



Perylene as an indicator of land-based plant biomarkers in the southwest Caspian Sea



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ARTICLE INFO

Keywords:
Caspian Sea
Perylene
Biogenic
PAHs

ABSTRACT

In this study, 84 surface sediment samples, from 28 Iranian rivers, 45 surface sediment samples and 31 samples from one core in the southwest of the Caspian Sea were collected and analyzed for polycyclic aromatic hydrocarbons (PAHs). The results showed high variability of perylene in coastal surface sediments (1.3–123.6 ng g⁻¹ dw) and river sediments (0.5–111.1 ng g⁻¹ dw). Core samples revealed high levels of perylene which increased with depth. Three diagnostic ratios (DRs) for source identification of perylene (Per/TPAH, Per/PAI and Py/Per) revealed a dominance of biogenic inputs to the surface layers (coasts and rivers) and diagenetic production of perylene in the sediment core. Hyrcanian forests with humid climates favor wood-degrading fungi and the production of perylene and its precursors. Biogenic production of perylene as a land plant derived biomarker can be used for the reconstruction of paleoclimatic conditions of the southwest Caspian Sea.

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1. Introduction

Perylene, a five ring PAH is believed to be mainly derived from natural sources but the source of perylene remains obscure and has been debated in recent years (Grice et al., 2009; Suzuki et al., 2010). The natural precursors of perylene (the structurally related perylenequinones and their derivatives), could be types of black pigments found in modern plants, insects, crinoids and fungi or have a diatomaceous origin (Venkatesan, 1988). It had been thought that terrestrial soil holds precursors of perylene (Jiang et al., 2000) which could be transported by rivers to the coasts (Boonyatumanond et al., 2006), although a report by Wakeham et al. (1979) suggested marine-derived precursors. Research on ancient sediments, however, has suggested that diatoms and crinoids are not the major potential sources of perylene and that the major precursor carriers are derived from terrestrial sources (Jiang et al., 2000). Recent researchers suggest that wood-degrading fungi are major producers of perylene precursor compounds (Bechtel et al., 2007; Grice et al., 2009; Itoh et al., 2010). However, high concentrations of perylene in new fungus combs of *Macrotermes gilvus* in Peninsular Malaysia (397 ng g⁻¹ dw recorded at one site) showed that perylene formation is facilitated in the anaerobic conditions present in the termite hind gut (Riyahi Bakhtiari et al., 2010). Itoh and Hanari (2010) found that perylene (1200 ng g⁻¹ dw) in Lake Biwa sediments originates mainly from the land, principally from

gymnosperms. Itoh et al. (2012) reported that a remarkable amount of DHPQ (4,9-dihydroxyperylene-3,10-quinone) exist in the humic acids of soils in the Lake Biwa catchment area. The fungi (*Cenococcium geophilum*) is responsible for DHPQ production and the authors concluded that this is the source of perylene found in Biwa Lake sediments, following transport to the lake by rivers. Marynowski et al. (2013) detected perylene in Mesozoic and Cenozoic fossil wood samples and concluded that wood degrading fungi are responsible for perylene production.

The different abundance and occurrence of perylene compared to those of other unsubstituted PAHs, especially combustion derived PAHs, provided the main insight to its different source. It is believed that perylene produced in anoxic conditions, and conversion of perylenequinone to perylene (diagenetic formation), results from a reduction process, requiring a reducing environment in sediments to prevent oxidation (Aizenshtat, 1973).

A number of studies have found high perylene concentrations in surface oxic sediments in tropical and subtropical environments (e.g., Zakaria et al., 2002). By contrast, however, it has been reported that perylene is either absent (Choudhary and Routh, 2010) or present only in minor concentrations in oxic surface sediments (e.g., Unlu and Alpar, 2006). Studies of the Caspian Sea sediments have shown surprisingly variable levels of perylene. Tolosa et al. (2004) reported 30–90% of perylene over total penta-aromatic isomers and high concentration levels of perylene with a natural origin in surface sediments in the southwest Caspian Sea, especially in the western and central Iranian coastal zones, and in particular south of the Kura River and near the Sefidrud River. The authors also

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reported significantly lower concentration levels ($<3 \text{ ng g}^{-1} \text{ dw}$) and percentage of perylene over penta-aromatic isomers ($<20\%$) in sediments from the Kazakhstan coasts and even eastern Iranian coasts. They hypothesized that Iranian river discharges are the main source of perylene transport to the Iranian coasts of the Caspian Sea. One of the main objectives of this study was to present first comprehensive survey of perylene and its DRs (diagnostic ratios) and to test this hypothesis in related Iranian river sediments. Another objective of the study was to assess the distribution pattern of perylene in surface sediments and in a core from the southwest Caspian Sea, to assist in perylene source identification.

2. Materials and methods

2.1. Study area and sampling

Caspian Sea, the biggest lake in the world, has virtually no tides and low salinity. Salinity varies, being lower in the north and west and higher in the south and east; salinity is approximately 13 g l^{-1} along the Iranian coastline. It has a diverse spatial PAHs distribution from mainly petrogenic sources. At all stations in the Iranian, Kazakhstan and Russian sectors, the PAH profiles were reported very similar except for perylene, which was reported as the dominant PAH occurring in the sediments of the Iranian coast (Tolosa et al., 2004). Selection of the Guilan Province for sampling in this study was based on these reported perylene hot-spots in the southwest of the Caspian Sea. The southwest shores of the Caspian Sea have a sub-tropic climate. Guilan Province is restricted by the Alburz mountains (mean height: 3000 m) at the west and south of the Iran plateau. The land area of the Guilan Province area is 1,067,736 ha; the main land uses being forest (52.89%, Hyrcanian forests), range land (22.94%), agriculture (23.73%) and residential (0.44%), respectively (Iran Statistical Yearbook, 2010). Precipitation is not homogenous all over the province, with majority in Anzali ($1827.5 \text{ mm year}^{-1}$, mean 1951–2010). The mean annual

precipitation of the province is 1226.4 mm, with the highest in October (204.6 mm) and lowest in July (38.5 mm). The relative humidity ranges from 52% to 98% with an annual mean of 84% (1951–2005). The average annual temperature is $16.2 \pm 1.39 \text{ }^\circ\text{C}$ (1951–2005), ranging between 14.3 and 17.5 $^\circ\text{C}$ in 1969 and 1966, respectively (Iran National Center of Climatology, 2013). General water circulation along the coast of the Guilan Province is affected by anticyclones located at the northwest of the south basin of the Caspian Sea (Tuzhilkin and Kosarev, 2005).

A total of 84 surface sediment samples were collected from 28 main rivers (at downstream locations, each river 3 replicate samples) of the Guilan Province (Fig. 1) during the period 19–22 September 2012. The coastal surface sediment survey was based on 45 samples collected at 15 stations (each station 3 replicate samples) from 28 May to 2 June 2012 in accordance with a Caspian Sea oceanographic excursion. Coastal stations with different depths (10, 20 and 50 m) were selected to describe the perylene concentration according to the depth gradient of the coastal area. All of the surface sediments were collected using a Van Veen Grab. Sediment from the surface ($\sim 3 \text{ cm}$) was sub-sampled. One sediment core was collected by gravity corer at Anzali shore (opposite of Anzali lagoon, a Ramsar site) at the depth of 20 m (same geographic location with T9 station) on 17 October 2012 (Fig. 1). The core length was exactly 85 cm with a 70 mm diameter. The core was sliced into 1, 2 and 5 cm sections immediately after sampling in the upper 10 cm, from 10 to 30 cm and higher than 30 cm to down of the core, respectively (a total of 31 samples). All samples were stored in clean aluminum foil and transported to the laboratory in a cool box before storage at $-21 \text{ }^\circ\text{C}$ to await further analysis.

2.2. Sedimentology

All samples were weighed and freeze-dried to calculate the water content. Dry bulk density profiles of the core samples were calculated based on dry weight of each slice divided by their volumes. Total organic matter (TOM) was determined by oxidation

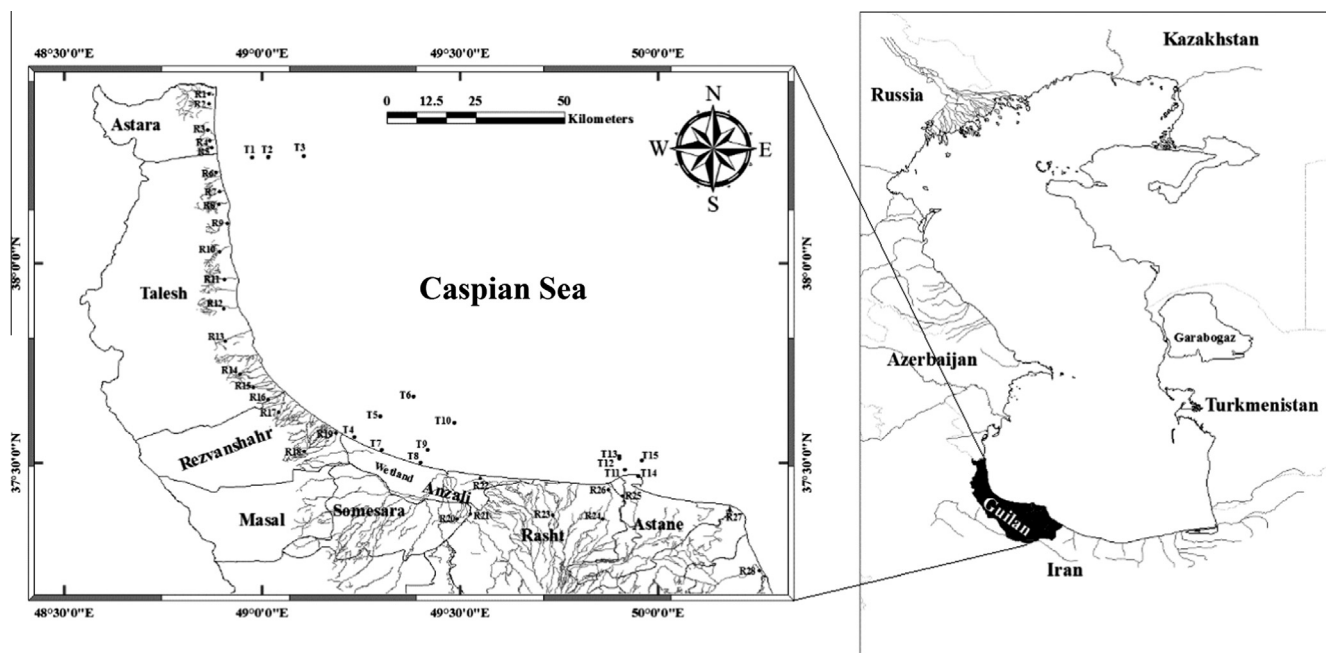


Fig. 1. Map of Caspian Sea and sampling points. Coastal (T1–T15) and River (R1–R28) stations, river names respectively, R1 (Khaje Karim Chay), R2 (Astara), R3 (Kanrud), R4 (Lavandevil Chay), R5 (Chalthvand), R6 (Lamir), R7 (Chubar), R8 (Havigh), R9 (Shirabad), R10 (Khotbesara), R11 (Lisar), R12 (Jokandan), R13 (Karganrud), R14 (Navrud), R15 (Khale Sara), R16 (Village 57), R17 (Dinachal), R18 (Shafarud), R19 (Chafarud), R20 (Pasikhan), R21 (Siahrud), R22 (Hasanrud), R23 (Khoshkbiyar), R24 (Lashte Nesh), R25 (Sefidrud), R26 (Zibakenar), R27 (Jirbagh), and R28 (Kohneh Sefidru).

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