Faculty and PostDoc, Energy and Environment

The Influence of Qatari Dust on the Element Composition of Marine Plankton

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ABSTRACT

The waters of Qatar are affected by dust making it an ideal location to examine the influences of the atmospheric depositions on the marine biological activity and its influence on biogeochemical cycling of elements. We examined the effect of dust on the elemental composition of plankton, and the variation with distance from shore. Size fractionated samples of bulk-plankton (50 µm) and zooplankton (200 µm) were collected in 2012 and 2014 from Qatar's waters, strong acid digested and analyzed by ICP-OES. The biogenic concentrations of trace metals were determined by correcting the results for lithogenic contributions using Al content of Qatari dust as a lithogenic tracer. The relative trace metal composition of plankton from EEZ of Qatar is Fe > Zn/Cu > V/Ni/Cr/As/Mo > Cd/ Co. Both plankton sizes' compositions were similar, except for Ba, Mn, Pb, Mo which were higher in zooplankton. It wasn't clear if this was due to differences in biology, proximity to the coast or interannual effects. The geochemical and statistical analysis suggested that the concentrations of Al, Fe, Cr, Co, Mn, Ni, Pb, Li were mostly of lithogenic origin and Cd, Cu, Mo, Zn are most likely of biogenic/anthropogenic origin. The excess concentrations relative to dust for most elements decreased with distance from shore.

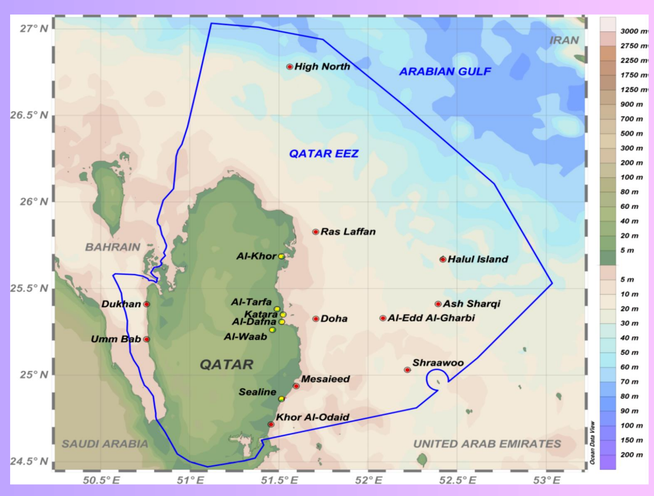

Fig. 1: Sampling locations for net-tow samples and marine borders of Qatar.

SAMPLING

The study region is the central Arabian Gulf (**Fig.1**). Biota samples were collected on board R/V Janan (**Fig.2**) for measurements of natural plankton assemblages (**Fig.3**) on October 2012 (11 sites from Qatar EEZ) and April 2014 (from Doha and Dukhan Bays only), using metal-free plankton nets (aspect ratio 4 : 1) with mesh sizes of 50 µm and 200 µm (**Fig. 4**). During biota sampling the ring nets were towed horizontally at 1 - 2m depth at 1.5 knot speed for 10 min (~ 0:5 km distance) from the board of R/V. Additionally, a set of dust samples were collected using automated passive dust samplers (**Fig.5**).

MATERIALS AND METHODS

All samples were analyzed using strong acid (HF, HNO_3, HCl & H_2O_2) digestion technique. Trace elemental concentrations were determined using ICP-OES. Abiotic material (lithogenic origin, e.g. dust) was calculated with Al as a tracer. Metal to Aluminum ([Me]/Al) ratios were calculated (Yigiterhan et al., 2018). After subtracting this value from the total concentrations, the remaining amount was assumed to be biogenic (non-lithogenic portion, e.g. zooplankton and a small fraction of other planktonic organisms).

Fig. 4 Marine plankton sampling

Fig. 5 Aeolian dust sampling

INTRODUCTION

The Arabian Gulf is one of the hottest, driest, most saline, and dustiest areas on earth. Limited number of studies exist in the Gulf due to sampling and analytical difficulties, abiotic contamination, interspecies, extreme climate, oil & gas fields and regional differences (Yigiterhan et al., 2018).

By locating at the center of the Gulf, the EEZ of Qatar is affected by extreme dust and extensive industrialization, making it an ideal location to examine influences of coastal biogeochemical processes on biological activity (e.g. plankton composition; Yigiterhan et al., 2020).

Our goal was to determine the influence of dust on the elemental composition of plankton in the surface waters.

Fig 2. QU Research Vessel Janan.

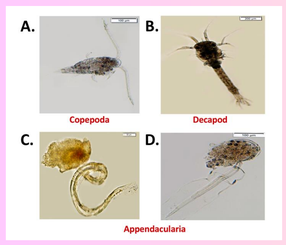

Fig. 3 Identified zooplankton species.

What did we study?

- the elemental concentrations in small-size (50 µm) and large-size (200 µm) fractions of net-tow particulate samples
- the influence of Qatari outdoor dust on the elemental composition of plankton
- The influence of distance from the coast on the spatial distribution of planktonic metal compositions

Why Qatari Dust is Important?

The composition of Qatari dust is carbonate rich, which is different from the composition of atmospheric dust from most other regions around the world, which is dominated by aluminosilicate (Al_2SiO_3) material.

Qatari outdoor dust is 4x depleted in Al, 5.3x enriched in Ca relative to UCC, reflecting Calcite ($CaCO_3$) and Dolomite ($CaMg(CO_3)_2$) rocks in the source areas on Qatar Peninsula.

What happen when the Dust Falls in to Seawater ?

We found that the $CaCO_3$ in Qatari dust does not dissolve upon entering seawater and Qatari dust is the major source of particles at most stations. *The big question is*:

Can biogenic and anthropogenic signals still be identified in the remaining concentrations?
If we use the following formula:

$$Me_{excess} = Me_{total} - Al_{total} \times Me/Al_{dust}$$

excess metal = biotic (biogenic origin)+ abiotic (authigenic & anthropogenic origin) So, the answer is *YES*
See the **Fig.6**.

RESULTS

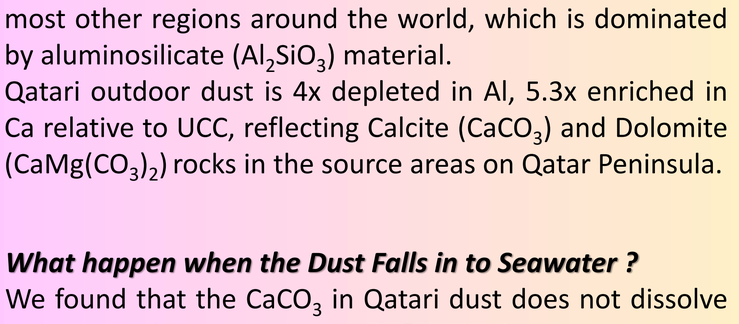

Fig. 6 Average excess metal composition (ppm) of plankton from 2012 and 2014 samples are given above. Small size fraction (phytoplankton, 50 µm) value for barium is not shown because lithogenic overcorrection resulted in a negative value (-3.71 ppm), which cannot be plotted on a logarithmic graph.

DISCUSSION

The biogenic portion was determined by subtracting the lithogenic portion from the total concentration. The lithogenic fraction was defined as the concentration of aluminum in the sample multiplied by a [Me]/Al ratio (Yigiterhan et al., 2011; **Fig.7**). Using average Qatari dust for these ratios generated a significant amount of overcorrection, so the correction was also made using average upper continental crust (UCC) (Yigiterhan, 2005; Yigiterhan et al., 2008). This method still caused some overcorrection for the lithogenic portion resulting in negative excess values for Ba, Mo, and Pb. Barium, Mo and Pb also showed the least consistency between measurements. For the other elements, a relative stoichiometry for plankton was determined as Fe > Cu≈Zn > As≈Cr≈Mn≈Ni ≈ V > Cd≈Co (**Fig.8**).

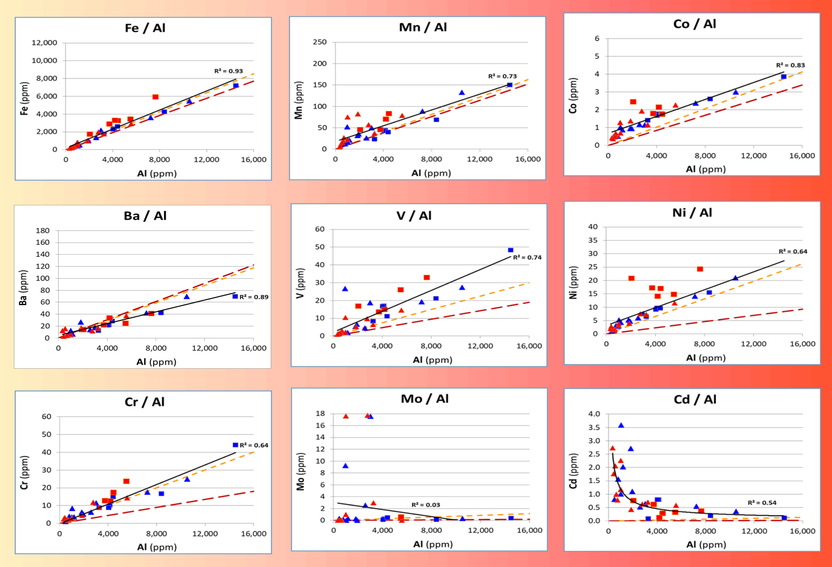

Fig. 7 The selected metal/Al ratios for the 2012 and 2014 net-tow samples. The dashed lines represent the Me/Al in average Qatari dust (Yigiterhan et al., 2018) and Upper Continental Crust (Rudnick and Gao, 2003) values. The solid line represent to best-fit line for cumulative values of plankton samples. All concentrations are given in ppm (Source: Yigiterhan et al., 2020).

1. some elements in net-tow samples could be mostly of lithogenic (dust) origin (E < 50% of the total); e.g. Al, Fe, Cr, Co, Mn, Ni, Pb, Li.
2. Some elements may be mostly of biogenic/anthropogenic origin (E > 80% of the total). These include As, Cd, Cu, Mo, Zn.

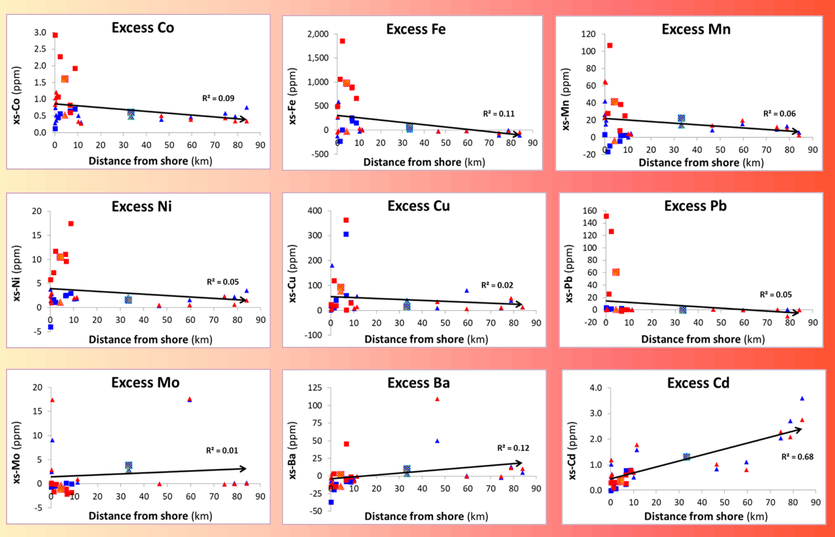

Fig. 8 The excess concentrations of selected trace elements were given above after lithogenic correction using average Qatari dust versus the shortest distance from the sampling site to land. The graphs show the combined data from four data sets: 50 µm and 200 µm mesh net tows for both 2012 and 2014 years (Source: Yigiterhan et al., 2020)

Regional Trends

The excess concentrations showed that 10 out of the 13 elements (As, Co, Cr, Cu, Fe, Mn, Ni, Pb, V, and Zn) had high concentrations in the 0–10 km range, indicative of a possible influence of coastal processes.
Co, Cu, Fe, Mn, Ni, Pb showed decreasing trend with distance from the shore. This variability could be due to differences in biology and/or non-biological (possibly anthropogenic) processes.

FUTURE WORK

The next step is to determine if leached or unleached Qatari dust should be used for the lithogenic correction. More data is needed for P, Ca, Ti, and leached dust. Phosphorus (P) has been used in many studies as a proxy for biogenic enrichments, via [Me]/P ratios. Adding Ca to our plankton analysis would be useful for understanding the biogeochemical cycling of this element and address the question about whether $CaCO_3$ in Qatari dust dissolves when entering seawater.

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