Baseline

Environmental characterization of a semiarid hyper saline system based on dissolved trace metal-macronutrient synergy: A multivariate spatio-temporal approach

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ABSTRACT

Trace metals and macronutrients play key roles in marine biogeochemical processes. Despite their higher availability, no reliable information is available on their ecological role in the hypersaline waters of NW Arabian Gulf. The present study identifies their synergistic effect on environmental characteristics and autotrophic biomass in the shallow coastal and offshore waters, off Kuwait on a seasonal basis. Surface water samples collected along four predefined transects were analyzed for physico-chemical and biological variables during summer (n = 27) and winter (n = 27) seasons. Multivariate analyses revealed clear spatial and seasonal trends, and identified the best suit of environmental variables responsible for the seasonal variability in phytoplankton biomass. Using statistically derived supply to demand ratios, carbon-trace metal stoichiometry, and bioavailability of trace metals, we propose possible growth regulating factors for phytoplankton on a seasonal basis in the NW Arabian Gulf, off Kuwait. This is the first report on trace metals from the entire Arabian Gulf, using clean techniques and multivariate statistical approach.

Rapid expansion of industrial activities along 500 km coastal stretch of Kuwait (Al-Rifaie et al., 2008; Al-Abdulghani et al., 2013) in recent years has inflicted negative changes on its marine environment as a variety of contaminants including petroleum hydrocarbons, trace metals, raw and partially treated sewage, and brine from desalination plants are released directly into coastal waters (Readman et al., 1992; Al-Ghadban et al., 2002; Bu-Olayan and Thomas, 2014; Uddin et al., 2011). These impacts are aggravated by seasonal dust storms, and particulate matter and sediment transport from the Shatt Al-Arab River system (Al-Ghadban et al., 2002; Al-Ghadban and El-Shammak, 2005). Thus, during the last two decades, these anthropogenic stressors have converted the shallow hypersaline waters (max. salinity 45) off Kuwait, a eutrophic system subjected to frequent outburst of phytoplankton blooms (Al-Yamani et al., 2004; Al-Kandari et al., 2009) and catastrophic decline in fisheries (Al-Said et al., 2017). From the NW Arabian Gulf, many studies are available on the physicochemical and biological characteristics (Al-Yamani et al., 1997a,b, 2002, 2004, 2008; Devlin et al., 2015; Lyons et al., 2015), but no attempts are made yet to understanding the cumulative effect of trace metals and macronutrients on the spatial and seasonal patterns of phytoplankton standing stock, and environmental characterization in the marine environment off Kuwait.

Recent use of clean trace metal analytical techniques suggest that concentration of micronutrients in the world oceans could be much lower than their earlier reports (Bruland and Lohan, 2004; Boye et al., 2012; Al-Said, 2008). Accurate estimates of total and biologically available trace metals along with information on inorganic macronutrients are therefore imperative in understanding the ecosystem function. Here, using clean analytical techniques, we studied the spatial and seasonal distribution of five bio-reactive trace metals (Cu, Co, Zn, Fe and Ni) and macronutrients (Nitrate-N (NO_3-N), Nitrite-N (NO_2-N), Ammonium-N (NH_4-N), Silicate-Si (SiO_3-Si) and Phosphate-P (PO_4-P)) in the Bay and offshore environments off Kuwait in the northwestern Arabian Gulf. In this study we engaged a multivariate statistical approach to understanding the hydrographic assemblage patterns, and environmental impact on phytoplankton standing stock (measured as chlorophyll *a*, and Chl *a* converted carbon). Using published information on organic chelation of different trace metals, we also have crosschecked the demand/supply scenario for micronutrients and their possible impact on phytoplankton standing stock. This is the first ever study from the NW Arabian Gulf on trace metal distribution using clean techniques, advanced instrumentation, and multivariate analytical
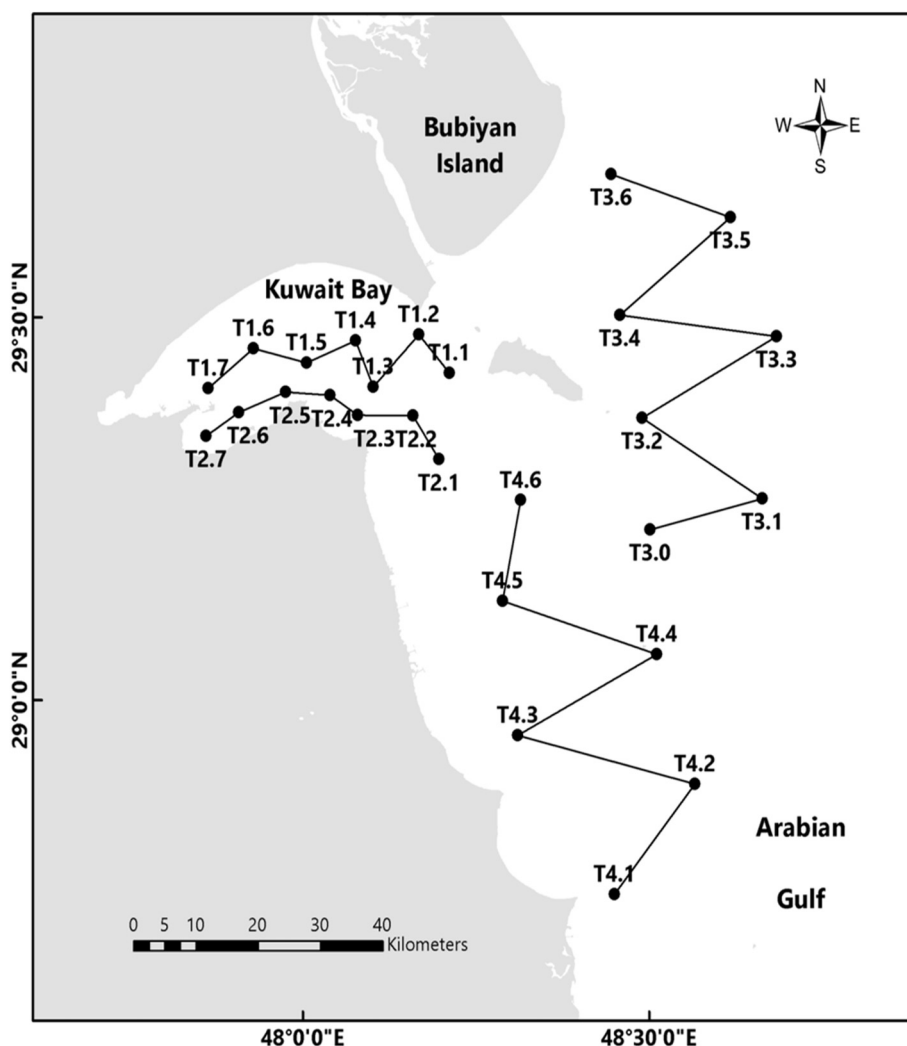
Fig. 1. Sampling locations in the NW Arabian Gulf, off Kuwait.

approaches. The new information will help us formulate experiments to redefining their biological availability and conduct detailed study on the importance of these micronutrients on autotrophic community dynamics in this semi-arid environment.

Surface water samples (0.2–0.3 m depth) were collected from 27 stations located along four different transects in the NW Arabian Gulf, off Kuwait on two different seasons (summer (June) and winter (November)) in 2015. Two transects were located in the Kuwait Bay (transects T1, T2) and two, in the offshore waters (transects T3, T4) (Fig. 1). Water temperature, salinity, dissolved oxygen, pH, turbidity, and PAR were measured using calibrated sensors attached to a Conductivity Temperature Depth (CTD) device (AAQ170 Rinko Alec Electronics). Samples meant for NO_3-N, NO_2-N, NH_4-N, SiO_3-Si and PO_4-P, and Chl-*a* measurements were collected using a 5-l Niskin sampler (General Oceanics, USA). Samples for NH_4-N were collected in triplicate (10 ml) test tubes with airtight caps. Water samples for nutrients were filtered through 0.7 μm filters (GF/F, Whatman) and stored at $-20\,°C$ in 125-ml acid-washed polyethylene bottles, until analysis following the colorimetric method as described in ROPME (2010). Quality control of nutrient measurements was assured using MOOS-3 Seawater certified reference material (CRM, National Research Council, Canada). NH_4-N measurements were carried out using a double-beam scanning spectrophotometer (Shimadzu UV-2450; wavelength 630 nm). For chlorophyll-a (Chl *a*), sample filtration (100 ml) was carried out under dim light conditions using 0.7-μm (GF/F, Whatman) filter paper. Chl *a* extracted from the filters using 10 ml of 90% acetone at $4\,°C$ overnight,

was analyzed before and after acidification (1 N HCL) using a pre-calibrated Trilogy fluorometer (Turner Design, 7200–000) following the United States Environmental Public Authority (US EPA) standard method 445.0 for aquatic fluorescence measurements (Arar and Collins, 1997).

Samples meant for trace metal analysis were collected and processed using acid-cleaned low-density polyethylene bottles (Nalgene) (Achterberg et al., 1999, 2003; Al-Said, 2008). Samples filtered through acid-cleaned 0.4-μm polycarbonate filters (Whatman) and subsequently acidified with HCl (6 N) (Romil) to pH $<$ 2 under a laminar flow hood, were stored until analysis at 20–23 °C. Adsorptive cathodic stripping voltammetry (Ad-CSV) system (Metrohm model 797 VA Computrace) was used to measure total dissolved trace metals: copper (Cu), nickel (Ni), cobalt (Co) and Zinc (Zn) (Achterberg and van den Berg, 1997; Al-Said, 2008; Achterberg and Braungardt, 1999). Ultra Violet (UV) digestion of trace metal samples was performed using a custom-made system. The samples were placed in quartz tubes (ca. 30 ml) around the lamp and exposed to UV light (4–5 h). The UV digested samples were kept at 20–23 °C for a period of minimum 24 h prior to analysis. Blanks were determined on a daily basis using Milli-Q water. Calibration curves of Co, Cu, Ni, and Zn were produced after optimizing measurements to assess the linearity of the method used. Samples meant for dissolved iron (Fe) were acidified with HCl (12 N) (Romil) to pH 1.9 and stored until analysis. The standard preparations were made from low Fe bulk seawater sample (1 l acidified to pH 1.9) by adding Fe standard solution (Standard 1–36.34 μM; Standard 2–3.64 μM).