Marine Pollution Bulletin 129 (2018) 35–42

Contents lists available at ScienceDirect

Marine Pollution Bulletin

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

High total organic carbon in surface waters of the northern Arabian Gulf: Implications for the oxygen minimum zone of the Arabian Sea

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ARTICLE INFO

Keywords:
Total organic carbon
Eutrophication
Hypoxia
Kuwait Bay
Tigris-Euphrates Delta region
Arabian Gulf

ABSTRACT

Measurements of total organic carbon (TOC) for two years in Kuwaiti waters showed high TOC levels (101.0–318.4, mean 161.2 μM) with maximal concentrations occurring within the polluted Kuwait Bay and decreasing offshore, indicating substantial anthropogenic component. Analysis of winter-time data revealed a large increase in density over the past four decades due to decrease in Shatt Al-Arab runoff, implying that the dissolved/suspended organic matter in surface waters of the northern Gulf could be quickly injected into the Gulf Deep Water (GDW). Our measurements together with an analysis of previously collected/published data suggest that the recent summer-time declining trend in oxygen in the GDW might be related to eutrophication. Higher preformed TOC and lower preformed dissolved oxygen contents of the high-salinity water mass that flows out of the Gulf and ventilates the mesopelagic oxygen minimum zone (OMZ) of the Northwestern Indian Ocean may cause expansion/intensification of the regional OMZ.

1. Introduction

The Arabian Gulf, hereafter referred to as the Gulf, is a Mediterranean-type, nearly land-locked marginal sea connected to the Sea of Oman/Arabian Sea through the narrow Hormuz Strait. Its geographical isolation, small basin size (area 251,000 km^2, volume 8600 km^3), shallow depths (maximum 90 m, average 36 m), and subtropical location combine not only to produce extremely large variability in hydrographic conditions, especially in surface temperature that varies seasonally from ~12 to 35 °C (Al-Yamani et al., 2004), but also make its environment and ecosystems highly vulnerable to human activities. Endowed with rich energy resources, nations surrounding the Gulf have witnessed rapid development in the past few decades, most of which has occurred in the coastal zone. This has led to huge changes in the Gulf's marine environment (Sheppard et al., 2010). One of the major threats faced by the Gulf's environment and ecosystems, as in many other coastal areas, especially the land-locked water bodies, is eutrophication, arising mainly from urban and industrial centers that have grown enormously in the past few decades (Naqvi, 2009; Sheppard et al., 2010; Devlin et al., 2015). The population of Kuwait (3.8 million today), for example, has undergone an approximately 27 fold increase since 1950. This has caused substantial increases in nutrient (especially ammonium) loading in coastal waters of Kuwait (Devlin et al., 2015).

Despite its relative isolation, water exchange between the Gulf and the Northwestern Indian Ocean (NWIO) through the Hormuz Strait is quite vigorous. This exchange is primarily driven by the massive evaporation within the Gulf (~2 m yr^{-1}). The Gulf receives negligible precipitation, and the combined runoff from rivers (mostly Tigris, Euphrates and Karun) is an order of magnitude smaller than the loss through evaporation (Al-Yamani et al., 2004; Sheppard et al., 2010). The resultant high salinity in conjunction with cooling in winter creates a dense, high-salinity water mass that sinks and flows out of the Gulf as a near-bottom current (Reynolds, 1993; Swift and Bower, 2003, and references therein). To compensate for this outflow, estimated to be ~6620 $km^3\ yr^{-1}$, and the excess of evaporation over river runoff, there is an inflow (7250 $km^3\ yr^{-1}$) of fresher surface water from the Sea of Oman to the Gulf (Sheppard et al., 2010, and references therein). Thus, with respect to the inflows and outflows, the flushing time of the Gulf is around 1.2 yr [Note: Brewer and Dyrssen, 1985 estimated a longer flushing time (2.5 yr) using lower estimates for water exchange provided by Hartmann et al., 1971]. The relatively rapid flushing, coupled with mixing caused by currents, waves and tides allows the Gulf to cope with some of the most severe human perturbation any semi-enclosed marine system is being subjected to. However, active exchange with the Indian Ocean, especially the export of saline, subsurface water, also underlines the capability of the Gulf to alter environmental conditions in the Sea of Oman and the Arabian Sea, which together constitute the NWIO.

After spilling over the Hormuz Strait, the outflow from the Gulf, referred to as the Persian Gulf Water (PGW) in the literature, sinks to

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https://doi.org/10.1016/j.marpolbul.2018.02.013
Received 21 September 2017; Received in revised form 4 February 2018; Accepted 5 February 2018

250–400 m depths, mixes with the surrounding cooler, fresher waters (Senjyu et al., 1998), and spreads over large parts of the Arabian Sea with its core, identified by a salinity maximum, centered around 26.6 σ_θ surface (Wyrtki, 1971). This density level corresponds to the core of the intense oxygen minimum zone (OMZ) of the Arabian Sea where denitrification is at its maximum (Deuser et al., 1978; Naqvi, 1987; Codispoti et al., 2001; Ward et al., 2009). In fact, the PGW is the only regionally- and freshly-formed water mass that directly ventilates the core of any OMZ in the world [the Red Sea Water (RSW), the other high salinity water mass of the NWIO ventilates the lower part of the OMZ (Wyrtki, 1971) that is not reducing]. Any changes in the production rate, physical characteristics or chemical composition of the PGW are, therefore, expected to affect OMZ processes. These changes are of special interest in view of the ongoing global intensification and expansion of the oceanic OMZs (Stramma et al., 2008; Banse et al., 2014; Schmidtko et al., 2017).

Thermohaline changes in the Gulf are taking place not primarily because of global warming, but because the Gulf is being steadily starved of the little freshwater runoff it receives due to the ongoing damming of major rivers (Euphrates and Tigris) in riparian states (Al-Yamani et al., 2004, 2017; Sheppard et al., 2010). Salinity in the Northwestern Gulf has already risen substantially as a result of the latter effect (Al-Yamani et al., 2017). Chemical alteration of PGW could occur as a decrease in its preformed oxygen content and/or an increase in its total organic carbon (TOC) content. While higher temperature and salinity in the Gulf would reduce the oxygen solubility, eutrophication and sewage discharge are expected to result in increased organic loading, thereby enhancing respiration in waters both inside and outside the Gulf. As it is, the PGW is associated with substantially higher (by 8–12 μM) TOC than the water it mixes with in the Sea of Oman and the Arabian Sea (Hansell and Peltzer, 1998). A substantial increase in the preformed TOC content of this water mass could have a significant impact on the intense OMZ of the NWIO. Here we investigate the TOC distribution in Kuwait waters, based on first ever TOC measurements made in the northern Gulf, a key site of dense deep water formation (Swift and Bower, 2003). We also evaluate the hydrographic changes that have taken place in this region over the past four decades that are relevant to transport of organic matter to the Gulf interior. Finally, we discuss the potential cause and implications of the recently reported hypoxia in the central Gulf (Al-Ansari et al., 2015) by utilizing other available data.

2. Materials and methods

As a part of an ongoing monitoring program on the health of Kuwait's coastal waters under the project “The Oceanography Operational Research Activity” being implemented by the Kuwait Institute for Scientific Research (KISR), samples were collected at 7 KISR stations (Fig. 1; Table 1) located in the Northwestern Gulf from March 2014 to March 2016. The sampling frequency was intended to be monthly, but it could not be achieved for logistic reasons. However, all stations were sampled adequately during each season (Winter: December–February; Spring: March–May; Summer: June–August; Autumn: September–November) with the exception of Station 18 in summer.

Observations were made using fiber glass speed boats. Water temperature and salinity were measured with a AAQ170 RinKo CTD (Conductivity-Temperature-Depth) profiler. The CTD sensors were regularly calibrated at the manufacturer's facility. Transparency measurements were also made on a routine basis using a Secchi disc. At each station a water sample was taken from 1 m depth with a 5-l Niskin sampler, taking due precaution to avoid contamination from the boat. Subsampling was carried out immediately for routine measurements - dissolved oxygen, nutrients (nitrate, nitrite, ammonium, phosphate and silicate), chlorophyll *a*, and phytoplankton composition. In addition, subsamples for TOC were taken in high density poly-ethylene (HDPE) bottles that had been treated with 1.2 M HNO_3 for 2 h followed by thorough rinsing with deionized water. The HDPE bottles are recommended for storing TOC samples (http://www.jodc.go.jp/geotraces/docs/PICESReport34_DOC_DON.pdf). Samples for TOC were immediately acidified with 50% sulfuric acid to bring the pH down to ~2 and stored at low temperature for analysis that was usually completed within a few weeks of collection.

Standard methods were used for measurements of dissolved oxygen and nutrients (Grasshoff et al., 1983). These data are presented and discussed in detail elsewhere (Al-Yamani et al., manuscript in preparation).

Carbon dioxide was purged out of the acidified samples by bubbling N_2 gas before the TOC content was determined following the high temperature (680 °C) catalytic oxidation method, using an Apollo 9000 TOC Analyzer with an NDIR detector (Teledyne Tekmar, Ohio, USA). Certified reference material procured from Analytik Jena was used for calibration before each set of measurements. Another TOC standard (1 mg C l^{-1}) and a blank (milli Q water) were run after each set of samples, and sometimes in between the samples, to check the performance of the instrument. In case of a shift in the area unit value relative to the initial calibration, appropriate correction was made.

For measurements of chlorophyll *a*, ~1 l of the sample was filtered through 0.70 μm glass fiber filter within 3 h of collection (during which time the samples were stored in an ice box in the dark). Chlorophyll *a* was extracted and measured following the fluorometric procedure as described by Strickland and Parsons (1972). While the lower limit of detection was 0.01 mg m^{-3}, the precision based on replicate analyses was better than 1%.

3. Description of sampling sites

The stations sampled (Fig. 1, Table 1) can be categorized under three groups based on the hydrographic conditions and/or the extent of anthropogenic impact. Stations A and B are located in the north in a region that receives runoff from the Shatt Al-Arab River, which is carried to these stations by the prevailing anti-clockwise circulation (Reynolds, 1993; Al-Yamani et al., 2004). Consequently, salinity dips to fairly low values during spring/early summer (the minimum value recorded in the present study was 34.77 at station A on 6 April 2014). Stations C and K6 are located in Kuwait Bay, a shallow embayment that receives large amounts of municipal wastes from Kuwait City as well as effluents from various industrial units, power and desalination plants, and vessels entering Kuwait port. Stations 3, 6 and 18 are in the open Gulf. Sta. 18 is the farthest from the shore, and the least impacted by human activities among all stations. All stations are shallow, with the water depth ranging from 5 m at Sta. B to 29 m at Sta. 18 (Table 1).

4. Results

The TOC concentrations in surface waters of the northern Gulf during regular KISR surveys conducted from March 2014 to March 2016 ranged from 101.0 to 318.4 μM with an overall seasonally-weighted mean of 161.2 μM (Table 2). Even higher values (336.7–543.3 μM) have since been measured in the inner Kuwait Bay during a phytoplankton bloom on 12 April 2017. The TOC distribution exhibited a clear spatial pattern in that the mean values decreased steadily away from the coast along both transects (Stas. A-B-3 and Stas. C-K6-6-18). The seasonal variability was less pronounced, especially in the open Gulf. However, in most cases mean concentrations were the highest in either winter or spring while the minimum generally occurred in autumn.

In order to understand factors controlling TOC distribution, linear correlations of TOC were examined with temperature, salinity, chlorophyll *a* and Secchi depth. The correlation coefficients varied from station to station (Table 3). Several stations in the north (but not K6) exhibited negative correlations between TOC and salinity. Significant