of spill oil; HPA: heavy pollution area of the spill accident.

In the marine environment, the spilled oil is subject to various weathering processes, including spreading and aggregation, dispersion, evaporation, emulsification, dissolution, settling, oxidation, and biodegradation. Among them evaporation, emulsification (forming the mousses material), dissolution and biodegradation are the most important processes for oil clear up from the water column (Lee et al., 2011; Li and Boufadel, 2011; Michel and Hayes, 1999; Payne et al., 2008; Peterson et al., 2003; Short et al., 1999, 2007). Dispersant can be sprayed on the water surface and shoreline to help dissipate oil spills. Meanwhile dispersant also change physicochemical properties of the spilled oil, which increases the solubility, stimulates biodegradation and speeds up sinking (National Research Council (US). Steering Committee for the Petroleum in the Marine Environment Update, 2003; Liu et al., 2010, 2012a). Except for partially recovered by salvage and evaporated into atmosphere, some spilled oil remains in water column, while others accumulate on the seafloor and migrate into subsurface sediments. The seafloor represents a potentially longer term sink for oil contamination than water column. Understanding the fraction of spilled oil deposited on the seafloor can help us to trace the fate of spilled oil.

The marine environment has a complex background of petrogenic, pyrogenic, and biogenic hydrocarbons from natural sources and anthropogenic activities. Geochemical evaluation of the fate and effects of the spilled oil requires the chemical fingerprinting of this oil and its residues to be distinguishable from the background. The distribution of petroleum biomarkers has been applied to identify various hydrocarbon sources and to distinguish quantitatively among mixed sources in the sediment samples and oil spills (Bence et al., 1996; Boehm et al., 2008; Liu et al., 2010, 2012a; Mulabagal et al., 2013; Tolosa et al., 2009; Venkatachalapathy et al., 2011; Wang et al., 2001, 2004, 2006, 2014). Here we explore the use of organic matter content in sediments, including total organic carbon (TOC) and extractable organic matter (EOM) to quantify the extent of pollution, and source-specific biomarkers to differentiate the origin of contamination. Aided by multivariate statistical analysis, residual oil has been identified in the sediments. This paper presents the first comprehensive survey of hydrocarbon contents and biomarker compositions in superficial sediments of the Dalian Bay on the basis of 3 core samples (located at the head, middle and mouth of bay, respectively) collected in May 2013 and July 2014. The main objective was to trace the oil spills in sediments and to assess the level of oil contamination due to accidental oil spills.

### 1.1. Geographical setting

Dalian Bay with an area of 174 $km^2$ is a semi-closed bay, surrounded by land on three sides with southeast part connected to Yellow Sea. It is a typical base-rock harbor coast with the zigzag coastline about 125 km (Chen and Wang, 2016). The bay has semi-diurnal tides, ranging from