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Spatial distribution and sources of organic matter and pollutants in the SE Mediterranean (Levantine basin) deep water sediments

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ABSTRACT

A study of deep sea sediment quality was conducted at 52 stations off the Mediterranean coast of Israel (50–1900 m depth). Total Organic Carbon (TOC), Polycyclic Aromatic Hydrocarbons (∑PAHs), Poly Chlorinated Biphenyls (∑PCBs) ranged between 0.58 and 1.44%, 12–190 and <0.3–7.7 μg kg^{-1}, respectively. The TOC distribution indicated the Nile delta as an important source of organic matter and the important effect of topography on deposition patterns in this region. PCBs and PAHs quantitative levels were associated with nearby gas well drilling (well below environmental criteria) and dredge-material dumping sites. A significant correlation between these pollutants and TOC was found in the southernmost stations suggesting a common source. PAHs isomer ratios in most of the stations indicated a petrogenic source, while the contribution of pyrogenic sources appears to be very small. These findings form a sound baseline for assessing the potential impact of future deep sea drilling activities that are expected to increase significantly in the Eastern Mediterranean basin.

Relatively higher levels of Total Organic Carbon (TOC) in deep water sediments are predominantly found along continental slopes in the bottom depth range of 200-2000 m (Premuzic et al., 1982). The processes and conditions determining this distribution are still not entirely clear, yet previous studies have demonstrated a number of important contributing factors (Hedges and Keil, 1995; Zonneveld et al., 2010). Hydrophobic organic contaminants such as Polycyclic Aromatic Hydrocarbons (PAHs) and Polychlorinated Biphenyls (PCBs) in the marine environment are often found at high levels in shallow coastal sediments with poor water exchange exposed to direct discharge or spills as well as contaminated urban runoff (e.g. Guitart et al., 2007; Guitart et al., 2010). Oil spills, have also been indicated as important sources of PAHs to both deep and shallow water marine sediments (e.g. Laflamme & Hites, 1978; UNEP-MAP, 2012). Few reports mentioned the hazardous discharge of PAHs and other pollutants with the drilling mud used for gas and oil explorations (Neff et al., 1992; OSPAR Commission, 2009; Iwegbue, 2011; Jagwani et al., 2011; Tornero and Hanke, 2016), which may cause enrichment of organic pollutants in deep water sediments at least in the immediate vicinity of well drilling sites. Atmospheric deposition of these pollutants is also considered an important source, especially in deep water sediments (e.g. Tsapakis et al., 2003; Tsapakis et al., 2006; Azoury et al., 2013; Theodosi et al., 2013), which are further away from the coast and therefore affected to a lesser degree by terrestrial sources (Louvado et al., 2015). Previous studies showed that PCBs (Lohmann, 2003) and PAHs (Oleszczuk & Baran, 2003; Nam et al., 2008) are strongly bound by sediments with high organic matter content, probably as a result of their high hydrophobic nature (Op. Cit.). Several studies demonstrated significant positive linear correlations between TOC and PAHs or PCBs in various coastal environments such as deltas (e.g. Nemr et al., 2007), harbors (e.g. Lohmann et al., 2005; Lohmann et al., 2006) and estuaries (e.g. Chiou et al., 1998; Oren et al., 2006). Finally, in deep sea sediments of the Eastern Mediterranean, PAHs were shown to correlate significantly with the Black Carbon (BC) fraction of TOC, suggesting that BC is an important transport vector for PAHs from the atmosphere to the oceans (Tsapakis et al., 2003). The results of a follow up study using sediment traps was able to demonstrate the significant correlation of PAHs and BC during the deposition processes as well (Theodosi et al., 2013).

Sparse measurements made throughout the Mediterranean Sea during the period 1950–1980 showed that the highest levels of TOC (1–2%) in deep water sediments were found in the Western Mediterranean Basin along the west coast of Italy, the northern Aegean Sea near the mouth of the Dardanelles and in the SE Levantine Basin, spreading to the north from the Nile River delta region along its eastern continental shelf (Romankevich, 1984). Yet, most (>50%) of the Mediterranean Sea bottom, primarily in the region east of the Sicily Strait throughout the central and eastern regions of the Levantine Basin and along the Mediterranean coast of Spain have relatively low TOC levels (0–0.5%) (Op. Cit.).

In the eastern Mediterranean Sea along the Egyptian coast, maximal contents of TOC in surface sediments on the shelf is up to 1.5% (Aly Salem et al., 2013), while in Israeli shelf sediments (<100 m depth) TOC levels vary between <0.1% in shallow water (10 m) along the

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coast and 0.8–1% near the shelf break (Almogi-Labin et al., 2009). Prior to the damming of the Nile during the 1960's, nutrient and organic matter loads were transported northward from the delta with the general circulation of the south-eastern (SE) Mediterranean (Sharaf El Din, 1977; Nof, 1978). After the damming of the Nile, this source diminished significantly, however, due to increased urbanization and use of fertilizers in the area around the Nile Delta, nutrient loads to the SE Mediterranean have returned to pre-damming levels (Ludwig et al., 2009; Oczkowski et al., 2009), but with an extremely smaller fresh water flux. Thus, the Nile has become again a significant source of nutrients and organic matter to the SE Mediterranean and while they are still being transported northward with the general circulation, it is possible that they propagate in a relatively wider band and to a limited distance as indicated in the modeling study of Suari and Brenner (2015). In addition, it is possible that in addition to nutrients and organic matter, organic pollutants (such as PAHs and PCBs) may also be carried northward by this current.

In the Mediterranean Sea, most measurements of PAHs and PCBs have been made primarily in coastal waters with relatively few observations in deep sea sediments (e.g. Gomez-Gutierrez et al., 2007; Azoury et al., 2013). Elevated levels of PAHs (<1–100 mg kg^{-1}) were detected in estuaries and harbor sediments, while much lower (<5–500 μg kg^{-1}) levels were reported for unprotected open coastal water sediments (Barakat et al., 2011; Kucuksezgin et al., 2013). In the SE Levantine basin along the Egyptian coastline maximal levels of ∑PAHs reached 1211 μg kg^{-1} in Alexandria harbor (Barakat et al., 2002) and 75 μg kg^{-1} in El-Arish or El-Mex (Aly Salem et al., 2013). Maximal ∑PCBs in western Mediterranean sediments in the open sea were up to 9 μg kg^{-1}, while coastal sediments reached 3.2 mg kg^{-1} and up to 21.2 mg kg^{-1} in sewage contaminated sediments (Tolosa et al., 1997). Considering factors such as shipping routes, oil spills, gas and oil exploration sites and polluted dredge material dumping (UNEP/MAP, 2012), it is possible that organic pollutants elsewhere in the deep sea may be elevated irrespective of atmospheric input (Mandalakis et al., 2014).

Although contamination hazards due to drilling and gas/oil production activities are well documented as mentioned elsewhere (Jagwani et al., 2011; Weis, 2014), there is almost no data describing the pollution levels in the vicinity of deep water drilling sites or even background levels of pollutants in the deep sea sediments of the SE Levantine basin. On a larger scale, while pollution levels in coastal sediments in the Mediterranean Sea have been sufficiently described, deep sea data is scarce, especially in the Eastern Mediterranean (Parinos et al., 2013).

In this study we analyzed and characterized the spatial distributions of TOC, PAHs and PCBs in the surface sediment (0–1 cm) of 52 stations in the SE Levantine basin (Fig. 1, SOM Table 1) and discuss the possible causes responsible for them. The analysis of PCBs data include measurements from the Epsilon and Alpha dredge material dumping sites that are located in the northern part of the study region at bottom depths of ca. 700 and 1400 m, respectively (Fig. 1, SOM Table 2). Both sites were surveyed using the same methodologies as this study, which are detailed in the supplementary online material (SOM), in 2004 and 2009–2010, respectively.

TOC levels in the study area were generally higher along the continental slope and substantially lower along the continental rise (Fig. 2A). In addition, there is an apparent south to north decreasing trend in TOC along the continental slope, which is interrupted by an increasing trend towards the northern boundary of the study area beginning approximately along the Carmel Head (northern Israel) parallel. The PCBs were above the level of detection (LOD) in only 22 stations (SOM Table 1) and out of these only 12 stations had concentrations above the limit of quantitation (LOQ) with a maximum total concentration of ΣPCBs = 8 μg kg^{-1} (far below the Effects Range Low (ERL); Long et al., 1995; Buchman, 2008). These levels are consistent with other observations made in the eastern Mediterranean (Mandalakis et al., 2014). The, relatively higher levels were found at five stations located on the continental slope along the southernmost east-west transect (stations S41–G27) (Fig. 2C, SOM Table 1). The dominant PCB congeners in all stations with exception of S11 were PCB-28 followed by PCB-52, both of which have lower toxicity and higher transportation ability compared to higher chlorinated PCBs (e.g. Hawker and Connell, 1988). However, at station S11, which is located 7NM from shore and on the same heading as the Epsilon and Alfa sites from Haifa Port, the dominant congeners were PCB-138,153,180. At the Epsilon site, PCBs were measured (>LOQ) at 6 stations that were concentrated in the southern half of the sampling area (see above) with a maximum value of ΣPCBs = 27.8 μg kg^{-1} (SOM Table 2). The dominant PCB congeners were PCB-138,153, while PCB-28 was <LOD. At the Alfa site, PCBs were >LOQ at all stations with ΣPCBs ranging between 0.7 and 33.0 μg kg^{-1}. The dominant congeners were PCB-118-180, however PCB-28 was >LOQ at some stations with relatively higher levels of ΣPCBs. PAHs were relatively low (Fig. 2B and SOM Table 1) and well below the ERL (Long and Morgan, 1990; Long et al., 1995; Buchman 2008). Only Naphthalene, 2-Methynaphthalene, Fluoranthene, Pyrene, Benz(a)anthracene, Benzo(b)fluoranthene, Indeno(1,2,3-cd)pyrene were >LOQ at all sites, while PAHs with the highest levels were Pyrene, Phenanthrene and Fluoranthene (SOM Table 1). Similar to ΣPCBs, relatively high ΣPAHs occurred along the southernmost east-west transect on the continental slope (stations S41–G27).

The higher TOC levels along the continental slope relative to deeper sediments in the study area (Fig. 2) are likely the result of the close proximity to shelf and coastal waters that are commonly enriched in land-derived nutrients and organic matter (Herut et al., 2000; Efrati et al., 2013). Yet, TOC levels on the shallow continental shelf (<30 m bottom depth) are very low (~0.1%) (Almogi-Labin et al., 2009), perhaps as a result of winnowing of fine grained sediments rich in organic matter (e.g. de Haas et al., 2002), and or higher remineralization rates in these relatively shallow coarse grained sediments, that are found in warmer, well oxygenated waters (e.g. Forster et al., 1996). Thus, it would be expected that peak TOC levels in the deep sea sediments occur near the edge of the continental shelf break. However, according to Fig. 3 it is evident that TOC peaks along the ca. 500 m isobath, midway down the continental slope. It is possible that the interaction between the general northerly long-shore current in the SE Levantine basin (Nielsen, 1912; Nof, 1978; Rosentraub and Bernner, 2007) and the relatively steep topography of the continental slope contributes to the entrapment of sediments and organic matter, originating from the shelf region. This assumption is based on earlier theoretical work demonstrating this mechanism, where reduced horizontal advection midway down the continental slope in a relatively narrow depth range, could result in elevated sedimentation rates relative to the shallower and deeper regions (Csanady & Shaw, 1983). Recently, a similar hypothesis was postulated for observed deposition patterns of fine sediments along the continental slope of the SE Levantine Basin (Schattner et al., 2015). Furthermore, in the deep water sediments of the western Levantine Basin it was shown that TOC was significantly correlated with the fine sediment fraction (<63 μm), suggesting that hydrodynamic sorting by resuspension and advection of fine sediments already enriched in organic carbon from the continental shelf plays an important role in the spatial distribution of TOC (Pedrosa-Pamies et al., 2015). However, this is not the sole case in our measurements (grain size distribution data not shown). The TOC distribution is also characterized by a general south to north decreasing trend along the continental slope (Fig. 4). Clearly, the close proximity of the study area to the Nile River delta, could provide an explanation for this distribution. Finally, TOC maxima along the continental slope correspond quite well to the approximate locations of the ridgelines and canyons that formed due to slumping along the continental slope (Fig. 5), also known as the Palmachim and Dor disturbances (Garfunkel and Almagor, 1987; Garfunkel et al., 1979). The high TOC levels measured along the northernmost east-west transect also correspond to a topographic feature (not apparent in Fig. 5) known as the Carmel Fault Canyon (Ben-Avraham et al., 2006).

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