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Trace metal bioaccumulation in Israeli Mediterranean coastal marine mollusks

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A B S T R A C T

During the period 1995–2012, trace metal levels were monitored on an annual basis in marine mollusks (*Donax trunculus*, *Mactra stultorum*, *Patella sp.* and *Cellana rota*) along the Mediterranean coast of Israel in polluted and unpolluted areas. In general, these records show that: 1) Mercury and cadmium concentrations declined precipitously in Haifa Bay specimens in response to pollution load reductions; 2) Nonetheless, Haifa Bay specimens still show higher trace metal concentrations compared to specimens from other sites along the Israeli shore; 3) Hot spots of pollution were identified along the Haifa Bay shore, demonstrating the sensitivity of these specimens to events of contaminated sediments re-suspension. These events were likely caused by winter flooding in Qishon and Na'aman rivers and dredging operations in Haifa Port; 4) Trace metal concentrations in *Patella* sampled north of Haifa Bay are higher than those measured in specimens sampled south of Haifa Bay, suggesting that the impact range is greater than previously considered and pollution loading in Haifa Bay could be projected northward via general transport processes; 5) Cadmium levels in *Patella* sampled along the coast displayed an increasing trend over time that could hypothetically be associated with ocean acidification and warming trends; 6) Excess of wet weight to shell length ratio in *Patella* specimens from Haifa Bay that exhibited higher trace metal accumulation, was lower than expected, possibly because of environmental stress, e.g. the energetic cost of detoxification. These findings provide supporting evidence for the importance and utility of trace metal bioaccumulation monitoring and sediment rehabilitation in polluted estuaries and other coastal regions as well as providing a basis for closer regulation and inspection of dredging operations.

1. Introduction

Trace metal accumulation in marine organisms has been shown to be a useful bio-indicator for the quality of seawater and sediments (e.g. Phillips, 1977; Rainbow, 1995; Phillips and Rainbow, 1998). Therefore, many monitoring programs have adopted this tool in order to follow long term trends in water and sediment quality including the national monitoring program of the Israeli Mediterranean coast (e.g. Herut et al. 1999; Deudero et al. 2007). The main objectives of this monitoring approach are to follow long term trends, identification of pollution hotspots and to assess the effectiveness of regulatory measures taken to improve water and sediment quality. However, there are relatively few reports in the scientific literature that show such long term monitoring records and responses to mitigation measures (e.g. Deudero et al. 2007; Kljaković-Gašpić et al. 2007; Kimbrough et al. 2008; Besada et al. 2014). Clearly, such records would provide a strong incentive or justification to continue these measurements considering their relatively high cost and labor intensity.

In Israel, trace metal levels in the soft tissue of marine organisms have been systematically monitored in Haifa Bay since 1980 (Hornung and Oren, 1981; Hornung et al., 1984; Hornung, 1989; Hornung et al. 1989; Herut et al., 1996; Fishelson et al. 1996, 1999; Herut et al. 1999). Measurements from the mid-1970s and early 1980s in Haifa Bay provided a strong baseline as well as alarming evidence showing relatively high levels of trace metal accumulation in commercial fish and benthic invertebrates (Hornung and Oren, 1981; Hornung et al., 1984; Hornung, 1989; Hornung et al. 1989; Fishelson et al. 1996, 1999; Herut et al., 1996; Herut et al. 1999). This evidence helped support the enforcement of government regulations on polluting industries in Haifa Bay and other sites along the Mediterranean coast of Israel

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resulting in almost complete reduction of trace metal and other pollutant loads.

Currently, trace metal loads into Haifa Bay are significantly lower compared to the early 2000s. In 2004, mercury (henceforth Hg) loads to the north of Haifa Bay from the Frutarom chlor-alkali plant ceased entirely. In 1999, the fertilizer producing plant situated above the Qishon River started using phosphate rock imported from the Kola Peninsula instead of the local Negev rock (Eshel, 2001). The Kola phosphate rock has a significantly lower content of cadmium (henceforth Cd) and Zinc (henceforth Zn) by a mean factor of 15 (Kharikov and Smetana, 2000). Together with implementation of effluent purification measures, Cd, Zn and Hg loads to the Qishon River decreased by 95–98% during the period 1999–2002 (Eshel, 2001).

South of Haifa Bay, nutrient loads to the Mediterranean are facilitated mostly by the discharge of treated sewage effluents into streams and rivers that flow into the sea. The total combined estimated loads of nitrogen and phosphorous from streams along the coast are greater than the total nutrient loads into Haifa Bay via the Qishon and Naaman Rivers by a factor of 3–4 (Herut et al., 2000). In contrast, the total combined trace metal load from the coastal streams is smaller by two orders of magnitude than the combined load from the Qishon and Naaman Rivers to Haifa Bay (Herut et al., 2000). Thus, it is anticipated that trace metal accumulation in specimens sampled along the coast will be lower than specimens sampled in Haifa Bay and should reflect relatively unpolluted conditions.

In this study, we present the findings of our long term bioaccumulation monitoring program using the most abundant species of bi-valves and gastropods found in Haifa Bay and along the Mediterranean coast of Israel. Other bivalves that are commonly used for this type of monitoring, e.g. *Mytilus edulis*, are not found along the Israeli coast. In this study we use the monitoring of trace metal levels in mollusks to identify long-term trends, environmental impacts of trace metal pollution, and the effectiveness of mitigation measures.

2. Material and methods

2.1. Biota collection and preparation for analysis

Specimens of the bivalves *Mactra stultorum* and *Donax trunculus*, and the gastropods *Pattela* sp and *Cellana rota* (hereafter *Mactra*, *Donax*, *Patella* and *Cellana*) were collected at several sites along the Israeli shoreline of the Mediterranean Sea (Fig. 1) once annually during the period 1995–2012. The systematic collection and monitoring of trace metal levels in *Mactra* and *Donax* specimens at all sites appearing in Fig. 1 started in 1995. Specimens of *Patella* were initially collected only at the Haifa Bay stations and MM during the period 1996–1999, after which they were collected at all sites indicated in Fig. 1. Monitoring of trace metal levels in *Cellana* specimens at all stations indicated in Fig. 1 started in 2002. Samples of *Patella* and *Cellana* were collected during March of each year from beach rocks and *Mactra* was sampled by SCUBA diving, during July of each year. Samples of *Donax* were collected along the sandy shoreline at a depth of 0.5–1 m using a rake. All specimens were kept frozen at −20 °C until analysis. Prior to analysis, the specimens were thawed, rinsed in distilled water, and the long diameter of their shells was measured. After this, the soft tissue of each specimen was removed completely from the shell and weighed (wet weight) after taking care to remove particles adhering to the soft tissue. The whole soft tissue of the mollusks was taken for analysis. Because of analytical limitations, low weight specimens (<250 mg wet wt.) of similar weight were pooled into composite samples and larger specimens were analyzed individually. The samples were then lyophilized (about 10–20% dry matter depending on the species) and digested with concentrated nitric acid in Uniseal, Teflon-lined, high pressure decomposition vessels as described by Hornung et al. (1989). In 2012 we began to digest samples in a Microwave oven (MarsX CEM).

2.2. Soft tissue trace metal analysis

Before 1998, the solutions were analyzed for Cd, copper (henceforth Cu) and Zn using a Perkin–Elmer 1100B flame atomic absorption spectrophotometer, and afterwards with a Varian AA220 flame atomic absorption spectrophotometer. After 2012, samples were analyzed with Agilent flame spectrophotometer 280FS AA. Following sample digestion for Hg analysis, 2% $SnCl_2$ in a solution of 5% HCl were added in order to reduce Hg^{+2} to Hg^0, which was then measured with a cold vapor atomic absorption spectrophotometer (until 2003 with a Coleman Mercury analyzer MAS-50B and since with a Merlin millennium System, PS Analytical equipped with a fluorescence detector). The method detection limit (MDL) in soft tissue samples for Hg was 0.005 μg/g wet wt. until 2003 and since 0.000035 μg/g wet wt. Until 1998 the MDL for Cd, Cu and Zn was 0.03, 0.03 and 0.07 μg/g wet wt., respectively, and since 0.05 μg/g wet wt. See Table SOM1 in the supplementary online material for the LODs and LOQs (Level of Quantitation) for the different atomic absorption instruments used during the monitoring period. Validations of sample preparations and all measurements with the different instruments were done following Eurachem (1998) and EPA (2005), and were also accredited by the Israeli Laboratory Accreditation Authority (ISRAC).

Quality control and quality assurance of trace metal determinations in the biota samples were performed with certified standard materials from the national Research council of Canada (NRCC) Dorm2, Dorm3 and Dorm4 and from the National Institute of Standards and Technology (NIST) Oyster 1566b and NIST-2976. The standards were digested and analyzed in the same manner as the samples, in each analytical run, and the results were usually within ±5% and not more than ±15% of the certified value according to the laboratory procedure. In addition, the IOLR laboratory participates regularly in international inter-comparison exercises (MEDPOL and QUASIMEME) with outstanding results. See Table SOM1 in the supplementary online material for detailed information on certified standard materials.

2.3. Statistical analysis

In the following description of the results we divide the data sets for *Donax, Mactra* and *Patella* into two periods 1995–2000 and 2001–2012 in order to highlight the changes associated with the significant load reductions that occurred in Haifa towards the end of the first period. Statistical analysis was conducted with XLSTAT 2013 software package. All mean values are reported with ±1 standard deviation of the sampling population values. Significant differences between sampling population values were determined using the student's t-test and one way ANOVA with 95% confidence intervals, i.e. $p < 0.05$ was considered significant. Values below the LOQ were not included in these analyses, but their percentage of the total number of observations is reported in the Supplementary online materials tables (Tables SOM2–4).

3. Results

3.1. Size and mass distributions of mollusks samples

Because of the difficulty of accurately differentiating between *Patella* and *Cellana* specimens at the sampling sites, we took a