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# Foraminiferal single chamber analyses of heavy metals as a tool for monitoring permanent and short term anthropogenic footprints

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## ABSTRACT

In order to establish environmentally sustainable industries there is a need for high-resolution temporal and spatial monitoring of heavy metal pollutants even at low concentrations before they become hazardous for local ecosystems.

Here we present single chamber records of Cu, Zn and Pb in shells of two benthic foraminifera species with different shell types from two shallow coastal stations in Israel: An area adjacent to an electrical power plant and desalination factory (Hadera) and an industrially free nature reserve (Nachsholim). Records of both foraminifera species show elevated metal concentrations in Hadera clearly identifying the footprint of the local industrial facilities. Moreover, short-term events of elevated Cu and Pb concentrations were detected by single chamber analyses. This study demonstrates the potential of using heavy metals anomalies in foraminiferal single chambers as a tool for detecting the industrial footprint of coastal facilities as well as short term events of elevated heavy metals.

## 1. Introduction

### 1.1. Heavy metals monitoring of marine environments

In recent years we have been witnessing a considerable growth of industrial facilities along coastal areas. Some of these have major economic importance, yet their operation can introduce a wide range of chemicals to the marine environment and severely impact the local ecosystems. Among some of these harmful chemicals are heavy metals that are introduced to coastal environments and may accumulate through the trophic chain leading to concentrations much higher than those in the ambient water (Zhou et al., 2008; Zuykov et al., 2013). Many of these metals could be toxic or seriously hazardous for many biological systems. These threats make it imperative to develop reliable proxies for detecting metals contamination in marine areas, before they are becoming a serious threat to local marine ecosystems.

Monitoring of heavy metals in the marine environment is traditionally done by combining analyses of water, sediments and tissues of the local biota. Each of these monitoring approaches has its pros and cons: Water analysis provides a direct measurement of metal pollutants, yet it may overlook specific events of elevated concentrations since it is limited by the frequency and spatial distribution of sampling. Analysis of sediment reflects time-averaged concentrations that are governed by many environmental parameters such as sedimentation rate, grain size and amounts of particulate organic matter (Phillips, 1977). Whilst both methods do not indicate the influence and possible toxicity (i.e. biological response) of the pollutants on the ecosystems (Zhou et al., 2008), indirect criteria is applied in certain monitoring programs (Buchman, 2008; Long et al., 1995). Analysis of organic tissues has the advantage of recording the presence of metals that are biologically available, as well as their effect and toxicity on the organisms (Zhou et al., 2008). However, different organisms exposed to the same conditions will display great variability in metal concentrations (i.e. vital effect) as well as different biological responses. Such differences are also expected among specimens of the same species that vary in size, gender, food availability, and in respect to other physiological parameters (Phillips, 1977). Moreover, the use of organic tissue only provides a snapshot of a specific time and the need for a long-term recording (i.e. bio-archive) is

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not resolved (Steinhardt et al., 2016). To overcome these disadvantages the use of geochemistry of shells was suggested as a bio-archive to document chemical changes in the organism's habitat (see recent discussion in Steinhardt et al., 2016, and references therein).

This approach, known as sclerochronology, has been already applied for environmental monitoring mostly based on analyses of calcareous shells of bivalves that benefit from the temporal context given by periodic banding (Steinhardt et al., 2016). Geochemical analyses of shells bears several advantages compared with that of organic tissues: 1. It is considerably less sensitive to vital effect and thus expected to provide similar values of metal concentrations among specimens inhabiting the same conditions (Bourgoin, 1990; Lingard et al., 1992). 2. It provides continuous records of metal concentrations over the whole period of shell formation (bio-archive). 3. The shells are preserved after the organisms death and could be easily collected from the field and maintained at low cost in the lab (Protasowicki et al., 2008). Despite these advantages, the approach of using calcareous shells has not yet received recognition in the regulatory sectors and has not been officially implemented in marine monitoring programs.

### *1.2. Foraminifera as geochemical proxies*

Foraminifera are highly diverse and abundant marine unicellular organisms, found in all marine environments (Sen Gupta, 2003). They are widely used in the community level as bio indicators of the environmental status of marine habitats because of their great abundance, fast turnover rates, high degree of specialization and the preservation of their shells in the sediment giving a reference to pre pollution conditions (Alve et al., 2016; Schönfeld et al., 2012). The geochemical properties of foraminiferal shells provide the foundation for the development of many paleoceanographic proxies (Katz et al., 2010). Under the same logic, the use of foraminifera shells geochemistry for monitoring marine pollution presents a new approach (de Nooijer et al., 2007; Frontalini et al., 2009; Herut et al., 2007; Munsel et al., 2010; Nardelli et al., 2013, 2016; van Dijk et al., 2017a, 2017b; Youssef, 2015). This approach relies on the known mechanism in which during precipitation of foraminiferal shells, different chemicals are incorporated within the calcite lattice or existed as interstitial elements. The general notion is that the concentrations of metals in foraminiferal shells are depended on their concentration within seawater (Delaney and Boyle, 1986; Elderfield et al., 1996; Erez, 2003; Russell et al., 1994).

Foraminifera have many advantages over other calcareous organisms in biomonitoring of heavy metal pollution:

- Their abundance is an order of magnitude higher than that of macrofauna (Schönfeld et al., 2012) reaching between 100 and 1000 individuals > 63 μm per 100 $cm^2$ surface area (Murray, 2006). This makes sampling easier as collection of smaller samples contain many specimens that gives a reliable representation of the environment. This is especially important in deeper water environment where macrofauna is scarce (Schönfeld et al., 2012).
- They are considered to be the most diverse group of calcareous organisms alive today (Sen Gupta, 2003) and the various species occupy different niches at the seafloor. Their coastal communities typically consist of 20–50 species per 300 individuals (Schönfeld et al., 2012). This is extremely valuable especially in areas such as the Eastern Mediterranean where benthic foraminifera are the most abundant and diverse component of the coastal ecosystems (Basso and Spezzaferri, 2000; de Rijk et al., 2000, 1999; de Stigter et al., 1998; Herut et al., 2005; Hyams-Kaphzan et al., 2008; Jorissen, 1987).
- They are easy to culture in the laboratory under variable environmental conditions. This is particularly important for the proxy calibrations of each metal. Specifically, it is essential to quantify incorporation of metals within shells that were cultured at different metal concentrations of seawater.
- They calcify their carbonate shell incrementally, so that each chamber documents the metal concentration of the water at the specific time of the chamber formation. This process of shell building combined with their high abundance makes their shells ideal recorders for continuous monitoring of metal concentrations in seawater

In this study, we demonstrate the potential of using foraminiferal shells as an effective tool for monitoring heavy metals industrial footprint based on geochemical investigation of their shells from shallow coastal areas along the Israeli shoreline which considered as relatively clean of significant industrial pollution.

## 2. Methods

This study is based on foraminiferal specimens collected monthly during 2013–2014 off a thermohaline polluted site (Hadera station) at the northern coast of Israel near the city of Hadera (32.4614°N, 34.8825°E) (Titelboim et al., 2017, 2016). This area displays a permanent heat anomaly, created by the release of cooling water from the electrical power plant “Orot Rabin”. Since 2010, a desalination plant is operated adjacent to the power plant, discharging brines together with the power plant cooling water. This creates a disturbed area, with warmer and slightly saltier seawater, extending about 1.5 km to the south and 1 km to the west. Material used in this study also includes specimens from the same monthly sampling campaigns of a Nature reserve station at Nachsholim, located about 18 km north of Hadera (32.6231, 34.9195) and serves as a reference of an industrially free, undisturbed station. According to annual monitoring reports of the national electrical company of Israel, the Hadera station is not significantly influenced in respect to heavy metals (e.g. Glazer, 2010).

Shells of living specimens of two common species *Lachlanella* sp. and *Pararotalia calcariformata* that are constantly present in both stations (Titelboim et al., 2016) were collected and analyzed (Fig. 1). All samples used in this study were collected from ~0.5 m water depth. Standard Rose Bengal staining technique was used to mark the foraminiferal cytoplasm in order to identify specimens that were living during collection (Schönfeld et al., 2012). Only specimens that were alive during sampling (stained) were analyzed in this study.

Metal concentrations were examined in 80 specimens of *P. calcariformata* and 120 specimens *Lachlanella* using Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICPMS). All analyses were conducted at the Department of Earth Sciences at the

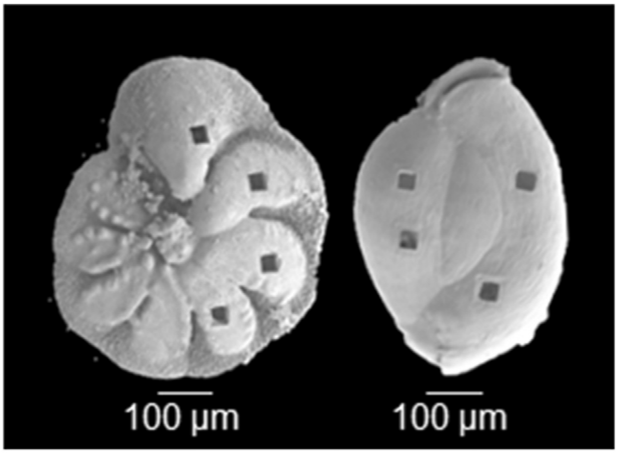

**Fig. 1.** SEM micrographs of *P. calcariformata* (left) and *Lachlanella* sp. (right) with laser-drilled spots on the shells where metal concentrations were measured. Note, the multiple visible chambers of the last whorl in *P. calcariformata* compared to *Lachlanella*. The former permits sequence analyses of different calcification episodes.