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# Distributions of persistent organic contaminants in sediments and their potential impact on macrobenthic faunal community of the Geum River Estuary and Saemangeum Coast, Korea

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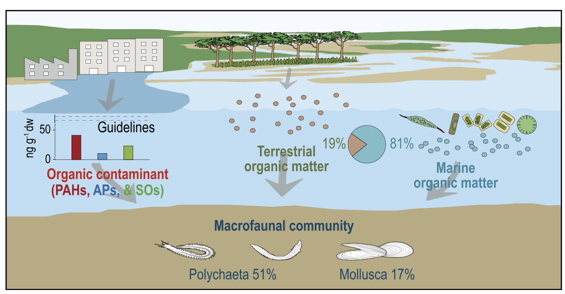
## HIGHLIGHTS

- Persistent organic contaminants in estuarine and coastal sediments were surveyed.
- Distribution of organic contaminants were affected by surrounding activities.
- Organic contaminants mainly originated from near industrial and municipal areas.
- Terrestrial organic matter found the inner estuary and near the watergate regions.
- Origin of sedimentary organic matter can be controlled macrofaunal community.

## GRAPHICAL ABSTRACT

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## ABSTRACT

Over the last 30 years, the Geum River Estuary and Saemangeum Coast have been subject to major environmental changes, including dike construction, reclamation, and development of industrial complexes. This study aimed to: 1) investigate the occurrence of polycyclic aromatic hydrocarbons (PAHs), alkylphenols (APs), and styrene oligomers (SOs), 2) identify the sources of sedimentary organic matter, and 3) determine key environmental factors controlling the macrozoobenthos community structure. A total of 58 surface sediments were collected from the estuary and coastal area in 2014. Specific persistent organic contaminants (POCs), including 24 PAHs, 6 APs, and 10 SOs were measured. PAHs, APs, and SOs were detected in the sediments at all sites, with concentrations varying among sites. Although POCs concentrations were generally below the Canadian sediment quality guidelines, relatively greater concentrations of POCs were found at some sites adjacent to industrial complexes and the estuarine area. Sediment organic carbon, total nitrogen, and the stable carbon isotope ratio ($\delta^{13}C$) were determined. Some sites near watergate had about 2–3‰ lighter $\delta^{13}C$ values compared to other areas, indicating that these sites are affected by terrestrial organic matter. The number of species in the macrofaunal

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community was significantly correlated with $\delta^{13}C$ values ($p < 0.001$), positively, suggesting that the origin of sedimentary organic matter is important for controlling the macrozoobenthos distribution. Overall, this research provides information about the level and sources of sediment pollution, the origins of organic matter, and the relationships with the macrofaunal community.



## 1. Introduction

The Geum River Estuary has been subject to major changes since the construction of a sea dike in 1990 and the establishment of the Gunsan-industrial complex in 1992 (Kim et al., 2006). Likewise, the Saemangeum Coast located to the south of the Geum River Estuary undergone major changes following the construction of the Saemangeum sea dike between 1991 and 2010 (Lee and Ryu, 2008; Lie et al., 2008). Gunsan is a major city in southwestern Korea that is located near the Geum River Estuary and Saemangeum Coast. Over the years, this city has expanded to support a manufacturing industry and an international trade port (Yi and Ryu, 2015), which might cause local contamination with persistent organic contaminants (POCs) (Hong et al., 2012). Moreover, dike construction and reclamation induced erosion and change to in surface sediments (Lie et al., 2008). These activities might alter the biogeochemical conditions of particulate organic matter in coastal areas and benthic environments (Lee et al., 2012).

Toxic chemicals, such as polycyclic aromatic hydrocarbons (PAHs), alkylphenols (APs), and styrene oligomers (SOs) have been found near industrial complexes and in waste from cities and large harbors in Korea (Khim et al., 1999; Koh et al., 2006; Hong et al., 2016). PAHs are ubiquitous POCs in various environments, particularly intensively used areas, such as dockyards, harbors, estuaries, and shallow coastal zones exposed to anthropogenic effects (Lipiatou et al., 1997; Rogers, 2002). PAHs are generally accumulated with relatively great concentrations in sediments due to their hydrophobic nature. PAHs can have also high degree of biota-sediment accumulation factors by being accumulated in coastal benthic organisms (Gewurtz et al., 2000). PAHs have long been considered as one group of major toxic contaminants found in coastal sediments to cause adverse effects on aquatic wildlife (Neff, 1979, 2002). Alkylphenol ethoxylates (APEOs), which include nonylphenol polyeothoxylates (NPEOs) and octylphenol polyeothoxylates (OPEOs), are extensively used as nonionic surfactants (White et al., 1994). APEOs can be degraded into products such as nonylphenol and octylphenol through biological and photochemical degradation (Li et al., 2013). However, the degradation products, endocrine disruptors, have harmful effects, including population decrease and the feminization of several aquatic species (Giesy and Snyder, 1998; Chen and Yen, 2013).

SOs have been reported as new pollutants in highly developed coastal areas (Hong et al., 2016). SOs are known decomposition chemicals that originate from polystyrene plastic materials, and have been listed as new contaminants of increasing concern; yet, few studies have reported the distribution of SOs (Saido et al., 2014; Kwon et al., 2015; Hong et al., 2016). SO analogues originate from the thermal decomposition of polystyrene at temperatures of 240–300 °C (Kwon et al., 2014). SOs have been reported to cause estrogenic effect *in vitro* and reproduction toxicity on daphnids (Ohyama et al., 2001; Tatarazako et al., 2002). Thus, sedimentary SOs may cause potential adverse effects on ecosystem, but effects on benthic community are not well known. Altogether, study on the occurrences and distributions of PAHs, APs, and SOs in sediments and benthic community responses would remain in question.

In general, sediment organic carbon (SOC) is positively correlated with organic contaminants (Warren et al., 2003). The SOC content and origin of organic matter is affected by inputs of freshwater. The origin of organic matter is generally determined by using the SOC to sediment nitrogen (SN) ratio and stable carbon isotopes (Sampei and Matsumoto, 2001; Meksumpun and Meksumpun, 2002). It is important to determine the origin because terrestrial organic matter is connected with an increase in macrofaunal community biomass and density (Hermand et al., 2008).

However, there have been few studies on organic contaminants, the sources of organic matter, and factors affecting the benthic macrofaunal community inhabiting the sediment of the Geum River Estuary and Saemangeum Coast. In the present study, we aimed to 1) investigate distribution of PAHs, APs, and SOs, 2) identify sources by analysis of chemical compositions, 3) investigate sources of sedimentary organic matter by use of carbon stable isotope ratio, and finally 4) determine macrobenthic community responses against sedimentary contamination.

## 2. Material and methods

### 2.1. Sampling areas and strategy

The Geum River Estuary and Saemangeum Coast are located on southwestern part of Korea. These areas are affected by three watergates. The inner part of the Saemangeum sea dike is influenced by freshwater originating from the Mangyeong and Dongjin Rivers. The Geum River Estuary and the Saemangeum Coast surround the industrial and domestic areas of the cities of Gunsan and Seocheon. Fifty-eight sediment samples were collected from the Geum River Estuary and Saemangeum Coast (Fig. 1). Thirty sediment samples were collected from the Saemangeum Coast in September 2014. The other samples were collected from the Geum River Estuary in December 2014. Surface sediments were collected for chemical analysis by use of Van Veen grab sampler. Upper 2 cm of the sediments were collected. All sediment samples for chemical analyses were transported with dry-ice and stored at −20 °C until analysis. For macrofaunal community, duplicate sediment samples were collected at each site. Macrofauna were separated by using a 1 mm mesh sieve on site, and were fixed with 5% buffered formalin.

### 2.2. Sample preparation

To analyze the organic chemicals, the samples were freeze-dried and homogenized and were extracted with 350 mL dichloromethane (DCM, Burdick & Jackson, Muskegon, MI) using Soxhlet extractor for 16 h. Five surrogate standards (SS, acenaphthene-d10, phenanthrene-d10, chrysene-d12, perylene-d12, and bisphenol A-d16) were added before extraction. The extracts were concentrated and replaced with hexane (Burdick & Jackson) using a rotary evaporator and activated copper (Sigma Aldrich, Saint Louis, MO) was added to remove elemental sulfur. The extracts were purified and fractionated by passing it through 8 g silica gel (70–230 mesh, Sigma Aldrich). The first fraction (F1) contained PAHs and SOs, and