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Establishing the baseline assessment levels for monitoring coastal heavy metals in seawater using benthic foraminiferal shells

Lin Hoober[1], Danna Titelboim[2], Sigal Abramovich[3], Barak Herut[4], Nadya Teutsch[5], and Adi Torfstein[6]

[1]Ben-Gurion University of the Negev, Department of Earth and Environmental Sciences, Israel (hoober.lin@gmail.com)
[2]Department of Earth Sciences, University of Oxford, Oxford, UK (dannati@post.bgu.ac.il)
[3]Ben-Gurion University of the Negev, Department of Earth and Environmental Sciences, Israel (sigalabr@bgu.ac.il)
[4]Israel Oceanographic and Limnological Research, Haifa, Israel (barak@ocean.org.il)
[5]Geological Survey of Israel, Jerusalem, Israel (nadya.teutsch@gsi.gov.il)
[6]Interuniversity Institute for Marine Sciences in Eilat, Israel (adi.torf@mail.huji.ac.il)

A considerable growth of industrial facilities has been taking place along coastal environments over the past century. Some of these facilities have major economical and national importance, yet their operation can introduce a wide range of potentially harmful chemicals, such as heavy metals (HM), that might impact local ecosystems and human health. Efforts to monitor the presence of HM at low concentrations before damaging the ecosystem are contingent for protecting and conserving these coastal environments.

Many recent studies have shown the applicability of benthic foraminiferal shell chemistry for monitoring HM in coastal environments. Foraminiferal shells grow by sequential addition of chambers, thereby yielding a chronological record of HM concentrations in ambient seawater. This study introduces a new concept of defining a HM baseline assessment levels (BAL) in coastal seawater environments using foraminiferal shells. The BAL provide an absolute reference for documenting the temporal variation in HM that can be used to quantify the magnitude and duration following pollution events.

We demonstrate the potential of this approach by examining a pristine site in a nature reserve along the Mediterranean coast of Israel. Our previous investigation of this site in 2013-14 using foraminiferal single chamber LA-ICPMS created a large dataset that consisted of HM measurements in the last few chambers of two species *Lachlanella* and *P. calcariformata*. This database was used to establish the BAL metals/Ca ratios of Zn, Cu and Pb, three HM associated with anthropogenic sources.

The BAL of each metal was defined as the 5th lower percentile value from the LA-ICPMS dataset of each species. To encompass the natural variability of non-contaminant natural sources in the BAL, 2 STDEV (in RSD%) of the observed variation of the alkaline earth metal Sr/Ca ratios were added. The potential biological variations between specimens to the resulting ratios based on laboratory culturing experiments of the two species.

In February 2021, a significant oil spill event affected the entire Mediterranean coast of Israel, and included a considerable out wash of tar onto the shore. The event provided a unique opportunity to test the applicability of foraminiferal BAL by revisiting the previously studied site. Our strategy was to compare whole shell ICP-MS measurements of the two species collected shortly after the event and six months later, and compare them with the established BAL values. Our results revealed a significant increase (2-20 folds) in Zn/Ca, Cu/Ca, Pb/Ca ratios between 2013-14 and 2021. Among these, the increase in Pb/Ca is the most substantial and observed in both species. This implies a possible linkage between the oil spill event and the substantially elevated metals/Ca ratios measured by the foraminifera in 2021. Our study also demonstrates that bulk ICP-MS analyses will most likely yield similar ratios as those of average values of single chamber LA analyses of shells from the same location and period. This observation confirms that once BAL values are established, the analysis of bulk shell ICP-MS is effective for monitoring HM contamination of coastal environments.