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# Historical trace element accumulation in marine sediments from the Tamaulipas shelf, Gulf of Mexico: An assessment of natural vs anthropogenic inputs



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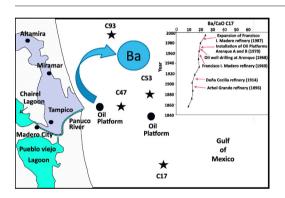
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#### HIGHLIGHTS

### Historic contaminant accumulation was examined in the Tamaulipas Shelf, Mexico.

- Dated sediment cores were used to examine trends in trace element input.
- CaO-normalized data showed increasing V, Cr, Zn, Cu, Pb, Zr and Ba over time.
- Ba and V exceeded the adverse effect index (AEI) in all cores.
- Ba/CaO data can be broadly correlated with increasing oil industry activities.

#### GRAPHICAL ABSTRACT



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# ABSTRACT

The Gulf of Mexico is considered one of the world's major marine ecosystems, supporting important fisheries and habitats such as barrier islands, mangrove forests, seagrass beds, coral reefs etc. It also hosts a range of complex offshore petroleum exploration, extraction, and refining industries, which may have chronic or acute impacts on ecosystem functioning. Previous work on the marine effects of this activity is geographically incomplete, and has tended to focus on direct hydrocarbon impacts, while impacts from other related contaminants (e.g. heavy metals, salt-rich drilling muds) which may be discharged from oil facilities have not been widely assessed. Here, we examine historical trace element accumulation in marine sediments collected from four sites in the Tamaulipas shelf, Gulf of Mexico, in the area of the Arenque oil field. Dated sediment cores were used to examine the sources, and historical and contemporary inputs, of trace metals (including those typically present in oil industry discharges) and their potential biological impact in the Tamaulipas aquatic environment over the last 100 years. CaO (i.e. biogenic component) normalized data showed increasing V, Cr, Zn, Cu, Pb, Zr and Ba towards the sediment surface in three of the four cores, with Ba and V (based on an adverse effect index) possibly associated with adverse effects on organisms. Dated Ba/CaO profiles show an increase of 30–137% after opening of oil installations in the study area, and can be broadly correlated with increasing oil industry activities across

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the wider Gulf of Mexico. Data do not record however a clear enhancement of Ba concentration in sediment cores collected near to oil platforms over more distal cores, indicating that any Ba released from drilling platforms is incorporated quickly into the sediments around the drilling sites, and once this element has been deposited its rate of resuspension and mobility is low.

Capsule abstract: Sediment core data from the Tamaulipas shelf show the influence of oil industry activities on selected trace element concentrations, with Ba/CaO broadly correlating with increasing oil industry activities across the wider Gulf of Mexico.

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# 1. Introduction

Many coastal and shelf sea areas around the world are heavily impacted by anthropogenic activities. The oil industry in particular can generate significant ecosystem damage through tanker and well-head accidents (Payne et al., 2008; Moreno et al., 2011; Qu et al., 2016; Jung et al., 2017), and routine operation and discharges. Hydrocarbonderived pollutants can cause direct mortality of benthic organisms or can modify the structure of benthic communities (Abdallah et al., 2016); causing impaired larval development, changes in oxygen consumption, nutrition, and growth, as well as molecular, biochemical and physiological modifications (Fokina et al., 2014). In addition nonbenthic organisms such as fish, seabirds, and aquatic mammals may suffer habitat loss or death due to oil coating or ingestion (Zhou et al., 2014).

Due to a high dependence on petroleum as an energy source, and the use of hydrocarbon-derived feedstocks in a wide variety of industries, the oil industry has increased its global production (notwithstanding oil crises, overproduction or price crashes) dramatically over recent decades. In 2014 global oil and gas production were 76,061 thousand barrels per day and 124, 444 billion cubic feet respectively (PEMEX, 2014) – 130% and 53,000% more than in 1989 (PEMEX, 1999). Around 30% of production is offshore (U.S.EIA, 2017): for example there are 800 offshore oil and gas platforms in the Arabian Gulf (Albano et al., 2016), 500 in the continental shelf of the North Sea (Fujii, 2015), 420 in the northern Gulf of Mexico and 258 in the southern Gulf of Mexico (PEMEX, 2014).

The Gulf of Mexico is considered one of the world's major marine ecosystems, supporting important fisheries and habitats such as barrier islands, mangrove forests, seagrass beds, coral reefs, river deltas and estuaries (Yáñez and Day, 2004a). In the north, south-west and south of the Gulf of Mexico however a range of complex offshore petroleum exploration, extraction, shipping, service, construction and refining industries have developed (Yáñez and Day, 2004b). Along the coasts of the Gulf of Mexico, a number of authors have reported adverse impacts on foraminiferal, Polychaete annelid, coral reef and benthic communities near to oil platforms or other oil installations (Hernández et al., 2005; Carriquiry and Horta, 2010; Sen Gupta and Smith, 2013; Magallanes et al., 2015; Qu et al., 2016). Current information is geographically incomplete however, and has tended to focus on direct hydrocarbon impacts, while impacts from other related contaminants (e.g. heavy metals, salt-rich drilling muds) which may be discharged from oil facilities have not been widely assessed. For example, the Tamaulipas coasts have supported a significant oil industry for the last 100 years, but there is little information on oil industry impacts in benthic systems in this area, particularly how sedimentary trace and major elements have increased or decreased in the last 100 years in relation to oil industry, and to other anthropogenic, activities (including urban and industrial development of the adjacent coastline and river drainage catchments). This article aims to partly fill this knowledge gap, via analyzing dated sediment cores to examine the historical and contemporary inputs of trace metals (including those typically present in oil industry discharges), and their potential biological impact, in the Tamaulipas aquatic environment over the last 100 years.

#### 2. Study area

The study area covers approximately 1612 km<sup>2</sup> of seafloor near to the Mexican state of Tamaulipas, within the third most important hydrocarbon field in the Mexican part of the Gulf of Mexico (Fig. 1). Its coordinates are 22° 27.03′ to 22° 5.99′ north latitude and 97° 56.99′ to 97° 21.04' west longitude. The area receives discharges from the Panuco River, which has the largest catchment area (85,956 km<sup>2</sup> CONAGUA, 2016) emptying into the western Gulf of Mexico, although only 16,499 km<sup>2</sup> of this catchment are in Tamaulipas state (INEGI, 2010). The coastal currents in this region vary seasonally, running southward from September to March and northward from May to August, and between each season there is a transition period that starts from late March to April and from late August to September (Zavala et al., 2003). The main anthropogenic influences consist of 11 point sewage discharges, 6 water treatment plants, the Madero oil refinery, the Altamira and Tampico ports located in the urban area formed by Altamira, Madero City and Tampico (INEGI, 2010), and the Arenque marine oil field (PEMEX, 2012).

The Panuco River has an annual discharge of 20,330 Mm<sup>3</sup> (CONAGUA, 2016) and crosses 13 municipalities from Tamaulipas with a population of 957,227 inhabitants (based on 2010 data), of which 73.8% are concentrated in the municipalities of Altamira, Madero city and Tampico (INEGI, 2010). The urban area formed by these three sites is considered the main industrial region of the Tamaulipas coastal zone (Ortiz et al., 2000), containing 1 major oil refinery (PEMEX, 2014), 2 of 13 ports in the western Gulf of Mexico, and other manufacturing industries (INEGI, 2010). Agriculture and livestock activities are also common in the catchment, with livestock production representing 27.7% of all state livestock production, and an agricultural production making up 33.6% of the total state agricultural produce value (based on 2011 data) (INEGI, 2010). The Tamaulipas Panuco catchment lithology mainly consists of 1) Cenozoic and Mesozoic clastic (sandstone, siltstone and shale) and calcareous (limestone) sedimentary rocks, and Quaternary alluvium. 2) Cenozoic volcanic rocks of mafic and intermediate composition and 3) metamorphic rocks comprising schist and gneiss of Paleozoic and Precambrian age (Armstrong Altrin et al., 2015; Moran-Zenteno, 1994 and Ortega Gutierrez et al., 1995).

# 3. Materials and methods

Four cores labelled as C17, C47, C53 and C93 were taken from the Tamaulipas shelf at water depths of 58, 38, 70 and 60 m respectively (Fig. 1). Coring locations were selected to sample bottom sediments in the area of the Arenque oil field, at locations proximal and more distal to the Panuco River mouth, and north and south of the oil field, to allow assessment of potential variations in sediment geochemistry caused by (a) different sediment sources (e.g. terrestrial vs biogenic); (b) inputs from oil exploitation activities in the Arenque field; and (c) inputs from industrial and other activities in the Panuco River catchment. The core lengths were 19, 27, 15 and 25 cm respectively. Cores were collected at 12.2 (C47), 30.1 (C93), 32.5 (C53) and 34.5 (C17) km from the Panuco River Mouth.

Cores were collected using a box corer and subsampled with a PVC pipe (10 cm inner diameter) aboard the O/V Justo Sierra, during the

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