# Accumulation of Metals in the Eastern Mediterranean Sea, Israel: Implications for the Marine Ecosystem and Human Health

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A THESIS SUBMITTED FOR THE DEGREE

"DOCTOR OF PHILOSOPHY"

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University of Haifa

The Leon H. Charney School of Marine Sciences

Department of Marine Biology

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*For the Ocean*

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Debra Ramon

Abstract

The accumulation of metals such as arsenic, mercury, cadmium, and lead in marine organisms has posed longstanding environmental and public health concerns due to their potential ecological and health impacts. Metals are released into the marine system either from natural or anthropogenic activity are accumulated by marine organisms from their surroundings depending on environmental conditions as well as species-specific accumulation dynamics. Particularly, seafood acts as a vector transferring metals from the marine environment, ultimately reaching the human population. With seafood constituting an important source of protein and providing certain health benefits to humans, metal associated health risks emphasize the significance of monitoring seafood products reaching the market for human consumption in order to reduce exposure. Despite the significant implications, there has been limited research on metal accumulation in Israeli coastal waters and minimal assessment of human exposure to metals in locally caught seafood. Therefore, this study aims to provide baseline information of the distribution of mercury, cadmium, lead, and arsenic within locally available marine biota, including edible seafood and ecological and economical important fish species, and investigate the potential driving factors for their accumulation. To do this, two extensive surveys were conducted, one focusing on commonly consumed seafood and the other on ecologically and economically important fish species. The results showed that in both surveys, arsenic had the highest prevalence, followed by mercury, lead, and cadmium. In Israel, arsenic concentrations are amongst the highest reported in the literature, possibly due to the unique environmental conditions of the Eastern Mediterranean Sea, characterized by high salinity and low phosphate, encouraging arsenic uptake by marine organisms. Mercury behavior was relatively expected with higher levels in fish in sediments or in adults, with interestingly higher levels in a marine protected area compared to pollution hotspots. The prevalence of lead and cadmium was relatively low, likely indicating the effectiveness of mitigation efforts in Israel. Species-specific life history traits, such as habitat and life stage, were identified as significant factors influencing metal accumulation in marine organisms. While comparing individual parameters provided insight to accumulation driving factors, accounting for all parameters simultaneously was conducted by developing a general additive mixed effect

(GAM) model for mercury and arsenic accumulation. Marine protected areas. The GAM model shows elevated mercury accumulation within the MPA as a factor of fish maturity. The study also highlighted the role of locally caught seafood as a pathway for metal exposure to the local population, with higher susceptibility among certain communities including fishing communities, fishermen and their families, and inhabitants of local markets (Jaffa, Kishon, Acre). This study provides a comprehensive assessment, offering large-scale observations and identifying areas for further research. The distinct behaviors of metals and the variability among species highlight the need for deeper investigations to better understand local metal dynamics in marine organisms and their environment. Ultimately, the findings underscore the complexities of metal impacts on Israel's marine ecosystems, guiding future research.

# Thesis Structure

The thesis will explore the impact of metal pollution on the marine environment of the Eastern Mediterranean Sea in Israel through one book chapter and two research articles.

Chapter 1: "Accumulation of Lead, Mercury and Cadmium in Coastal Sediments in the Eastern Mediterranean Sea"

This chapter, presented as a published book chapter, aims to provide regional context for metal pollution in the Eastern Mediterranean Sea. It addresses the knowledge gap in regional information of metal accumulation in sediments, which was chosen as a proxy for ecotoxicological potential in marine organisms due to the abundance of sediment-oriented studies. The chapter breaks down the eastern basin into smaller segments with unifying characteristics and explores individual countries by providing descriptions of the state of the marine environment and anthropogenic activities influencing local pollution levels. An overview of sediment metal research per country is provided, integrating scientific published material and gray literature to offer a comprehensive assessment for many countries in the region.

Chapter 2: "A survey of arsenic, mercury, cadmium, and lead residues in seafood (fish, crustaceans, and cephalopods) from the south-eastern Mediterranean Sea"

This chapter, presented as a published research article, focuses on the accumulation of metals in locally caught seafood in Israel. It emphasizes human health by comparing metal levels in different fish species and highlights exceptionally high arsenic concentrations not previously reported in the literature. The study provides a first-time assessment of metal accumulation in seafood from the southeastern Mediterranean Sea, illustrating the complexities of metal pollution in the marine environment and establishing a baseline for future research.

Chapter 3: “Metal accumulation in marine fish of the Eastern Mediterranean Sea: behavior and driving factors”

This chapter, presented as a research article ready for submission, builds upon the findings of Chapter 2 by focusing on the accumulation of metals in economically and ecologically important fish species throughout Israeli waters. It assesses species-specific accumulation and contamination levels in comparison to standards, providing deeper ecological context by evaluating differences in accumulation behavior between fish from a marine protected area, a relatively pristine area, and highly industrialized area. The study sheds light on the driving force for accumulation and the impacts of high industrial areas and marine protected areas on metal accumulation in fish, offering valuable insights for biodiversity conservation efforts.

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# Introduction

## Marine Ecosystem Services and Anthropogenic Impacts

The Ocean serves as a vast interconnected body of water, playing a pivotal role in sustaining life on Earth through essential biological, chemical, and physical processes. Among its numerous responsibilities, the Ocean is crucial for climate regulation, biodiversity support, and oxygen production. To effectively regulate these critical global processes, which are essential for ecological balance and human well-being, it is a priority to maintain healthy marine ecosystems. The health of marine ecosystems directly influences their ability to provide and ensure the quality of ecosystem services, defined as the array of benefits humans derive from healthy ecosystems (Barbier, 2017). These services encompass four key categories: provisioning (products obtained from marine ecosystems), regulating (services related to the marine environment's role in regulating natural processes that affect environmental factors), supporting (services that form the basis for other ecosystem services), and cultural (non-material services contributing to human well-being) (Future Ocean et al., 2015). Therefore, the health of human populations is intricately linked to the health of marine ecosystems.

Until the 1950s, there was a prevailing belief that the Ocean was resistant to human influence and was considered an expansive dumping ground capable of absorbing countless anthropogenic inputs, including brine, pollutants, and heat, without consequence. This mindset, often referred to as 'pollution dilution,' suggested that inputs were endless and had no discernible thresholds. However, it is now understood that the Ocean does respond to human activities and that there are critical tipping points. Once these tipping points are exceeded, returning to previous conditions becomes impossible, leading to the establishment of new steady states. Presently, marine environments are experiencing rapid changes across various components due to the cumulative impact of multiple stressors including, climate change, overfishing, exploitation of resources, habitat degradation, and pollution (Future Ocean et al., 2010). Specifically, pollution can manifest in various forms, and can broadly be categorized into physical pollution, chemical pollution, biological pollution, nutrient pollution, noise pollution, and light pollution. From these pollutants, chemical pollutants are further sub-categorized to pharmaceuticals, agriculture chemicals, antifoulants, disinfectants, hydrocarbons, radioactive substances, metals, and xenobioticss. When addressing chemical pollutants in the environment, key concerns revolve around their environmental retention time, bioaccumulation potential, and their toxic levels - both chronic and acute - for both biota and humans (Future Ocean et al., 2010). These concerns are particularly true for legacy contaminants such as metals, which are the focus of this thesis.

## Metal Pollution

Metals are referred to as legacy contaminants, which are pollutants that exhibit high persistence in the environment even after being released from industrial sources. Although naturally occurring in the Earth's crust, the introduction of metals into the environment through anthropogenic activities dates back to ancient times with the advent of mining and metalworking (Nriagu, 1996). However, it was the onset of the Industrial Revolution that intensified the release of metals into the water and atmosphere as industrialization expanded (Nriagu, 1996). The primary pathways through which metals enter the environment include atmospheric deposition, water runoff via storms and rivers, and discharge from industrial and domestic sources (Solan & Whitely, 2016). Unlike many chemical compounds that degrade over time, metals in their elemental form remain stable, perpetuating their presence in the environment and posing a continuous environmental threat. Conversely, chemical transformations of these metals within the environment can enhance their bioavailability and toxicity, facilitating their transfer throughout ecosystems.

Of all the metals, four are particularly concerning due to their significant impacts on human health and include mercury, arsenic, cadmium, and lead. These metals have been designated by the World Health Organization (WHO) as the WHO 10 Chemicals of Major Public Health Concern. Arsenic is classified as a carcinogen, and chronic exposure to high levels can increase the risk of skin cancer, as well as negatively affect pregnancy outcomes, child health, and development (World Health Organization, 2019). Cadmium, also a recognized carcinogen, can result in kidney, bone, and lung diseases following chronic exposure (World Health Organization, 2010a). Mercury, a neurotoxin, has the potential to disrupt central nervous system development, with high exposure leading to kidney disease, respiratory failure, and even death (World Health Organization, 2007). Lead is identified by the WHO as a substance of major public health concern, with significant impacts on the human body (World Health Organization, 2010). High exposure of lead in pregnant women can result in fetal and birth complications, while exposure in young children can affect the development of their nervous system and brain.

Throughout history, there have been numerous instances of citizen exposure to metals through food and water sources, resulting in catastrophic outcomes that have severely impacted entire communities. One of the most infamous incidents occurred in 1956 in the Japanese town of Minamata, where residents were exposed to high concentrations of methylmercury due to the Chisso Co. Ltd chemical plant dumping untreated waste containing mercury directly into Minamata Bay (Harada, 1995). The released mercury proceeded to accumulate in seafood caught for local consumption, leading to a variety of symptoms among citizens, including numbness, difficulty walking, speech impairments, convulsions, and loss of motor control (Harada, 1995). Additionally, residents observed unusual deaths among marine organisms, including fish, shellfish, and birds, while local cats displayed neurological symptoms and many perished (Harada, 1995). The long-term impacts of the disease persisted for years, with fetal exposure through contaminated mothers resulting in congenital cerebral palsy in born children, and chronic neurological disorders continuing to affect the local population for subsequent decades (Harada, 1995). Similarly in Japan, beginning in the early 1900s, cadmium exposure resulted in many citizens falling ill with what was called Itai-Itai disease (‘it-hurts it-hurts disease), medically known as osteomalacia or the softening of bones due to renal tubular dysfunction (Yoshida et al., 1999). The major polluter in this case was the Mitsui Mining and Smelting Co., which was releasing cadmium into the air and water through the disposal of cadmium-loaded tailing slurry from the Kamioka mine into the Jinzu River, ultimately contaminating surrounding rice paddy fields (Yoshida et al., 1999). Consequently, civilians were exposed to cadmium through the rice grown in the region (Yoshida et al., 1999). These and other similar incidents worldwide have raised global awareness of the potential dangers of environmental metal contamination and its profound impact on human health.

When evaluating the impacts of pollutants on the marine environment, there is often a disproportionate emphasis on human health compared to the state of the marine ecosystem, despite the inseparable connection between the two. Extensive standards exist for acceptable levels of metals in food products for human consumption, including seafood, at both on national (Israel Ministry of Health Public Health Services – Food Control Services Regulation 01022007) and international level (Commission of the European Communities Commission Regulation EC No 78/2005) (for human health standards, refer to Chapter 2 – Supplement Table 2: Summary of standards). However, equivalent environmental standards are lacking as well as toxicity thresholds for different marine species in their various life stages. In the literature, considerable attention is devoted to assessing the human health aspect by comparing acceptable levels to the established standards. While standards provide a common comparison point between studies, they contribute little to the environmental aspects of metal pollution. Even after decades of research, our understanding of marine biogeochemical cycle of metals remains limited. Though certain metals such as mercury have been well researched with their biogeochemical cycle largely established, other metals like arsenic lack a well-understood biogeochemical cycle. Furthermore, our understanding of how exposure to pollutants impacts wildlife, from plankton to large top predators, is inadequate, particularly in cases of chronic contamination.

As metals persist in the environment, they undergo constant redistribution through physical and chemical processes. Physical processes like transportation and chemical processes, such as speciation, play pivotal roles in this redistribution. Marine sediments exhibit a higher affinity for metals compared to the water fraction, serving as both a sink for pollutants and a substrate that drives chemical speciation. Within sediments, metals undergo transformations as they speciate into various chemical configurations distinct from their original input species. Speciation is driven by a combination of biogeochemical parameters and biological activity, with sediments serving as reaction centers due to factors such as higher microbial concentrations, redox conditions, pH changes, organic carbon content, and more (Solan & Whitely, 2016). Often, these speciated forms are more biologically available, leading to increased toxicity in marine organisms (Solan & Whiteley, 2016). Consequently, processes that disturb sediments and mix them into the water column, such as dredging or high intensity storms, can serve as secondary pollution sources, potentially more toxic than the primary input itself.

Once in the environment, biologically available chemical species interact with marine organisms through processes such as bioaccumulation, bioconcentration, and biomagnification. While these concepts share similarities, they differ in their accumulation mechanisms. Bioaccumulation involves the gradual accumulation of pollutants within an organism over time, sourced from both biotic and abiotic origins (Gray, 2002). Bioconcentration, on the other hand, refers to the accumulation of a compound from the abiotic environment, resulting in higher concentrations within the organism (Gray, 2002). Biomagnification occurs as pollutants traverse through a trophic system, accumulating in higher trophic levels and concentrating within the organisms occupying those levels (Gray, 2002). Textbook descriptions often depict metal accumulation as increasing with organism size over time (age) and through dietary intake based on trophic position. However, it is crucial to recognize that while metals share categorical similarities, their behaviors vary significantly from one another. Among the four metals addressed in this thesis, only mercury conforms to the textbook mechanisms of bioaccumulation and biomagnification. Therefore, biomagnification may be considered an exception to the rule, with other metals exhibiting different behaviors (Gray, 2002) and caution should be exercised when evaluating numerous metals together.

While detailed discussions of the specific biogeochemical cycles for these metals follow below, the overarching narrative remains consistent for all metals in the environment. Following their release, metals can integrate into various environmental fractions, including water, sediments, and biota. The biologically active chemical speciation of each metal is heavily influenced by environmental abiotic factors. Exposure to these metals can manifest as chronic, characterized by sublethal levels over time leading to long-term risks, or acute, involving sudden exposure to high concentrations resulting in immediate health risks and potential mortality.

**Mercury**

Mercury is released into the Earth's atmosphere and water bodies through both natural phenomena and human activities. Natural sources include geological processes, biomass burning, weathering, and degassing, while anthropogenic sources encompass various industrial processes such as oil refining, smelting, chlor-alkali production, cement manufacturing, petrochemical industries, mining activities, coal combustion, agricultural fertilizer use, and waste incineration (Chen et al., 2012). Following release, it is mobilized through the atmospheric and aquatic fraction, where it can then reach the marine environment. Marine deposition is dominated by atmospheric transport responsible for 90% of the mercury that enters its waters, compared to 10% from rivers (Chen et al., 2012).

Once mercury enters the marine water fraction, it occurs initially as inorganic mercury and undergoes transformation facilitated by microorganisms and organic particles to form methylmercury, its more toxic species. Methylmercury can be degraded back into its inorganic form, incorporated into marine biota, or sink into benthic sediments. Due to its hydrophobic properties, mercury exhibits a high affinity for sediments, acting as a significant sink and a reaction center for chemical and biological transformations into methylmercury. This methylmercury is readily accumulated by marine organisms, particularly fish, where it bioaccumulates and biomagnifies through the marine food web, resulting in higher concentrations in organisms at higher trophic levels.

Impacts on fish health are well documented and include negative impacts on physiological, histological, biochemical, enzymatical, and genetic levels (Morcillo et al., 2017). Exposure experiments on zebrafish and impacts on reproductivity showed that concentrations at ppb levels in wet weight in reproductive organs was enough to have negative impacts on early life stages (Xie et al., 2020). Human exposure and impacts of mercury are well documented in the scientific literature, with one of the largest human exposure events in Minamata, Japan (described in the previous section). Following on the events in Minamata, fish consumption continues to act as the major pathway of methylmercury into the human population globally (Sundeland, 2007). The associated health risks on humans have also been well studied, and include neurological effects, impaired fetal and infant growth, and cardiovascular disease (summarized in Gray 2002). Women of childbearing age, pregnant women, breastfeeding women, and young children are particularly vulnerable to methylmercury exposure due to its potential neurological impacts and adverse effects on child development (Chen et al., 2012). Acceptable concentrations in fishery products and muscle for both the European Commission and Israeli Health Standards are set at 0.5 ppm (Chapter 2 – Supplement Table 2: Summary of standards).

Though the release of mercury has dramatically decreased with improvements in mitigation, especially following the signing of the Minamata convention, it is still considered a global pollutant and source shifts in mercury reaching the marine environment will require a global approach. As atmospheric concentrations change, a relatively quick reduction in concentrations is expected to be observed in the open Ocean while the coastal areas are expected to have a delayed response. However, concerns surrounding the impacts of climate change will exacerbate the secondary input of mercury in the environment.

**Arsenic**

Arsenic is an earth crust element and naturally released through the weathering of rocks, sediments, hydrothermal activities, sulfide minerals, forest fires, and windblown dust (Flora, 2015). Alternatively, it can be released through anthropogenic activity including the burning of coal, mining and smelting of sulfide ore, runoff from tailings, arsenical pesticides/herbicides, semiconductor production, lead acid batteries, glass industry, copper refining, and wood preservation (Flora, 2015). Initially, arsenic is mobilized through the air and water fraction, where it then enters the marine environment and undergoes speciation depending on environmental conditions. As with many metals, the speciation is critical for its movement and toxicity, with inorganic species being more toxic than their organic counterparts. Arsenic is biochemically similar to phosphorus, resulting in its biological uptake (Anninou & Cave, 2009; Wurl et al., 2013). Under low phosphate conditions, arsenic can act as a reciprocal to phosphate and thus is incorporated through the phosphate transport system by photosynthetic organisms. Inorganic arsenic incorporated by microorganisms undergoes speciation producing arsenosugars, a mobile organic chemical species which is highly soluble in plant membranes and fats (Azizur Rahman et al., 2012). These arsenosugars can either be removed in a proposed a detox strategy (Kumari et al., 2017) or metabolized through the food chain and accumulated as the arsenobetaine in the marine food chain. Arsenobetaine, also known as fish arsenic, is the dominant chemical speciation within marine organisms, functioning as an osmolyte and not considered toxic. Biota are then able to excrete aresnosugars and it reaches sediment deposition, there marine bacteria degrade the sugars into organic/inorganic arsenic and is then released back into the water column to continue the cycle.

Based on current research, it is unclear what the bioaccumulation and transfer patterns throughout the food web are, as there are many inconsistencies between studies (Azizur Rahman et al., 2012). Some research has supported that arsenic accumulation in marine organisms is not biomagnified as a factor of increasing trophic position or feeding mode, with Rahman et al., 2012 showing that arsenic decreases with trophic level, and appears to be related to their diet (Azizur Rahman et al., 2012). Kirby et al. 2002 showed the accumulation differences based on the following feeding styles; detritivores >> primary producers > herbivores > omnivores, with omnivores showing a large variability within the functional group. This variability may be due to the a combination of the species-specific assimilation capacity and retention times within marine biota. Additionally, environmental factors may influence the accumulation, as studies have shown the connection between arsenic and salinity (summarized in Byeon et al., 2021). The impacts of arsenic on fish have been described to impact the following pathways; hematological, biochemical, and ionoregulatory pathways (Kumari et al., 2017). Negative health outcomes in aquatic organism including poisoning, reduced reproduction and growth, immune disorders, cell and tissue damage, and cell death (Byeon et al., 2021). Lethal concentration of marine species to various arsenic species are summarized in Byeon et al. 2021 Table 2.

While the human impacts from arsenic exposure have been extensively documented, the precise mechanisms underlying its health effects are unclear (Jomova et al., 2011). The primary pathway for arsenic exposure from the marine environment to human populations is through consumption, particularly of seaweeds, although no acute toxic risks have been reported. Health issues resulting from arsenic exposure in humans manifest as oxidative stress and genotoxicity, leading to various diseases affecting the skin, cancer, cardiovascular system, gastrointestinal tract, liver, kidneys, nervous system, and reproductive organs (Jomova et al., 2011). Despite arsenosugars being considered non-toxic, it is suggested that upon ingestion, they may undergo speciation in the digestive tract, potentially transforming into alternative metabolites associated with carcinogenesis, thus establishing a plausible chronic exposure pathway. Due to this lack of consensus, standards for acceptable concentrations in seafood are difficult to define. Currently, there are no defined acceptable concentrations or arsenic species in any seafood category for both the European Commission and Israeli Health Standards (Chapter 2 – Supplement Table 2: Summary of standards), though the Israeli Health Standard was once defined at 1 ppm. The Australia New Zealand Food Standards Code has set acceptable arsenic in fishery products and muscle at 2 ppm.

**Cadmium**

Cadmium is a natural element in Earth's crust and is naturally released into the environment through volcanic outgassing and weathering of rock and easily mobilized through the atmosphere through windblown dust (Cullen & Maldonado, 2013). It has important industrial applications and used in the manufacturing of rechargeable batteries, pigmentation, stabilization of plastics, and in the protection of electroplating of metal surfaces (Cullen & Maldonado, 2013). Atmospheric release through anthropogenic activity is the main source of cadmium in the environment, and is mostly due to non-ferrous metal production, fossil fuel combustion, iron and steel production, waste disposal and cement production (Cullen & Maldonado, 2013). Once released in the atmosphere, cadmium can be dispersed over long-distance thousands of kilometers away from its original point source (Cullen & Maldonado, 2013). In addition, it is also highly mobile within freshwater systems and is transported by rivers from inland areas to the Ocean.

Cadmium is easily transported through the atmosphere and reaches the Ocean surface, exhibiting high solubility in seawater (Cullen & Maldonado, 2013), with concentrations in the water fraction of coastal areas, notably higher compared to open waters. As cadmium readily forms complexes with chloride, there is an inverse relationship between salinity levels and free ionic cadmium in the water, with ionic cadmium considered the most toxic chemical species of the metal (Neff, 2002). The bioavailability of cadmium decreases with increasing salinity, impacting the availability of toxic ionic cadmium species (Baars et al., 2014; Neff, 2002). In open waters, cadmium distribution aligns with phytoplankton nutrient profiles, mirroring the vertical distribution patterns of phosphate in the water column (Baars et al., 2014). Specifically, phytoplankton is responsible for the accumulation of cadmium from the water column via either the Mn or the Zn transport system (Xu & Morel, 2013). While cadmium may potentially play a significant biological role in phytoplankton function (Cullen & Maldonado, 2013), an ongoing debate questions whether this uptake represents a biological error or actual utilization by phytoplankton (Morel, 2013) and whether it arises from a biological or chemical requirement (Roshan & DeVries, 2021). Ultimately, at threshold concentrations (i.e. 0.11 μg L(-1) Echeveste et al., 2012), cadmium becomes toxic for phytoplankton (Xu & Morel, 2013).

Similar to arsenic, the accumulation behavior of cadmium is unclear, with past studies indicating bioaccumulation potential while current studies highlighting its complexities as it is transferred though the food web (Saidon et al., 2024). Marine organisms are exposed to cadmium through either dissolved ionic cadmium via their in their gills (Neff, 2002) or with their diet. Studies have shown that cadmium does not necessarily biomagnify in marine food webs from the bottom trophic levels to the top. Within a system, different trophodynamics have been observed based on the organism category with invertebrates exhibiting biomagnification while fishes displaying biodilution (Espejo et al., 2018). However, when liver tissues were assessed bioaccumulation patterns did emerge (Rohonczy et al., 2024), indicating that muscle may not be an appropriate indicator of accumulation. Fish health toxicity includes damage to fish tissue structure, to fish reproduction, to development, to endocrine system, to energy metabolisms system, to nervous system development, and to blood plasma parameters (Liu et al., 2022). Acceptable concentrations in fishery products and muscle for both the European Commission and Israeli Health Standards are set at 0.05 ppm (Chapter 2 – Supplement Table 2: Summary of standards).

**Lead**

Lead is a natural earth element and is non-essential for biological process, characterized by high toxicity. Natural sources include release from volcanoes, biogenic, wind-borne dust, terrestrial biomass burning and sea-salt spray (Cullen & McAlister, 2017). It has important industrial uses such as the used in lead acid batteries, ammunition and ballistics, oxides for glass, ceramic hardening, casting metals, weight, and shielding application (Cullen & McAlister, 2017). However, of all the uses, much goes to the production of lead batteries, being allocated 80% of lead used in the United States (Cullen & McAlister, 2017). Lead was also formally used in leaded fuels, which has been phased out worldwide since the early 2000's. Despite this, the global production of lead continues to rise annually. Anthropogenic sources have become the dominant input in lead's global biogeochemical cycle, with input coming from electricity and heat production, vehicular traffic, mining of lead, mining of copper, mining of zinc, iron and steel production, waste disposal, and cement production (Cullen & McAlister, 2017). Once released in the atmosphere, it becomes highly mobile and can disperse at distances thousands of kilometers from its point source.

Lead is readily washed out of the atmosphere through precipitation, eventually finding its way into Ocean surface waters where it interacts with chlorine, carbonate, and hydroxide. Upon entering the Ocean via rivers, lead forms complex organic ligands, the stability of which depends on environmental abiotic factors such as salinity. Much of the lead reaching the marine system is buried through sedimentation. Phytoplankton in the water column can concentrate lead to higher levels than those found in seawater, thus introducing it into the trophic food web. Fish accumulate lead from both accumulation from the water fraction via their gills as well as ingestion, while benthic organisms are additionally exposed to lead from sediments. Lead readily binds to sulfur and oxygen atoms in proteins and is stored in various tissues and organs such as the liver and kidneys, with fish liver possessing detoxification mechanisms to counter this accumulation (Lee et al., 2019). Negative health impacts on fish due to lead exposure are both physical and biochemical, including oxidative stress, induced immune response, and neurotoxicity. Acceptable concentrations in fishery products and muscle for both the European Commission and Israeli Health Standards are set at 0.3 ppm (Chapter 2 – Supplement Table 2: Summary of standards).

## Israel

The Israeli coastline stretches for 273 km of continuous shoreline, encompassing a vast maritime space of 26,000 $km^2$ (Maritime Policy for Israel's Mediterranean Waters), surpassing its terrestrial area. Despite the harsh environmental conditions of this highly oligotrophic environment and high-water temperatures, it fosters a thriving marine ecosystem, though its true richness and diversity of which are just coming to light with more research. The local Israeli population highly benefits from these healthy seas, with the Mediterranean offering a variety of critical ecological services. Among these, desalination of seawater for fresh water, a highly limited resource in Israel and the rest of the region. An estimated 85% of the drinking water in Israel was produced through desalination in 2022, with a max capacity of 815 million $m^3$ (Israel Desalination & Water Treatment Society, 2024). Fisheries and aquaculture also play vital roles, though more modest compared to other countries surrounding the Mediterranean. While commercial fisheries solely serve the local market as landings are limited, artisanal fisheries remain generationally and culturally important for certain Israeli communities. Furthermore, a modest marine aquaculture sector exists, that utilizes either Ocean-based fish cages or pumped seawater used for limited land-based aquaculture. The sea also serves as a major hub for leisure and recreation, both local and tourism, including beaches for recreational swimming, recreational fishing, surfing, swimming, SCUBA/free diving, kite/wind surfing, and watercrafts. Similarly, the sea provides both spiritual and inspirational components that are ingrained in the history of the land. Additionally, Israel's two major ports of Haifa and Ashdod facilitate shipping and trade, serving as a critical link between the east and west. Natural products such as gas reserves have emerged as a major economic and political service, potentially independence from oil dependency. Moreover, the sea harbors biomedical compounds with potential for future utilization. Lastly, its ecological value cannot be overstated, maintaining biodiversity and crucial marine habitats that form the backbone of the marine ecosystem and support all services outlined here.

Israel's history with chemical pollution is quite similar to that of many other countries around the world. Prior to the 1960s, the sea served as a dumping ground for industrial and residential waste, releasing considerable quantities of harmful chemicals, including metals, into its waters. Historically, several major sources of metals from anthropogenic sources in Israel have been identified, notably wastewater and atmospheric emissions. Prior to mitigation, effluent and runoff emerged as primary sources, with untreated industrial, agricultural, and domestic waste finding its way to the sea. Among these, industrial wase, particularly from petrochemical plants around Haifa Bay and the Kishon area, stood out as major contributors to metal contamination. Atmospheric release also played a significant role, with industries and the use of leaded fuels being major contributors. Prior to the transfer of cleaner fuels like gas, the burning of coal contributed to the atmospheric release of metals. Despite the improvements in mitigation, which has reduced atmospheric lead through the successful transfer over to leadless fuels and the reduction in coal-based fuels, mercury sources are still dominated by atmospheric inputs (Erel et al., 2002). Additionally, ocean-based release, including activities such as marine infrastructure, shipping industry, and gas platforms, poses another source of contamination is Israel's marine environment. Beyond Israel's direct influences, regional inputs also play a role in metal contamination in the Eastern Mediterranean, with neighboring countries like Egypt, Cyprus, Gaza, Lebanon, Syria, and Turkey contributing pollutants through both aquatic and atmospheric sources. As a shared basin, all activities along the Mediterranean influence one another, with long-range atmospheric transport further complicating the sources of contamination. However, the extent to which these regional dynamics impact metal levels in Israel's marine environment has not been investigated.

### Research in Israel

Extensive research on metal pollution in Israel's marine environment has largely been conducted through the monitoring program of Israel Oceanographic and Limnological Research Center (IOLR), which has been monitoring sediments since 1978 (Bareket et al., 2016; Herut et al., 1993; Hornung et al., 1989) and biota since 1981 (Shefer et al., 2015a). A significant portion of their research has centered on the Kishon Estuary – Haifa Bay (Bareket et al., 2016; Hornung et al., 1989; Shoham-Frider et al., 2020), recognized as a major pollution hotspot due to intense anthropogenic activities. This area is characterized by urban development, a major harbor, multiple industries discharging wastewater, and a river collecting water and runoff from its entire basin, making it a focal point for pollution. For decades, it was regarded as one of Israel's most polluted waterways, with detrimental effects on the local biota as well as human health (Richter et al., 2003). The closure of notable mercury and cadmium sources, such as the Frutarom chlor-alkali plant in 2004 and a fertilizer plant utilizing Negev rock with elevated cadmium levels, resulted in a significant reduction — between 95-98% — in mercury and cadmium loads in the bay (Shefer et al., 2015b, 2015a). Monitoring of marine biota from the bay has reflected similar trends observed in sediment studies (e.g. benthic fauna and mollusks) (Hornung et al., 1989; Shefer et al., 2015a). Apart from specific hotspots like the Kishon and Yarkon estuaries, sediment analysis indicates that most areas along the Israeli coastline do not exhibit major contamination (Herut et al., 1993).

In addition to the limited assessment of benthic fauna and fish within the IOLR monitoring program, there has been occasional research on the accumulation of metals in other marine organisms. Studies beyond the monitoring program have explored the potential of ascidians to serve as bioindicators of metal pollution (Tzafriri-Milo et al., 2019). Furthermore, there have been investigations on cetaceans, including the common bottlenose dolphin (Shoham-Frider et al., 2009), fin whale (Shoham-Frider et al., 2014), minke whale (Shoham-Frider et al., 2014), Cuvier's beaked whale (Shoham-Frider et al., 2014), rough-toothed dolphin (Shoham-Frider et al., 2014), and Risso's dolphin (Shoham-Frider et al., 2014). However, these studies on cetaceans have been predominantly exploratory and lack substantial context regarding accumulation behavior. Moreover, while these studies offer valuable baseline information, the highly migratory nature of cetaceans limits their usefulness in understanding local metal behavior in Israel.

Several studies have investigated lead pollution in Israel, identifying three primary sources of contamination. Firstly, atmospheric aerosols, both local and remote, have been identified as significant contributors (Erel et al., 2002). Secondly, sludge discharge, notably from the Dan

Region Wastewater Plant (commonly known as Shafdan), has been identified as another major source. Thirdly, stream sediments have also been implicated (Erel et al., 2002). The presence of lead in Israel's atmosphere has been linked to leaded gasoline, with a phased reduction beginning in 1995 and a complete transition to unleaded fuels by 2001 (Harlavan et al., 2010). Sludge from wastewater treatment plants has been shown to transport lead to marine sediments, with studies indicating seasonal accumulation and rapid removal during turbulent winter storms (Harlavan et al., 2010). Approximately half of the total lead load has been estimated to enter the Mediterranean, turning it into a lead pollution sink, which subsequently becomes a source of lead pollution into the Atlantic Ocean (Harlavan et al., 2010).

Research on metals in Israel has underscored the significance of accounting for secondary pollution sources, where previously released metals are reintroduced into the ecosystem. One major contributor to secondary pollution is the resuspension of sediments, which serve as a sink for metals in Israel (Bareket et al., 2016). In Haifa Bay, for instance, dredging activities are conducted to maintain appropriate minimum depth for ship passage by removing sediment buildup within the harbor, thus initiating resuspension. Additionally, beach sand enrichment, aimed at counteracting sand erosion along Israel's beaches, also leads to resuspension. Furthermore, increasingly severe storms, exacerbated by climate change, contribute to sediment mixing. Another category of secondary pollution stems from historic point sources, where metals leached over time are reintroduced into the system. An example of this phenomenon is observed in the passive release of mercury from the electrochemical plant in Haifa Bay (Shoham-Frider et al., 2020). Despite a notable decrease in direct metal releases into the environment, secondary pollution poses a significant concern as it reintroduces pollutants into the marine trophic system, particularly worrisome in areas like Haifa Bay utilized for commercial fisheries.

**Mitigation in Israel**

Around the 1960s, heightened awareness of ecosystem service issues and observable problems along the coastline prompted steps towards mitigation and a shift in the approach to the marine ecosystem in Israel. Significant changes were made regarding atmospheric emissions, including the enforcement of standards, the phase-out of lead-based fuels from transportation, transitioning from coal to cleaner alternatives like gas and solar, and advancements in technologies to incorporate Best Available Technologies across industries. Efforts to address effluents involved stricter enforcement on industries releasing problematic wastewater, mandating treatment before discharge into the general water treatment system, and overall improvements in wastewater treatment practices.

In addition to stopping pollution at its source, restoration efforts have been initiated in areas long exposed to metal contamination. A notable project was the restoration of the Kishon Estuary, where contaminated sediments underwent treatment to mitigate the impacts of surrounding industrial activities in Haifa Bay. Specific polluted transboundary rivers entering Israel, such as the Alexander River, undergo simplified treatment processes to facilitate the flow of cleaner waters, promoting healthier ecosystems along its route, with less polluted water reaching the sea.

Moreover, the Israeli Ministry of Health has recognized the potential risks of metal ingestion through food consumption. It has established standards for acceptable metal concentrations in food items, including eggs, meat, and seafood (Israel Ministry of Health Public Health Services – Food Control Services Regulation 01022007). While imported seafood undergoes assessment according to these standards, as well as seafood from local aquaculture, there are currently no requirements for local seafood to undergo such assessments before being sold or consumed by the general public.

## Research Objectives, Motivation, and Innovation

Metal pollution continues to be a threat to both the marine ecosystem and to human health. In this thesis, I aim to provide better understanding of the behaviors of the metals mercury, arsenic, cadmium, and lead in Israel's marine ecosystem, particularly the accumulation behaviors in the local marine biota.

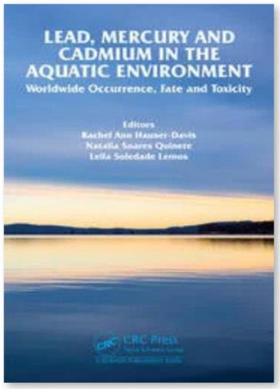
The first chapter aims to provide a regional summary of metal research in the Eastern Mediterranean Sea, by using well studied and standard defined sediment contamination as a proxy for potential biota contamination. This review incorporates both scientific and gray literature to provide better background context to this issue. Such a review is the first of its kind for this topic in the Eastern Mediterranean Sea as it applies a regional lens to metal pollution through an understanding that contamination is interconnected and does not respect man-made political boundaries. It also accumulates knowledge that is not necessarily available in scientific literature to provide important insight to this region.

The second chapter focuses on the local waters of Israel to provide a first-time assessment of the exposure of the local Israeli population to local seafood caught along the Israeli coastline within territorial waters. This chapter emphasizes the human health aspect of metal accumulation in the marine environment. Though health standards exist for seafood, locally caught seafood that reaches the local Israeli market is not required to undergo any assessments to ensure public safety.

The third chapter continues in the local territorial waters, however, it emphasizes the environmental aspect of metal accumulation in the marine environment. This chapter uses a combination of ecologically and economically important fish species, including keystone species like groupers. We also incorporate a non-conventional model to assess the driving factors of metal accumulation. By doing so, this paper provides context to species specific accumulation, the impact of marine protected areas on the accumulation of metal pollution in fish, and the potential human health impacts from eating fish caught locally.

This thesis integrates several innovative components, distinguishing it from similar studies in the field. First, a complex sampling strategy was adopted, encompassing a large dataset that includes numerous species and multiple metals, which are rarely addressed simultaneously in conventional studies. Importantly, this work examines each metal individually, considering the environmental and biological conditions influencing accumulation behavior, which is an aspect that is often overlooked in comparable research. To provide deeper context to arsenic accumulation, speciation data was incorporated, offering insights into the dominant arsenic species and their potential toxicity. Additionally, trophic positions and food sources of locally caught species were determined using compound-specific amino acid stable isotope analysis, eliminating reliance on literature-derived estimates that do not accurately represent the Eastern Mediterranean Sea. Finally, a multi-parameter assessment of metal accumulation through a Generalized Additive Model (GAM) sheds light on the key factors driving accumulation patterns. This thesis uniquely combines aspects of both environmental and human health—an integration often overlooked in studies that tend to focus exclusively on one or the other.

# Chapter 1: Accumulation of Lead, Mercury and Cadmium in Coastal Sediments in the Eastern Mediterranean Sea




Chapter

## Accumulation of Lead, Mercury and Cadmium in Coastal Sediments in the Eastern Mediterranean Sea

*By Debra Ramon, Malka Britzi, Nadav Davidovich, Dan Tchernov, Danny Morick*

Book Lead, Mercury and Cadmium in the Aquatic Environment

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# Statement of Authorship

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By signing the Statement of Authorship, each author certifies that:

I. the candidate's stated contribution to the publication is accurate (as detailed above);
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Chapter 5

# Accumulation of Lead, Mercury and Cadmium in Coastal Sediments in the Eastern Mediterranean Sea

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## MEDITERRANEAN SEA: A BRIEF BACKGROUND

The Mediterranean Sea is a semi-enclosed oligotrophic basin fed by the Atlantic Ocean through the narrow Straights of Gibraltar and is characterized by its high salinity and temperatures. It is bound between three different continents with Europe to the north, Africa to the south, and Asia to the east. Compared to the world's ocean, the continental shelf of the Mediterranean Sea is more dominant, making up 20% of the sea floor (Coll et al., 2010; Pinardi and Zavatarelli, 2006).

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While the Mediterranean Sea is considered small compared to other areas of the ocean, contributing to only 0.82% of its surface area and 0.32% of the volume (El-Geziry and Bryden, 2010), it hosts 4–18% of the world's marine biodiversity that includes many endemic species (Durrieu de Madron et al., 2011). It is also home to numerous emblematic species and habitats (Coll et al., 2010) including the Mediterranean monk seal, cetaceans, sea turtles, bluefin tuna, elasmobranchs, seagrass beds, and unique deep sea habitats.

The sea is considered an evaporate basin due to its low precipitation and high evaporation, which influences its unique circulation and biogeochemical processes. Upper Atlantic Ocean waters, already depleted in nutrients, enter the Mediterranean Sea through the narrow Straights of Gibraltar, which is 13 km wide and does not exceed 1,000 m in depth. A strong west-east gradient exits, with surface waters becoming increasingly warmer, saltier, and depleted of nutrients. This results in a corresponding decrease in the productivity as well. External sources of water input into the Mediterranean include the Black Sea and river basins. While the Nile River is one of the largest rivers in the world, the construction of the Aswan Dam has limited its flow into the Mediterranean. Other river inputs are mainly from the European boundary as very few perennial rivers flow from the African Coastline. However, the geology of the coast combined with its short shelf means that these European drainage systems contribute very little to the overall input (El-Geziry and Bryden, 2010).

The basin can be divided into two sub-basins, a western and an eastern basin (El-Geziry and Bryden, 2010) with the Straits of Sicily acting as a physical divider between the two. The geographic structure of the Sicilian-Tunisian sill in the Straits of Sicily, found at 400 m in depth, limits the hydrological transfer between the two (El-Geziry and Bryden, 2010). Thus, essentially, the Mediterranean Sea acts as a lagoon for the Atlantic Ocean, and the eastern basin a lagoon for the western basin. The two differ in their characteristics, with the eastern basin being larger by two folds and is more complex than its western companion. While the western basin is characterized by five different seas, the connectivity between them is non-confining, unlike in the eastern basin. The eastern basin comprises of four sub-seas: the Ionian Sea, the Levantine Sea, the Adriatic Sea, and the Aegean Sea (Figure 5.1). Directly eastward to the Straits of Sicily, the basin opens into the Ionian Sea, located between Italy and Greece. The deepest point of eastern basin is found here with a depth of 5 km just south of Greece (El-Geziry and Bryden, 2010). Eastward to the Ionian Sea lies the Levantine Sea, with its deepest point near Rhodes at 4.5 km. North of the Ionian Sea is the Adriatic Sea, which is separated by the 75 m wide Strait of Otranto with a sill at 800 m depth. The Adriatic Sea elongates into the European continent and is confined on either side by two major mountain ranges. To the north of the Levantine Sea lies the Aegean Sea, bound by Greece to its west and Turkey to its east. The Aegean Sea is quite shallow compared to the rest of the basin, with a maximum depth of 1.5 km. It is not an open basin, and unlike the other sub-basins in the eastern basin, it consists of many islands scattered within. The Black Sea highly influences the Aegean Sea, which flows directly into it, bringing a significant load of fresh water and nutrients.

There is immense human pressure around the entire Mediterranean basin. Coastal urbanization is particularly intense as the coast hosts a large population with 132 million people (Durrieu de Madron et al., 2011). Agricultural runoff via rivers brings heavy loads of pollutants (i.e., hydrocarbons, pesticides, herbicides, fertilizers, litter) from both coastal and inland areas, with rivers acting as trans-boundary transports. Industrial activities are scattered around the basin, with 161 identified marine pollutant hotspots often associated with large industrial areas and harbors (Antonio et al., 2014; EEA, 2006). While not up-to-date, the European Environmental Agency (EEA) has summarized such hotspots around the entire Mediterranean Sea, many of which are still relevant today (EEA, 2006). These industries include sectors such as petro-chemical infrastructure, chemical production, plastic production, metal treatment, and more (EEA, 2006). There is also particular concern with obsolete chemicals which are stockpiled near coastal areas and can leach into the marine environment (EEA, 2006). With urbanization and industrialization, treatment of both domestic and industrial wastewaters are problematic (EEA, 2006). The Mediterranean Sea is utilized by all coastal countries as a final release point for different levels of treated waste, with wastewater treatment regulations unique to each individual continent and country. Often, large harbors are coupled with heavily industrialized areas in order to logistically transfer goods between countries. Maritime traffic in the Mediterranean is particularly dense as the Suez Canal acts as a maritime bridge between the east and the west. Approximately 30% of the global merchant shipping fleet and 20% of the oil shipping fleet passes through the Mediterranean Sea each year (Antonio, et al., 2014). With intense maritime traffic, marine-based pollution is a prominent threat, resulting in chronic shipping discharge as well as acute incidents such as oil spills. In addition to the added anthropogenic input of metals, it has been suggested that natural background levels of metals in the Mediterranean Sea may be higher compared to other areas of the ocean due to tectonic activity around the central and western basin (Copat et al., 2014). Furthermore, due to the oligotrophic nature of the of the Mediterranean, the system is more sensitive to bio-accumulation processes as the bio-dilution of contaminants by organic carbon is reduced (Durrieu de Madron et al., 2011).

## METAL RESEARCH IN THE EASTERN MEDITERRANEAN SEA

The Eastern Mediterranean Sea (EMS) is an interesting study area in many aspects of marine sciences, yet research in this entire area is highly lacking. Sixteen countries border the EMS including Italy, Malta, Slovenia, Croatia, Bosnia and Herzegovina, Montenegro, Albania, Greece, Turkey, Cyprus, Syria, Lebanon, Israel, Egypt, Libya, and Tunisia. Some countries have had more focus on metal research in their local waters (i.e., Italy, Turkey, and Greece), others with moderate research (such as Israel, Libya, and Tunisia), while some have almost no studies to come by (i.e., Syria, Albania, and Montenegro). As basin wide studies are extremely limited, there is little understanding of basin wide

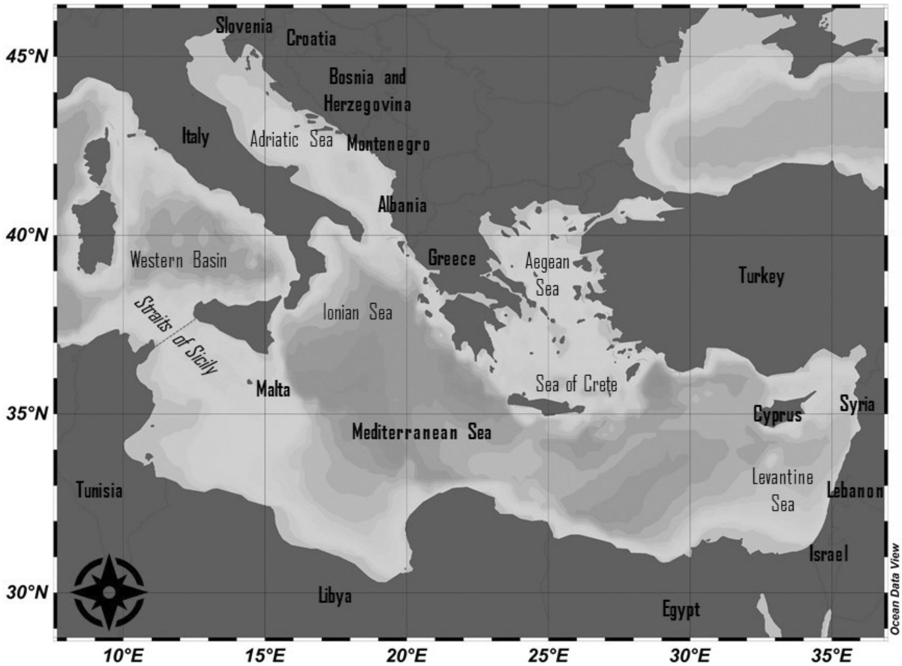


**Figure 5.1** Map of the Eastern Mediterranean Sea.

metal dynamics. Regional focused studies (such as those assessing the Aegean) are much more common, with a wealth of information coming from these areas. Yet, these regions are just a minor makeup of the entire EMS, still limiting our understanding of accumulation patterns. Therefore, understanding metal accumulation in the EMS comes from locally produced research originating from individual countries. Unfortunately, these studies, especially more recent ones, have never been collected and assessed on a more regional scale. Thus, through this chapter, we hope to contribute to a more regional understanding as we provide a brief summary of metal assessment studies in sediments from the different sub-regions of the EMS.

This summary focuses on the accumulation of mercury, cadmium and lead in sediments as an indicator of ecotoxicological potential due to both the availability of studies in the field as well as the comparison ability due to a relatively normalized set of standards. Currently, sediment analysis can be advantageous over biota studies as precise sediment pollution indexes exist that allow for the determination of enrichment, contamination, and potential transfer to biota. In comparison, metal levels in marine biota are open to ecotoxicological interpretation, with existing standards focusing on the human health aspect. Sediments play a major role in metal accumulation and are highly relevant to ecotoxicology studies. While the major route in which metals reach the marine environment is through either aerosols or land-based effluents, and the initial interface interaction is within the aquatic phase, only a small fraction of these contaminants remains suspended in the water column (Bonsignore et al., 2018). Instead, it is the sediments which act as the major sink for metals through processes such as adsorption and absorption onto sediment, precipitation, and interaction with the organic fraction (Gargouri et al., 2011). More than 90% of marine inorganic pollutants bind to sediments (Damak et al., 2019), thus acting as major reservoirs for pollutants. The level of absorption depends on its sediment qualities such as grain size, geochemical composition, and organic fracture, as well as environmental factors like salinity, temperature, and pH (summarized in El Baz and Khalil, 2018). With sediments acting as a concentrator for metals, as well as acting as sites for chemical speciation which can improve its bioavailability, they are an important source of metal transfer to biological systems. Therefore, by assessing sediment concentrations, the level of contamination can be assessed for potential ecological risk.

Coastal areas in particular are adequately studied as they are logistically more accessible and point sources of pollution are more easily identifiable. Seawater enrichment of metals often occurs intensively throughout coastal areas due to the high urbanization of coastlines, which contribute to industrial, urban, and agricultural inputs into the marine environment (EEA, 2006; UNEP/MAP, 2012). Regardless of the origin of the land-based metal source, contaminated coastal sediments constitute an important secondary non-point pollution source as they release metals into the overlying water. As metals tend to precipitate after their introduction into the coastal marine environment they accumulate in sediments and biota. This occurs especially in sheltered areas that enhance accumulation such as harbors and semi-enclosed bays (Merhaby et al., 2018) in the vicinity of land-based metal sources. Increased metal concentrations have been identified in many coastal areas in the Mediterranean Sea, such as the coast of Tuscany (Tyrrhenian Sea), Kastella Bay (Adriatic Sea), Haifa Bay and the coast of Alexandria (eastern Mediterranean), and Izmir Bay and Elefsina Bay (Aegean Sea) (EEA, 2006). With the EMS being used by numerous countries with varying social economic backgrounds and research advancements, coastal waters remain the primary focus for contaminant studies.

In this chapter we provide a brief overview of the different regions of the EMS including the; (1) north African coastline, (2) Levantine Sea, (3) Aegean Sea, (4) Adriatic Sea, and (5) Ionian Sea. Though the north African coastline is not considered an official sub-region of the EMS, it is included as a sub-division in this chapter due to the similarities between the countries it borders. Within each region, a brief description is provided for each individual country on the state of the marine environment as well as the anthropogenic activity that may affect local pollution levels. Additionally, a brief overview of the metal research in sediments is provided.

## NORTH AFRICAN COASTLINE

The North African coastline of the EMS is bordered by Tunisia, Libya, and Egypt (Figure 5.2). Despite the emergence of increased research of the marine system from this region over recent years, the scientific literature is still quite limited with baseline studies on biodiversity often lacking. Sampling efforts for this region center mostly in the vicinity of industrial areas, especially surrounding the harbors and ports of sizable cities. Therefore, while some studies can identify specific industries as sources of metal enrichment of marine coastal sediments, others are influenced by a cocktail of polluters from both the industrial and domestic sector. Most studies focus on areas identified as hotspots according to the EEA (EEA, 2006). Sediment enrichment along the North African coastline is shown in Figure 5.2 and concentrations are shown in Table 5.1.

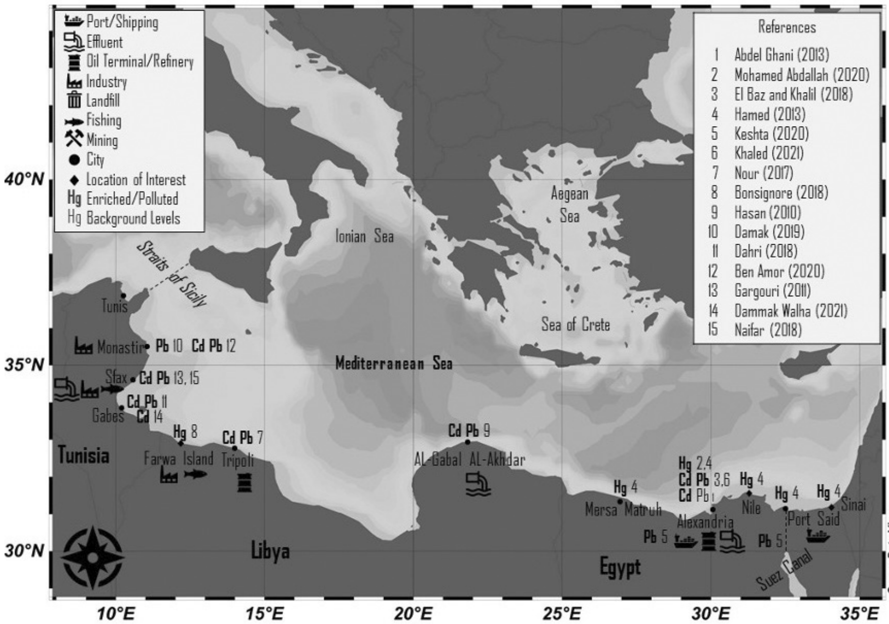


**Figure 5.2** Metal enrichment in sediments along the North African Coastline including Tunisia, Libya, and Egypt.

## Tunisia

Tunisia divides its 1,300 km coastline between both the western and eastern basin of the Mediterranean Sea. It is currently undergoing rapid urban growth and industrialization along the coastline, and the marine system suffers negative impacts from wastewater discharge, industrial activities (i.e., textiles, cement, and phosphate), agriculture, and urban development. Additionally, Tunisia hosts Mediterranean tapeweed (*Posidonia oceanica*) meadows, which compose a highly valuable marine ecosystem for many species (Telesca et al., 2015).

Over the recent years, Tunisia has shown a boost in research focusing on marine contaminants. In the eastern basin, the waters in front of the cities Gabes and Sfax have been identified as pollution hot spots (Figure 5.2) (EEA, 2006). Both cities are situated on the Gulf of Gabes, a highly productive area responsible

**Table 5.1** Studies assessing metal accumulation in sediments along the North African coastline. Metal concentrations (µg.g$^{-1}$, dry weight – dw) are reported depending on data provided from within the studies as either mean value ±SD, range within parentheses, or both. Values in bold indicate that sediments were considered either contaminated or enriched by the study

| Location | Hg | Cd | Pb | References |
|---|---|---|---|---|
| Egypt (Abu-Qir Bay – Alexandria) | – (–) | **2.93 (0.31–4.89)** | 8.2 (1.9–16.79) | Abdel Ghani et al. (2013) |
| Egypt (Eastern Harbor – Alexandria) | – (–) | **1.11 (0.3–1.83)** | **40.57 (1.3–112.09)** | Abdel Ghani et al. (2013) |
| Egypt (Western Harbor –Alexandria) | **4.07 (1.01–6.6)** | – (–) | – (–) | Abdallah (2020) |
| Egypt (Central Zone – El Mex to Port Said) | – (–) | 0.16 (0.06–0.42) | 14.75 (5.3–57) | El Baz et al. (2018) |
| Egypt (Coastline) | – **0.01–0.02** | – (–) | – (–) | Hamed et al. (2013) |
| Egypt (Alexandria) | – (–) | **0.29±0.07 (–)** | **32.55±6.49 (–)** | Khaled et al. (2021) |
| Libya (Sabratha) | – (–) | 0.83 (0.19–2.19) | **11.69 (2.16–38.22)** | Nour and El-Sorogy (2017) |
| Libya (Farwa) | – **(0.01–0.16)** | – (–) | – (–) | Bonsignore et al. (2018) |
| Libya (Al-Gabal Al-Akhda) | – (–) | – **(0.79–1.4)** | – **(1.4–7.5)** | Hasan et al. (2010) |
| Tunisia (Monastir Bay) | – (–) | – (–) | **5.29±3.54 (1.48–13.04)** | Damak et al. (2019) |
| Tunisia (Gabes Catchment) | – (–) | **0.68 (0–5.62)** | **28.12 (0.13–162.7)** | Dahri et al. (2018) |
| Tunisia (Monastir Bay) | – (–) | – **(0.01–3.45)** | – **(0–47)** | Ben Amor et al. (2020) |
| Tunisia (Sfax Coast) | – (–) | 5.9±0.5 (5.5–7) | **32±17** (18–88) | Gargouri et al. (2011) |
| Tunisia (Gulf of Gabes) | – (–) | **0.4±0.14** (–) | – (–) | Dammak Walha et al. (2021) |
| Tunisia (Gulf of Gabes) | – (–) | – **(0.55–24.52)** | – (3.68–39.7) | Naifar et al. (2018) |

for 40% of the country's fish landings and important habitats for many marine organisms (Béjaoui et al., 2019). Due to its economic and ecological importance, the gulf has been well researched. This area in particular is negatively impacted by industrial activity like phosphate factories (EEA, 2006), which has been attributed to elevated Cd contamination in sediments (Dammak Walha et al., 2021; El Zrelli et al., 2018). The metals Pb and Cd were also found elevated near channel outlets leading into the gulf due to effluents released throughout the catchment by both industrial and domestic activity (Ben Amor et al., 2020; Naifar et al., 2018), though industrial sources appear to be the major source (El Zrelli et al., 2018). Concentrations were higher especially in muddy sediments (Ben Amor et al., 2020; Gargouri et al., 2011), with decreasing levels of contamination further from shore with increasing grain size and organic matter levels. Additionally, a study investigating the impacts of fish farming showed that Pb was enriched directly below the fish cages (Damak et al., 2019).

## Libya

Libya is particularly limited in research despite having the most dominant coastline in the southern border of the Mediterranean Sea, comprising of approximately 1,970 kilometers (IUCN, 2011). Many pristine areas exist along the coast with the gray literature describing the Libyan marine system as a wealthy one with three key Mediterranean hotspots (IUCN, 2011) home to a range of marine species such as fish, larger pelagic fish, elasmobranchs, benthic organisms, sea turtles, and sea birds (Regional Activity Centre for Specially Protected Areas, 2016). Anthropogenic activity including coastal urbanization, discharge of sewage water, construction debris, petrochemical industry, oil terminals, ports, and other industries (Bonsignore et al., 2018; Regional Activity Centre for Specially Protected Areas, 2016; IUCN, 2011) have been noted as considerable threats to the health of the marine ecosystem and the fisheries that depend on it. The country has no perennial rivers that provide a constant supply of water throughout the year (EEA, 2006).

Libyan research is highly limited with only a handful of articles published on sediment contamination (Figure 5.2, Table 5.1). Pollution hotspots have been identified around the ports of Tripoli, Benghazi, and Tobruk (EEA, 2006) with Tripoli and Benghazi being the two largest cities in the country with populations exceeding one million inhabitants. On the western border of Libya, an area with active chemical industries as well as known fishing area (Farwa Island) observed that sediments closer to shore were found to be enriched and diluted with depth (Bonsignore et al., 2018). Additionally, commercially important fish species showed Hg accumulation, with sediment sifting *Mullus* species (a known bioindicator for metals in the Mediterranean Sea), particularly susceptible to bioaccumulation (Bonsignore et al., 2018). Less than 100 km east of Farwa Island is the city of Sabratha, which hosts a fishing port as well as the Mellitah Complex Oil and Gas just beyond the city, which is the main point in western Libya for gas and oil export to Italy. Sediments here were shown to be enriched with both Pb and Cd, with particularly elevated Cd levels near the fishing port and highest levels of Pb were observed near the oil and gas complex (Nour and El-Sorogy, 2017).

## Egypt

Egypt's 950 km coastline is mostly dominated by sandy beaches with occasional rocky shores (Fouda, 2017). It is the endpoint of the Nile River, which drains into the Mediterranean Sea. It also hosts the Suez Canal, which creates a water bridge between the Red and Mediterranean Sea, thus making the Mediterranean one of the busiest waterways in the world and susceptible to an elevated risk of oil spills. While it's marine biodiversity has been described as relatively poor in comparison to other regions of the Mediterranean Sea, it still hosts a diversity of marine organisms many of which are endangered (Fouda, 2017). The Sinai Mediterranean coast has remained quite pristine, while other sections of Egypt's coastline are influenced by anthropogenic activity. Due to urbanization, 20% of the population have settled in coastal areas and over 40% of the local industry centered around coastal zones includes ports, petroleum, and mining (Fouda, 2017). River drainage systems ultimately reaching the sea faces pollution threats from wastewater discharge (domestic and industrial) as well as from agricultural runoff (Fouda, 2017). Additionally, large lagoons/urban lakes situated along the coast act as accumulation points of metals before flowing into the sea (Keshta, et al., 2020).

In Egypt, major research focus has been placed on the central zone, defined between Alexandria and Port Said (Figure 5.2). This area is considered some of the most industrialized areas of the Mediterranean, particularly in port cities, due to the amount of shipping that passes through Egypt's Suez Canal. As a result, this area is considered a pollution hotspot by the EEA (EEA, 2006). The sediment of Alexandria has been particularly well sampled, showing enrichment of Hg (Abdallah, 2020; Hamed et al., 2013), Cd (Abdel Ghani et al., 2013; Khaled et al., 2021), and Pb (Abdel Ghani et al., 2013; Khaled et al., 2021) (Figure 5.2, Table 5.1). While Alexandria's harbor receives a cocktail of inputs including wastewater, petrochemical, and cement factory discharge, the elevated contamination levels of Hg within the harbor has been shown to come from a local chlor-alkali plant (Abdallah, 2020). As a result fish feeding on the organic material in the bottom sediments were shown to have corresponding elevated Hg levels (Abdallah, 2020). Cadmium is believed to originate from the industrial sludge from wastewater treatment while Pb is a result of the manufacturing of batteries and petrol fuel (El Baz and Khalil, 2018). These metals also accumulate in the Egypt's northern lakes located in urban areas adjacent to the coastline (Keshta et al., 2020), showing the contamination potential in such urban environments from runoff.

# THE LEVANTINE SEA

The Levantine Sea is the eastern most section of the Mediterranean Sea. It is bordered by Egypt, Gaza, Israel, Lebanon, Syria, the island of Cyprus, and eastern Turkey (Turkey's Mediterranean region). This area is considered extremely oligotrophic with saline and warm waters. Due to the long shore current traveling north along the eastern boundary, the Nile River plays a major influence in this area. Additionally, the opening of the Suez Canal, which allows ship passage between the Red Sea and Mediterranean Sea, has brought with it a number of invasive species (i.e., *Pterois miles*—common lionfish, *Surida lessepsianus*—lizardfish, *Siganus rivulatus*—marbled spinefoot rabbitfish) in the Lessepsian migration (EEA, 2006) resulting in changes in the marine ecology of the entire region. The region has become a major source of economic interest with the discovery of gas fields, leading to both exploration of this resource as well as the establishment of infrastructure used for its extraction. Importantly, this region is highly impacted by socio-economic issues, ultimately influencing the quality of marine management and the research of the marine system. For this section, we focus on exploring Gaza Strip Palestine, Israel, Lebanon, Syria, Cyprus, and the Mediterranean region of Turkey. The accumulation of metals in this region is summarized in Figure 5.3 and Table 5.2.

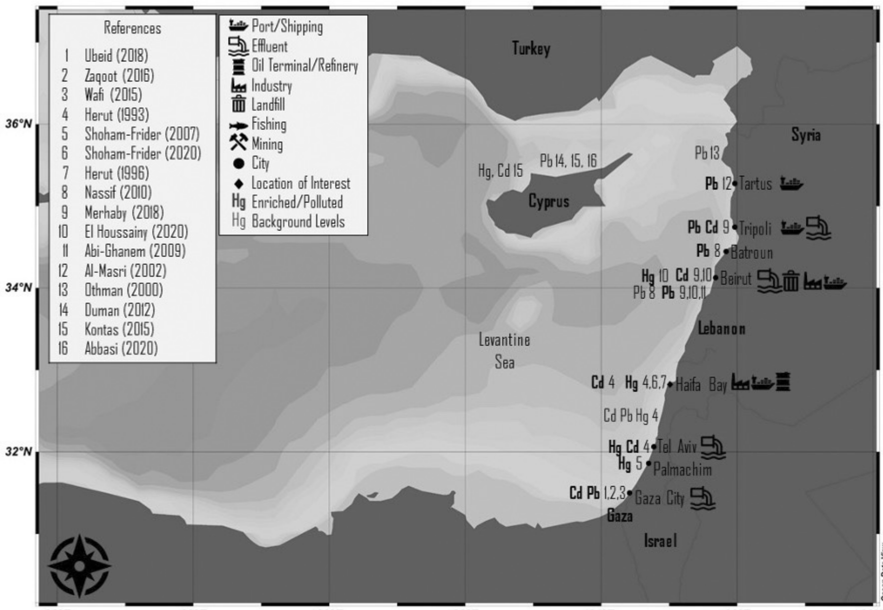


**Figure 5.3** Metal enrichment in sediments along within the Levantine Sea including Gaza, Israel, Lebanon, Syria, Cyprus, and Turkey.

## Gaza

The coastline of Gaza extends only 42 km and is characterized by sandy habitats (Ali, 2002) similar to that of southern Israel. Unfortunately, there is little information available on the status of the marine environment for Gaza. However, it has been reported that the coastal marine ecosystem has been greatly impacted, leaving little to no pristine areas (Adel Zaqoot et al., 2012). Despite this, artisanal fisheries fleet do exist in this area and there has been documentation in the gray literature (Ali, 2002) as well as local reports of elasmobranch species

**Table 5.2** Studies assessing metal accumulation in sediments along the Levantine Sea. Metal concentrations (μg $g^{-1}$ dw) are reported depending on data provided from within the studies as either mean value ±SD, range (), or both. Values in bold indicate that sediments were considered either contaminated or enriched by the study.

| Location | Hg | Cd | Pb | Reference |
|---|---|---|---|---|
| Gaza (Gaza Coastline) | – (–) | **1.1 ± 0.63 (0–3.72)** | 15 ± 9.7 (3.4–63.7) | Ubeid et al. (2018) |
| Gaza (Gaza Fishing Harbor) | – (–) | 1.07 (–) | 7.27 (–) | Wafi et al. (2015) |
| Israel (Coast) | – (0.004–0.07) | – (0.04–0.31) | – (3.59–10.3) | Herut et al. (1993) |
| Israel (River Mouths) | – (0.002–0.46) | – (0.04–1.8) | – (3.19–48.3) | Herut et al. (1993) |
| Israel (Palmachim) | **0.26 ± 0.24 0-1** | – (–) | – (–) | Shoham-Frider et al. (2007) |
| Israel (Haifa Bay) | – **(0.09–2.2)** | – (–) | – (–) | Shoham-Frider et al. (2020) |
| Lebanon (Coast) | – (–) | – (3.29–13.47) | – (1.2–443.3) | Merhaby et al. (2018) |
| Lebanon (Beirut Harbor) | – (0.1–0.7) | – (0.4–1.1) | – (25.1–376.1) | El Houssainy et al. (2020) |
| Lebanon (Akaar) | – (–) | – (–) | – (6.2–15.7) | Abi-Ghanem et al. (2009) |
| Lebanon (Dora) | – (–) | – (–) | – (70.7–101.4) | Abi-Ghanem et al. (2009) |
| Lebanon Selaata | – (–) | – (–) | – (4.8–34.5) | Abi-Ghanem et al. (2009) |
| Syria | – (–) | – (–) | – (2.6–24) | Othman et al. (2000) |
| Northern Cyprus | – (–) | – (–) | – (1.6-9.2) | Duman et al. (2012) |
| Northern Cyprus | – (0.02–0.07) | – (0.03–0.32) | – (1.1–2.4) | Kontaş et al. (2015) |
| Northern Cyprus | – (–) | – (–) | – (11–22) | Abbasi and Mirekhtiary (2020) |

caught in Gaza that have been less frequently observed in Israeli waters. The human population of the entire area is one of the densest in the world resulting in numerous environmental problems that impact the marine environment. The release of untreated wastewater is one of the greatest problems to the area (Adel Zaqoot et al., 2012) with 80% of it untreated and released directly into the sea (IUCN, 2015). This includes local waste as well as trans-boundary pollutants that originate from beyond Gaza's borders (Israel and West Bank) that flow to the coast via seasonal rivers. The central area of Gaza is particularly polluted owing to the discharge of wastewaters from Gaza City (Adel Zaqoot et al., 2012). Industrial pollution also contributes to the release of metals and other pollutants into the marine system (EEA, 2006) via wastewater treatment which also remains untreated similar to domestic wastewaters. Industries shown to release Pb, Cd, and As include the pharmaceutical industry, cosmetic industry, textile industry, electroplating factories, galvanic factories, detergent factories, textile washing factories, soft drink factories, and car washing workshops (Adel Zaqoot et al., 2012). Additionally, solid hazardous waste disposed in open landfills also act as a source for pollutants entering the marine environment.

Research on metal accumulation in both sediments and biota are limited to a few papers. Focus has been emphasized around Gaza Fishing Harbor, which is a major outlet for wastewater disposal. Overall, wastewaters have been blamed as the major culprit contaminating the waters, sediments, and fish for this area. Sediments along the Gaza coastline show enriched levels of Pb and Cd, with concentrations increasing deeper off shore where grain size decreases (Ubeid et al., 2018). Work assessing the all three mediums (water, sediment, and biota) indicate that the accumulation within the indicator species flathead grey mullet (*Mugil cephalus)* is higher than the local seawater yet lower than that of sediments (Wafi 2015; Zaqoot et al., 2017). Sediment concentrations were particularly elevated following rainy periods (Wafi, 2015) possibly as rivers are flushed from the entire inland watershed (Israel and Palestine/West Bank) out into Gaza Harbor.

## Israel

Israel's coastline extends approximately 200 km and is characterized by mostly sandy beaches with occasional rocky habitats (Scheinin et al., 2013). While the marine richness is less compared to the western basin, and despite the harsh conditions of this area, research on the marine environment shows that it sustains a wealth of life and is an important habitat for larger marine species including elasmobranchs, cetaceans, sea turtles, and large pelagic fish (Scheinin et al., 2013). The coastline is highly urbanized with over half of the population living along the coastal plain (Israeli Ministry of Foreign Affairs). There are two major ports along its waters with intense industrial activity centered in these areas. Numerous rivers flow through Israel into the Mediterranean Sea with some of the larger ones including the Yarkon, Alexander, and Kishon rivers. While the release of untreated sewage has dramatically decreased over the years, the release of raw sewage either into rivers or directly into the sea does still occur, especially during the winter months. Additionally, as numerous rivers originate in the Palestinian West Bank, where wastewater management is less efficient compared to Israel, untreated urban and industrial effluents are also transferred via river systems directly into the sea. Pollution hotspots are concentrated around areas like harbors and river outlets (EEA, 2006).

Long term monitoring of metals in Israel's marine environment has been conducted continuously for almost 40 years by Israel's National Monitoring Program (Herut et al., 1993). Coastal sandy sediments were found to be relatively unpolluted, except for hotspot areas like river outlets along the coastline (Herut et al., 1993). A major research focus has been placed on the pollution hotspot of Haifa Bay (Bareket et al., 2016; Herut et al., 1993, 1996; Shoham-Frider et al., 2020) (Figure 5.3), which is a major harbor, fishing port, river outlet, and industrial area in Israel. Due to the intense industrial activities in the area, a considerable Hg signature was observed in the sediments and biota of the harbor (Herut et al., 1996). However, the level of metals entering the marine environment in Israel has dramatically decreased over recent years with the reduction of over 99% of land-based sources, specifically the disposal of raw sewage, due to improved legislation on source water treatment (Malster, 2019). This reduction can be directly observed in both the sediment and biota of Haifa Bay (Herut et al., 1996). Additionally, locally consumed seafood show low presence of Cd and Pb, though Hg is still present (Ramon et al., 2021). Despite this, point problems still remain which can be seen, for example, with the passive release of Hg from an abandoned electrochemical plant which has led to elevated levels in the Haifa Bay sediments (2,200 $ng.g^{-1}$) and local biota (Shoham-Frider et al., 2020). While the land-based sources may have decreased, sediments continue to act as a secondary source as winter storms result in the resuspension of buried contaminated sediments (Bareket et al., 2016).

## Lebanon

The Lebanese coastline extends 235 km and is characterized by mostly rocky formations (Abboud Abi-Saab, 2012), differing from the sandy habitats dominating Gaza and Israel to its south. With these unique habitats, Lebanon's marine environment is a hotspot for marine biodiversity (Badreddine, 2018; Bitar et al., 2018). Over 1,500 species have been recorded in Lebanese waters, from macrophytes, cetaceans, elasmobranchs, bony fish, sea birds, and sea turtles (Bitar et al., 2018). However, these natural resources also compete against rapid urbanization, with over 55% of the population living on the coast (Abboud Abi-Saab, 2012). The shoreline hosts four commercial ports, 15 fishing harbors, dozens of oil terminals, three power plants, and intense agriculture (Abboud Abi-Saab 2012; Badreddine, 2018). Effluents from wastewaters from both urban and industrial sources are released untreated into the coastal waters (Badreddine, 2018; Abboud Abi-Saab, 2012) while rivers carry effluents from inland areas (Abboud Abi-Saab, 2012). Coastal dumping of both solid wastes are a major issue (EEA 2006), with landfills situated directly on the shoreline (Ghosn et al., 2020). Such dumpsites in Lebanon, many of them illegal, have been reported to be major sources of trace elements being released into the marine environment (Ghosn et al., 2020; Merhaby et al., 2018) Political conflict, like the Syrian Civil War, has brought in a large influx of refugees, further pushing population stress and urbanization while national conflict has resulted in industrial development with little overseeing management (Badreddine, 2018).

Research on metals in Lebanon has focused on major cities like Beirut and Tripoli, both of which are characterized as major industrial areas with commercial harbors (Figure 5.3). Beirut, in particular, is faced with a combination of anthropogenic inputs that has led to metal enrichment of Hg, Cd, and Pb in the marine sediments and is considered a highly polluted area (El Houssainy et al. 2020; Merhaby et al., 2018). With solid wastes in coastal areas still a major national issue, a local dumpsite in close proximity to Beirut has been identified as a source of leached Pb with extremely high coastal marine sediment concentrations of 70.7–101.4 $\mu g.g^{-1}$ (Abi-Ghanem et al., 2009). These elevated concentrations have been shown to have similar isotopic signatures to that of gasoline (Abi-Ghanem et al., 2009). Despite these high levels, the biota-sediment transfer factor to commonly consumed seafood species like spiny oysters (*Spondylus spinosus*) and kuruma shrimp (*Marsupenaeus japonicus*) collected in Beirut show a low transfer of Hg, Cd, and Pb, indicating that highly contaminated sediment does not always equate to certainty of bioaccumulation (Ghosn et al., 2020). In comparison, Tripoli's biota-sediment transfer factor does indicate that Hg does indeed transfer from sediments to kuruma shrimp, perhaps due to the shrimp's lifestyle which is associated with the benthos (Ghosn et al., 2020). While some marine species have been investigated in Lebanon, studies are still quite limited, and focus on species relevant to human consumption. Additionally, no recent comparisons have been conducted on highly polluted areas of Lebanon compared to more pristine areas. In order to gain a more comprehensive view of the state of marine environment of the country, more detailed local research is required.

## Syria

The Syrian coastline stretches 182 km with sandy beaches making up 20% of the coastline (Ibrahim, 2009) and the rest characterized as rocky. As little information exists in the literature on the marine biodiversity of Syria, its similarities to that of Lebanon may indicate a comparable potential as a marine biodiversity hotspot. In contrast, there is less urbanization compared to Lebanon with around 10% of the population living on the coastline (EEA, 2006; Ibrahim, 2009), and a quarter of coastal population is centered in four cities (Ibrahim, 2009). Only three major cities are situated along the coastline; Latakia, Baniyas and Tartus (Othman, et al., 2000). Along the coastline there are four commercial ports and 14 fishing harbors, as well as a variety of industrial activities such as half of the country's oil processing industry (Ibrahim, 2009). Direct disposal of both domestic and industrial untreated wastewater mas well as the slicks from the oil industry are direct inputs into the marine environment (EEA, 2006). More recently, in August 2021, a major oil spill was reported in the international media (including CNN, BBC) along the Syrian coastline, spreading to deeper waters and nearing neighboring countries likes Cyprus and Turkey.

Unfortunately, published research on the topic of metals in Syria's marine environment is limited to a few studies from 20 years ago. This is probably attributed to the nation's political situation leading to a lower priority in environmental research. The little scientific information available shows radionuclide Pb enrichment around Tartus, which hosts the second largest port in Syria and is particularly known for its phosphate loading (Al-Masri et al., 2002).

Beyond this, very little scientific information on metals along Syria's coastline is provided in the literature.

## Cyprus

Cyprus is the third largest island in the Mediterranean Sea. Its coastline extends 735 km and is characterized by rocky shores and fringed with sandy beaches. Similar to other countries of this region, there is limited published literature on the marine habitat of Cyprus. Literature describes the soft sandy substrates hosting seagrass beds of *Posidonia oceanica*, holding important ecological significance to species like turtles, monk seals, and dolphins (Kletou et al. 2020). While Cyprus is characterized by a relatively small industrial sector, a mining industry does exist on the island (EEA, 2006). Additionally, anthropogenic activities like fish farming, cement factories, and oil terminals have been reported adjacent to sensitive habitats adjacent of seagrass meadows (Kletou et al. 2020). While urban wastewater has been noted as a coastal environmental problem in the past (EEA, 2006), as the country is water limited, much effort is placed by waste water treatment facilities to treat waters for both agricultural use and replenishing aquifers (Nicos Neocleous, 2018), thus wastewater discharge directly to the sea has been practically eliminated.

Cyprus also lacks published scientific literature addressing the accumulation of metals in its marine system, though some sediment and biota studies do exist. Sediment studies focus on northern Cyprus, which observed low Pb pollution (1.6–9.2 mg $kg^{-1}$ Duman et al., 2012) (1.12–23.8 μg.$g^{-1}$; Kontaş et al., 2015) (1.6–9.2 mg.$kg^{-1}$; Abbasi and Mirekhtiary, 2020), Hg (0.02–0.07 μg.$g^{-1}$; Kontaş et al., 2015), and Cd (0.03–0.32 μg.$g^{-1}$; Kontaş et al., 2015). It would appear that Cyprus' almost non-existant industrial complexes, as seen in other countries around the Mediterranean Sea, plays a major role on the local contamination levels. In regards to biota, one of the only published studies is on the local nesting sea turtle population which showed that concentrations of metals appear to impact turtle health (Godley et al., 1999). While turtles may be using Cyprus as a nesting site, their accumulation of contaminants is not local, and thus does not provide direct indication of the local pollution. However, as they are a sentinel species that travel throughout the Mediterranean Sea, they can be important indicators to the overall marine health.

## Turkey

Turkey's coastline extends for 8,333 km and is divided between the Black Sea, Sea of Marmara, Aegean Sea, and the Mediterranean Sea. Only 1,707 km of coastline is situated along the Mediterranean Sea (PAP/REP, 2005). Its marine environment has been described as a rich one due to its strategic location (Sustainable Development Turkey, 2012). It is also an important exporter in fisheries and aquaculture (Sustainable Development Turkey, 2012), though only 5% of its catch comes from the Mediterranean Sea (PAP/REP, 2005). The coastal dunes of the Mediterranean Sea act as key nesting grounds for multiple sea turtle species while limestone structures provide a habitat for the endangered Mediterranean monk seal (Sustainable Development Turkey, 2012). The seas that Turkey borders are influenced differently by pollutants, yet ultimately all these water bodies are in contact with one another and flow into the Mediterranean Sea. Coastal pollution is mainly due to land-based sources from both direct inputs in coastal areas as well as transfer by local and trans-boundary rivers (Sustainable Development Turkey, 2012). Similar to many other countries around the Mediterranean, wastewater from major cities were once directly released into the sea, though untreated sewage outflow from the major cities of Istanbul and Izmir has been reportedly stopped since 2002 (Sustainable Development Turkey, 2012). Though industrial wastewater output is relatively smaller compared to domestic, it has been noted that they contain high loads of metals, thus creating major hotspots around coastal industrial areas (Sustainable Development Turkey, 2012). Agricultural runoff also continues to be a major contributor of pollutants that eventually reach the sea (Sustainable Development Turkey, 2012). There is a strong presence of marine traffic, with the Turkish Mediterranean region hosting numerous seaports including the major contributors Port of Mersin, İskenderun Harbor, and Port of Isdemir, and the other minor contributors Port of Antalya, Taşucu Seka Harbor, Port of Assan Iskenderun, and Port of Yesilovacik. Additionally, the Port of Ceyhan hosts three oil terminals that transfer crude oil from landlocked areas.

The coastal regions of Turkey relevant to this chapter include the Mediterranean region, the Aegean region, the Marmara region, and the Black Sea region. For this sub-section, the relevant region for the Levant Basin is the Mediterranean region alone. Despite Turkey hosting a wealth of information with regard to metal research, it appears that a majority of the scientific information focuses on other regions (particularly the Aegean and Black Sea regions) and emphasis is placed on biota-based studies rather than sediments. This emphasis may be attributed to the economic importance of fisheries to the local public as well as exports. However, these studies often focus on the human health effects rather than the ecotoxicological significance. From the few investigations on the bioaccumulation of metals from the Mediterranean region of Turkey, Cd and Pb levels have decreased in edible fish species compared to prior studies (Korkmaz et al., 2019; Türkmen et al., 2005) perhaps due to a decrease of industry in this area (Türkmen et al., 2005). In contrast, shrimp and fish species were found to exceed permissible human health standards (Aytekin et al., 2019). Overall, this area remains relatively uninvestigated with regard to the metal accumulation and the potential impacts on the environment.

## AEGEAN SEA

The Aegean Sea is a 215,000 km$^2$ semi-closed extension of the Mediterranean Sea located between Turkey and Greece, with its southern limits being the islands of Crete and Rhodes. It is one of the few locations in the Eastern Mediterranean where deep water is formed, specifically near Rhodes (Simboura et al., 2018). The coastline is characteristically irregular with thousands of islands distributed throughout its waters (Tanhua et al., 2013). It is considered a biodiversity hotspot, hosting important habitats like seagrass meadows, coralligene reefs, and marine caves (Panayiotis et al., 2020). This area is considered highly rich in species, with species richness comparing to that of the richer western basin (Simboura et al., 2018). Additionally, it hosts marine mammal species including numerous cetacean species and the Mediterranean monk seal (Simboura et al., 2018). Besides the Mediterranean, the Aegean Sea is fed by Black Sea and the Sea of Marmara. Due to the introduction of nutrient rich waters from the Black Sea, the Northern Aegean in considered particularly productive (Ozsoy et al., 2016). Similar to other areas around the Mediterranean Sea, the Aegean Sea is threatened by anthropogenic activity including coastal development, pollution, shipping, and more (Katagan et al., 2015). It is a major maritime route that links the land-based industries to the Black Sea and out to the Mediterranean, and major ports in the Aegean Sea exist both in Turkey and Greece. Additionally, the Aegean Sea plays an important role connecting the route for oil between the Black and Mediterranean Seas. One fifth of the cargo ships passing through the Turkish straights carry transporting dangerous and hazardous cargo (Oral, 2015). The Black Sea is highly polluted as different countries use it as a resource, the intense industrialization of the area, and the number of large rivers that act as a transport for inland pollutants. The Sea of Marmara is polluted from maritime traffic as well as inputs of untreated domestic and industrial wastewaters (Ozsoy et al., 2016). Research conducted on sediment accumulation mostly targets major cities and harbors, and particular interest around the Maramara and Black Sea (Figure 5.4). The accumulation of metals in this region is summarized in Figure 5.4 and Table 5.3.

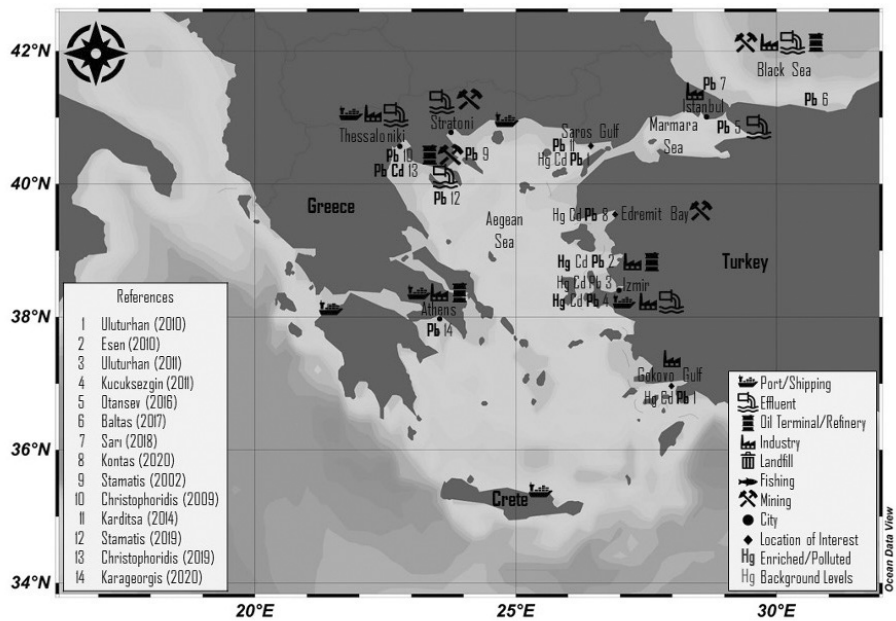


**Figure 5.4** Metal enrichment in sediments along the Aegean Sea including Turkey and Greece.

**Table 5.3** Studies assessing metal accumulation in sediments along the Aegean Sea. Metal concentrations (μg $g^{-1}$ dw) are reported depending on data provided from within the studies as either mean value ±SD, range (), or both. Values in bold indicate that sediments were considered either contaminated or enriched by the study

| Location | Hg | Cd | Pb | References |
|---|---|---|---|---|
| Turkey (Black Sea) | – (–) | – (0.02–0.9) | – (<0.05–84.2) | Balkıs et al. (2007) |
| Turkey (Saros Gulf) | – (0.07–0.19) | – (0.01–0.04) | – **(3.9–48.2)** | Uluturhan (2010) |
| Turkey (Gokova Gulf) | – (0.07–0.17) | – (0.01–0.05) | – **(10.0–21.8)** | Uluturhan (2010) |
| Turkey (Nemru Bay) | – **(1.70–9.6)** | – (0.005–0.25) | – **(22.3–89.4)** | Esen et al. (2010) |
| Turkey (Homa Lagoon-Izmir) | 0.33 ± 0.08 (0.22–0.48) | 0.107 ± 0.03 (0.06–0.19) | 10.49 ± 5.05 (2.43–17.2) | Uluturhan et al. (2011) |
| Turkey (Izmir Bay-Outer) | – (0.05–0.99) | – (0.005–0.25) | – (9.8–119) | Kucuksezgin et al. (2011) |
| Turkey (Izmir Bay-Inner) | – (0.12–1.3) | – (0.01–0.82) | – (3.1–94) | Kucuksezgin et al. (2011) |
| Turkey (Sea of Marmara) | – (–) | – (–) | 32.9 (9.1–73.1) | Otansev et al. (2016) |
| Turkey (Eastern Black Sea) | – (–) | – (–) | 97.33 ± 3.2 (3.7–177.75) | Baltas et al. (2017) |
| Turkey (Black Sea) | – (–) | – (0.5–14.3) | – (17–129) | Sarı et al. (2018) |
| Turkey (Edremit Bay) | – (0.03–017) | – (0.10–0.27) | – (5.32–47) | Kontas et al. (2020) |
| Greece (Athens Sewage Outfall) | – (0.38–3.1) | – (–) | – (–) | Papakostidis (1975) |
| Greece (Thermaikos Gulf ) | – (2.9–8.88) | – (0.87–1.08) | – (20.9–27.8) | Fytianos and Vasilikiotis (1983) |
| Greece (Strymonikos and Ierissos Gulf) | – (–) | – (–) | 61.9 (23.4–92.5) | Stamatis et al. (2002) |
| Greece (Thermaikos Gulf) | – (–) | – (–) | 72 (10–218) | Christophoridis et al. (2009) |
| Greece (Alexandroupolis Gulf) | – (–) | – (–) | 50.5 ± 30.1 **(9–113)** | Karditsa et al. (2014) |
| Greece | – (–) | – (–) | 166.23 (–) | Stamatis et al. (2019) |
| Greece (Kavala Gulf) | – (–) | – (–) | 52.79 ± 36.21 (18.12–203.28) | Stamatis et al. (2019) |
| Greece (Strymonikos Gulf) | – (–) | – (–) | 91.1 ± 35.06 (23.41–130.46) | Stamatis et al. (2019) |
| Greece (Ierissos Gulf) | – (–) | – (–) | 637.66 ± 713.82 (52.91–2233.09) | Stamatis et al. (2019) |
| Greece (Thessaloniki Bay) | – (–) | **2.51 (0.2–13)** | **84.19 (29.4–195.4)** | Christophoridis et al. (2019) |
| Greece (Saronikos Gulf) | – (–) | – (–) | **69 ± 69 (5–374)** | Karageorgis et al. (2020) |

## Turkey (Aegean Sea)

Expanding on the background provided in Turkey in the Levantine Basin section, the Turkish regions relevant to the Aegean Sea include the Aegean, Marmara, and Black Sea regions. These regions are collectively highly influenced by anthropogenic activity, with major urbanization and industrialization. Many rural areas have rapidly developed over the years due to tourism, often without adequate infrastructure to accommodate its expansion (Ozsoy et al., 2016). Maritime traffic is particularly prominent in this region, with Turkey bordering a large segment of the Black Sea as well as the entire Sea of Marmara. The major Turkish port sitting directly on the Aegean Sea is the Izmir Port, which also hosts a major oil terminal. However, the bulk of maritime movement is seen in the Marmara Sea, with major ports including Port of Haydarpaşa (Istanbul) and numerous oil terminals. With the major industrial activities taking place in both the Black and Marmara Sea area (Ozsoy et al., 2016), these basins can act as pollution accumulation points and as a secondary pollutant source into the Mediterranean Sea. Additionally, the behavior of the currents in the Aegean Sea bring pollutants from the rest of the Aegean Sea as well as the Mediterranean towards Turkey's Aegean region (Izdar et al., 2015). These regions also encompass large catchment areas with high urbanization, resulting in fresh water drainages to the sea acting as transport of land-based pollutants (Izdar et al., 2015). Istanbul, in particular, has been noted as a major polluter to this area with over 60% of its industry directly located on the coast of the Sea of Marmara.

Investigations in the Aegean region of Turkey have focused on metals in industrialized areas and harbors rather than pristine regions along the coast. Particular focus has also been placed on the Black and Marmara Sea and have been shown to accumulate metals in their surface sediments (Balkıs et al., 2007; Otansev et al., 2016; Sarı et al., 2018). Through sediment cores, a major increase in metals was shown to have taken place in the 1970s/1980s as anthropogenic activities increased in this area (Sarı et al., 2018). In addition to the direct industrial and domestic waste acting as a major contributor (Otansev et al., 2016) pollution sources are not only local, and European rivers have been shown to act as a means of transport to the western and north-western Black Sea (Sarı et al., 2018). Such studies emphasize how the Black and Marmara Seas act as accumulation points and are a source of metals into the Aegean Sea. Looking directly at the Aegean Sea, the coastal areas are less industrialized compared to the Black Sea. One of the largest Turkish cities on the Aegean coastline, Izmir, is home to Izmir Bay which is a major commercial harbor and a release point of domestic wastewater discharge (Katagan et al., 2015). The bay was found to have enriched levels of Hg from mining and enriched levels of Pb due to previous use of leaded fuels (Kucuksezgin et al., 2011). In comparison, the less industrialized Edremit Gulf showed a decrease in Pb levels since the early 1990s, which has been reported to be potentially related to the removal of leaded gasoline in Turkey since 2005 (Kontas et al., 2020). The Homa Lagoon, located near to Izmir Bay, is one of the most productive lagoons in the Eastern Aegean Sea, and has important ecological and economic value for the area. Despite no point sources of Hg, Cd, and Pb pollution observed in the area, sediments contamination was reported to originate from landlocked cities via the Gediz River.

## Greece (Aegean Sea)

Greece has an extensive coastline estimated to exceed 18,000 km (Simboura et al., 2018). Due to the extent of its thousands of islands, a majority of the Aegean Sea is filled with Greek islands. Greek waters are considered rich in biodiversity and are an important resource for the country (Simboura et al., 2018). A majority of its southern islands, categorized by a high quality ecological status, with much of the Greek Aegean coastline categorized with good to high ecological status (Simboura et al., 2018). However, the Greek coastline is highly urbanized with over a third of the population living just a few kilometers from the coast. Similar to other regions, such intense coastal urbanization developed without accommodating adequate infrastructure (Simboura et al., 2018). The major Aegean coastal cities include Athens, Thessaloniki, and Volos also act as important ports for the region. These city ports are important industrial areas, with over 80% of the industry taking place in these urban centers (Simboura et al., 2018). Land-based pollution sources include electric power plants, sewage treatment plants, industrial waste, and agricultural activity (Simboura et al., 2018). With many small communities around the Aegean Sea, especially on islands, domestic wastewater is required to undergo at least secondary treatment for population sizes exceeding 2,000, yet this requirement is not always complied with (Simboura et al., 2018). Many of the major river catchments that reach the Aegean Sea along the Greek coastline are trans-boundary, originating in other countries (Simboura et al., 2018). The use of the marine realm in Greek culture is highly important, with intense ship traffic and the marine based pollution that comes with it. There are over 900 ports (22 international) throughout Greece that are important in both international trade and connecting more than 100 inhabited islands to important resources (Simboura et al., 2018). Harbors and ports are a major source of pollution from the mechanical activity that takes place there. Additionally, the marine transport of liquid goods like oil and energy products are a dominant trade (Simboura et al., 2018).

Similar to Turkey, pristine areas from Greece are also data deficient. With Greek ports acting as major centers of urbanization, industry, and maritime traffic, they are a major focus in sediment research. The Saronikos Gulf, home to the busiest Greek port Piraeus (Athens), presents enriched Pb levels that have been decreasing over the past 20 years due to tougher pollution management policies (Karageorgis et al., 2020). The second largest Greek Port in Thessaloniki, has been frequently assessed and shows that sediments are heavily polluted with both Cd and Pb (Christophoridis et al., 2019). Unlike in the Levantine Basin and North African coast, an active mining industry still exists in Greece. Mining activity often requires coastal access to load and transfer raw materials. With mining comes effluent discharge directly from the mining operations, and marine sediments around unloading terminals have been shown to be enriched with Pb (Stamatis et al., 2019). Recently, fish framing has become more pronounced throughout the basin, with research indicating that metals such as Cd and Pb are enriched directly below the cages (Kalantzi et al., 2013; 2021). In a similar trend within harbors, concentrations of metals below the cages decrease with distance from the point source.

## ADRIATIC-IONIAN SEA

The Adriatic Sea is a shallow, semi-closed sea situated between the Apennine and Balkan Peninsulas. It comprises 5.6% of the Mediterranean Sea, and is considered its most extensive gulf, connected by the Straits of Otranto in its southern limits. Six countries border the Adriatic Sea including Italy (1,272 km coastline) to its west, and to its east Slovania (47 km), Croatia (5,835 km), Bosnia and Herzegovina (21 km), Montenegro (294 km), and Albania (406 km) (Joksimović et al., 2021). Similar to the Aegean Sea, the Adriatic is full of islands (over 1,200) that are mostly located on the eastern coastline. Over 20 large rivers flow into the Adriatic, most significant being Italy's Po River, which is responsible for a third of the freshwater and a fourth of the sediment input into the Adriatic Sea (Lopes-Rocha et al., 2017). Due to the environmental conditions, the Adriatic Sea is considered rich with over 7,000 marine species (Zonn et al., 2021) and is a habitat for numerous endemic species in addition to endangered species. The richness of this habitat is expressed through the importance of fishing in the region, especially in the northern Adriatic (Zonn et al., 2021). A large population dwells along the Adriatic coastline, approximately 3.5 million people, with major cities including Italy's Bari, Venice, Trieste, Ravenna, and Rimini; Croatia's Split, Rijeka, and Zadar; Albania's Durrës and Vlorë; Slovenia's Koper; and Montenegro's Budva and Bar (Zonn et al., 2021). The Northern Adriatic is considered particularly urbanized with pollution hotspots in Italy, Slovenia, and Croatia (EEA, 2006). Intense urbanization in this area, especially due to the encouragement of tourism, has been connected to inadequate infrastructure management of coastal areas. Ports also play an important role in this region, 19 major ports, with Trieste in Northern Italy being the largest (Zonn et al., 2021). Large bays in the region include the Gulf of Venice, Gulf of Trieste, Gulf of Manfredonia, and Bay of Kotor. A unique problem in this area are obsolete chemical stockpiles (EEA, 2006) as well as marine buried chemical weapons from WWII (Zonn et al., 2021). Directly south of the Adriatic Sea, divided by the Straits of Otranto, lies the Ionian Sea, which is highly influenced by the Adriatic Sea. It is bounded by southern Italy to its west, and southern Albania and Greece to its east. From all the sub-basins withing the Mediterranean Sea, it is the deepest and reaches a depth of 5,000 meters (UNEP/MAP, 2012). The shoreline is characterized by mostly rocky shores with occasional coarse beaches (Rivaro et al., 2004). Unfortunately, the literature describing the overall marine ecology of this area is highly lacking.

Metal research in the Adriatic Sea is dominant on its western side (Italy) compared to east and is summarized in Figure 5.5 and Table 5.4. Additionally, much research is focused on the northern Adriatic where major pressures are located including the Po River, in addition to a more developed coastal industry.

With rivers in the Adriatic holding such importance in the area, understanding the potential transfer of metals, especially with fine sediments, has been prioritized. The Po River has been shown to have an impact on not only the coastal sediments of the areas surrounding the Po River Delta, but of the entire Adriatic Sea, with a contamination signal taking 10 years to reach the southern Adriatic Sea (450 km south) (Lopes-Rocha et al., 2017). By the Otranto Strait, where the Aegean meets the Ionian Sea, the signal reduces to background levels. Anthropogenic contaminants are shown to reach the Po River from land-based sources, with sediments from tributaries of the Po River (like the Lambro River) showing elevated Pb, Hg, and Cd (Marziali et al., 2021). However, with Italy establishing regulations on wastewater treatment in the mid 80s, the signal intensity of the region has gradually decreased over time (Lopes-Rocha et al., 2017). In Albania, rivers have been shown to be a source of metal pollution from mining activities up-stream, though the coastal Pb in sediments did not appear to be enriched by this output (Rivaro et al., 2004). A long-term study conducted in Italy shows the enrichment in the coastal sediments began around 1910s, potentially associated with the industry surrounding World War I (Lopes-Rocha et al., 2017). Enrichment of Pb was shown to be related to shipping activity, particularly around shipyards and marinas (Obhodaš and Valković, 2010). Lead in the sediments collected from the Sicilian Channel were also attributed to the ship traffic in the area (Tranchida et al., 2010). In Croatia, enriched Pb levels were attributed to an oil terminal, though levels have noticeably decreased with the elimination of leaded fuels (Cukrov et al., 2011). In regard to Hg, numerous studies conducted in the area focus on the historical release of Hg from industry and the residual levels and enrichment that it continues to have today. Point sources identified include oil terminals (Cukrov et al., 2011), sewage outflow (Cukrov et al., 2011), mining enrichment (Acquavita et al., 2012; Covelli et al., 2001) and chlor-alkali plants (Acquavita et al., 2012). Such combination of sources makes areas like the Marano-Grado Lagoon (Italy) hotspots for metal accumulation and will continue to act as a secondary source for many years to come.

Studies in the Ionian Sea are highly lacking, with research coming mostly from Italy summarized in Figure 5.6 and Table 5.5. Hotspots within the Ionian Sea include Taranto Bay and Sicily's Augusta Harbor (EEA, 2006), both considered highly industrialized areas. Taranto Bay, in particular, is considered by the Italian government as an area of high environmental risk (Di Leo et al., 2013) with the presence of steel factories, petroleum refineries, marine traffic, and urban waste. Mercury pollution in the bay has been considered problematic (Di Leo et al., 2013; Spada et al., 2012) with military areas, harbors, and shipbuilding work considered major contributors. Augusta Harbor became a major industrial center following WWII, considered an European petro-chemical hub (Romano et al., 2021), with an active chlor-alkali plant active between 1958–2003. Additionally, breakwater construction enclosing the bay has led to the entrapment of fine terrestrial sediments that also allow for the accumulation of metals within the bay (Romano et al., 2021) and can act as a secondary source of metal pollution. Despite the high bioaccumulation factor of Cd and Hg within these sediments, sediment contamination alone was shown to not be sufficient enough to lead to biological transfer, and the sediment's physicochemical properties was reported to be a major driving force (Signa et al., 2017). Though not within the Ionian Sea itself, the Straights of Sicily have shown overall low Hg levels, yet are still considered enriched (Di Leonardo et al., 2006; Tranchida et al., 2010).

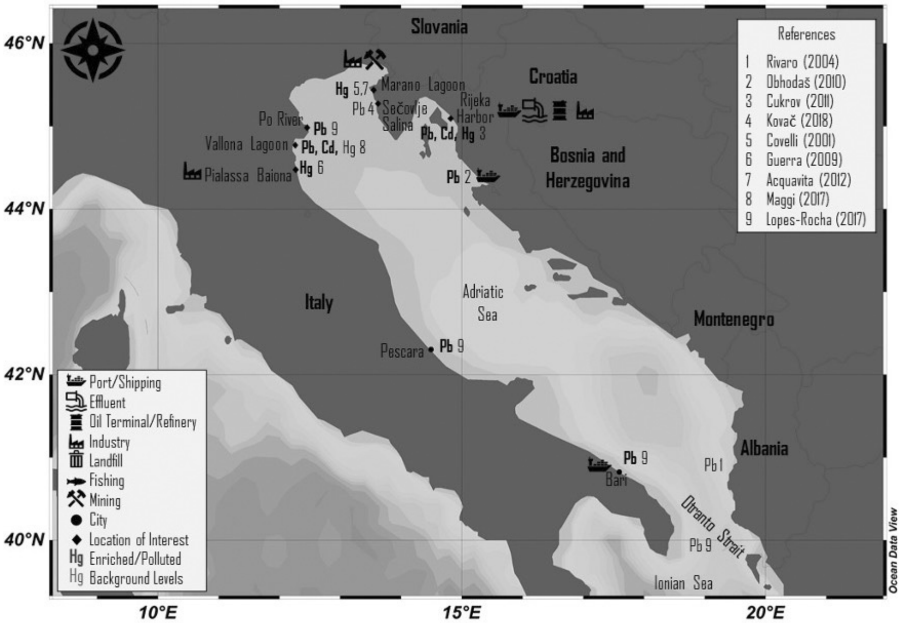


**Figure 5.5** Metal enrichment in sediments along the Adriatic Sea including Italy, Slovania, Croatia, Bosnia and Herzegovina, Montenegro, and Albania.

Compared to the other countries in the area, studies from Italy have given great attention to investigating metal accumulation in sediments from both the Adriatic and Ionian Sea. Italy recognizes the intense and uncontrolled industrialization that took place following World War II as a major influence on the accumulation of marine pollutants of all kinds in their local waters. While most sediment-oriented studies focus on the surface sediments around particular hotspots to provide insight on specific point sources, Italy has provided numerous long term monitoring studies that evaluate the change of metal levels over longer time periods, some even dating back to 1920s (following World War I). These studies provide immense input, and have allowed for the proper legislative measures to be established. Distinctively, from all the papers reviewed throughout the entire Eastern Mediterranean region, studies from Italy describe the Environmental Quality Standard for the metals Pb, Hg, and Cd in marine sediments and coastal zones as established by the Italian Parliament. With defined measures and strict legislation in place, Italy has actively reduced metal discharge into the Adriatic-Ionian Sea (Lopes-Rocha et al., 2017).

**Table 5.4** Studies assessing metal accumulation in sediments along the Adriatic Sea. Metal concentrations (μg $g^{-1}$ dw) are reported depending on data provided from within the studies as either mean value ±SD, range (), or both. Values in bold indicate that sediments were considered either contaminated or enriched by the study

| Location | Hg | Cd | Pb | References |
|---|---|---|---|---|
| Albania (Coastline) | – (–) | – **(0.07–0.753)** | – (22–69) | Rivaro et al. (2004) |
| Croatia (Coastline) | – (–) | – (–) | 9.8 (2.1–65.6) | Obhodaš et al. (2010) |
| Croatia (Rijeka harbor) | **2.2 ± 1.99 (0.1–8.06)** | 1.07 ± 0.87 (0.14–4.66) | **227 ± 152 (23.6–637)** | Cukrov et al. (2011) |
| Slovania (Sečovlje Salin) | – (–) | – (–) | 24.88 ± 2.97 (20.32–28.29) | Kovač et al. (2018) |
| Italy (Isonzo River Mouth – Gulf of Trieste) | **5.04 (0.06–30.38)** | – (–) | – (–) | Covelli et al. (2001) |
| Italy (Pialassa Baiona lagoon) | – (0.4–5.5) | – (–) | – (–) | Guerra et al. (2009) |
| Italy (Marano & Grado Lagoon) | – (0.68–9.95) | – (–) | – (–) | Acquavita et al. (2012) |
| Italy (Vallona Lagoon) | – (0.01–0.27) | – **(0.09–0.58)** | – **(4.7–31.05)** | Maggi (2017) |
| Italy (Po River Delta) | – (–) | – (–) | **28 ± 6 (13–39)** | Lopes-Rocha et al. (2017) |
| Italy (Pescara) | – (–) | – (–) | **16 ± 3.6 (11–26)** | Lopes-Rocha et al. (2017) |
| Italy (Bari) | – (–) | – (–) | 24 ± 4 (19–36) | Lopes-Rocha et al. (2017) |
| Otranto Strait | – (–) | – (–) | 11 ± 2 (9–18) | Lopes-Rocha et al. (2017) |

**Table 5.5** Studies assessing metal accumulation in sediments along the Ionian Sea. Metal concentrations (μg $g^{-1}$ dw) are reported depending on data provided from within the studies as either mean value ±SD, range (), or both. Values in bold indicate that sediments were considered either contaminated or enriched by the study.

| Location | Hg | Cd | Pb | References |
|---|---|---|---|---|
| Italy (Taranto Gulf) | 0.12 (0.04–0.41) | – (–) | 57.8 (44.7–74.8) | Buccolieri et al. (2006) |
| Straits of Sicily | **48 (15–70)** | – (–) | – (–) | Di Leonardo et al. (2006) |
| Italy (Sicily-Augusta Industrial Area) | – **(0.02–1.67)** | – (–) | – (–) | Di Leonardo et al. (2008) |
| Italy (Taranto Gulf) | – **(0.10–1.79)** | – (0.12–0.17) | – (14.28–29.19) | Di Leo et al. (2013) |
| Italy (Taranto Gulf) | **2.7 (0.04–7.73)** | – (–) | – (–) | Signa et al. (2017) |

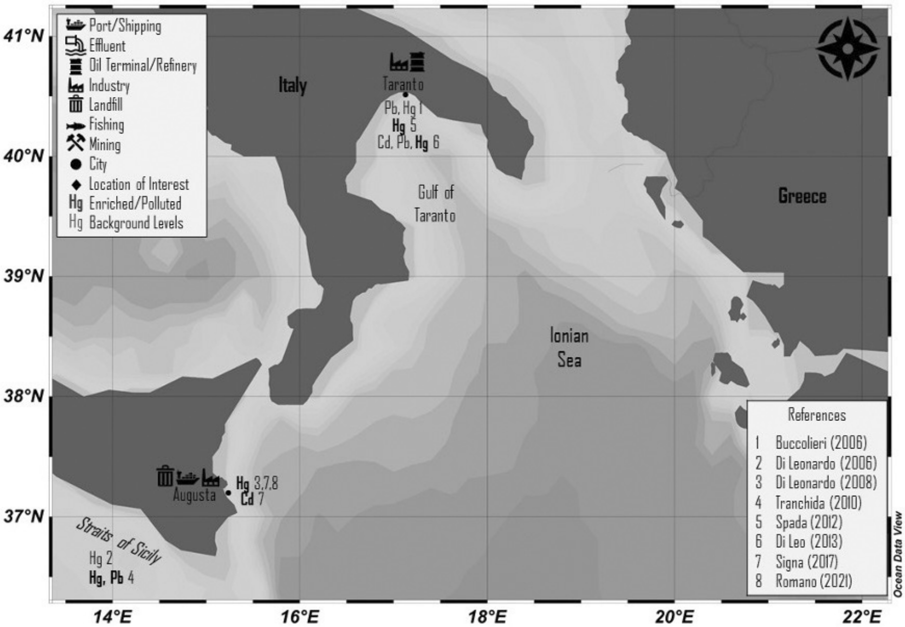


**Figure 5.6** Metal enrichment in sediments along the Ionian including Italy and Greece.

# CONCLUSION

This chapter provides a brief summary on the accumulation of metals in the coastal sediments of the EMS. While pollution inputs are influenced by the unique socio-economic conditions of each country, there are evident similarities between studies of different sub-regions. Areas of high industrial and economic importance are a major research focus in all countries, and indeed show enrichment of metals as a result. Unfortunately, many pristine areas that could provide a baseline comparison are lacking in almost all countries of the EMS. Even basic information describing the marine environment for this region is highly lacking, emphasizing the importance of further research efforts in the future. Major reviews per individual country are also lacking, and summaries of basin wide pollutants are mainly conducted by bodies like the United Nation Environmental Program. Another major issue, which is just briefly touched upon throughout this chapter, is legislation. With many different countries belonging to multiple continents using the Mediterranean Sea, uniform legislation is challenging. Despite this obstacle, the Barcelona Convention (The Convention for the Protection of the Mediterranean Sea Against Pollution) aims to reduce eliminate pollution in the Mediterranean Sea and protect the marine environment. From the EMS, all countries are contracting parties of the Barcelona Convention including Albania, Bosnia and Herzegovina, Croatia, Cyprus, Egypt, Greece, Israel, Italy, Lebanon, Libya, Malta, Montenegro, Slovenia, Syria, Tunisia, Turkey, and the European Union. On a final note, it is important to emphasize that sediment studies can provide highly important information regarding the accumulation of metals in local sediments in a way that is relatively feasible logistically. There are also uniform standards that have been accepted internationally regarding both protocols and measurement indexes that indicate sediment pollution or enrichment. However, sediment contamination does not always equate to biological transfer. Therefore, in regard to ecotoxicology, while acceptable concentrations in food stuffs exists for marine organisms, ecotoxicological context is indeed lacking.

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# Chapter 2: A survey of arsenic, mercury, cadmium, and lead residues in seafood (fish, crustaceans, and cephalopods) from the south-eastern Mediterranean Sea

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## A survey of arsenic, mercury, cadmium, and lead residues in seafood (fish, crustaceans, and cephalopods) from the south-eastern Mediterranean Sea

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# A survey of arsenic, mercury, cadmium, and lead residues in seafood (fish, crustaceans, and cephalopods) from the south-eastern Mediterranean Sea

Debra Ramon, Danny Morick, Peter Croot, Ran Berzak, Aviad Scheinin, Dan Tchernov, Nadav Davidovich, and Malka Britzi

**Abstract:** Seafood is capable of bioaccumulating heavy metals (HM), making it a potentially major dietary source of HM for humans. Presently, little data exists on seafood from the eastern-most boundary of the Mediterranean Sea. This study aims to provide exposure insight of the Israeli population to HM through the consumption of locally caught seafood by assessing the levels of arsenic, mercury, cadmium, and lead in raw tissues of seafood. A wide survey of local fisheries was conducted providing 296 samples from 11 different species, including seven fish, two crustacean, and two cephalopod species. Total arsenic, cadmium, and lead were analyzed by graphite-furnace atomic absorption. Total mercury was measured by cold-vapor mercury analyzer. Arsenic speciation was performed by anion chromatography-inductively coupled plasma sector field mass spectrometry. Results suggested that the total arsenic concentrations were significantly higher in crustaceans and cephalopods than fish. Arsenic speciation revealed two samples that exceed 1 mg/kg of inorganic arsenic, whereas methylated arsenic was below the detection limit. Elevated mercury levels were detected in the commercial benthic species *Mullus barbatus* (red mullet), cadmium was detected in one-third of the samples, and lead detected in eight samples. Comparing the results to health guidelines, 99.4% of seafood tested in this study abide with acceptable levels of heavy metals in seafood, as defined by both Israeli and European Union guidelines.

**Keywords:** arsenic, cadmium, lead, Mediterranean Sea, mercury, seafood

## 1. INTRODUCTION

The accumulation of heavy metals (HM) in marine organisms is an important environmental issue due to its ecological and public-health implications. HM are released into the marine system from either natural or anthropogenic activity (Millward et al., 2019), and are accumulated by marine organisms from their surroundings (Copat et al., 2012; McIntyre & He, 2019). The level of accumulation depends on a number of different environmental factors (Copat et al., 2012; Storelli & Marcotrigiano, 2001), as well as an organism's bioaccumulation capabilities and biomagnification up the trophic food chain (Millward et al., 2019). Consequently, such behavior has led to seafood acting as a vector for HM from the environment to humans through consumption (Millward et al., 2019; Ross et al., 2017) and may subsequently lead to negative health issues associated with HM exposure (Millward et al., 2019). Four HM are of particular concern due to their occurrence in the environment and impacts on public health and include arsenic (As), mercury (Hg), cadmium (Cd), and lead (Pb) (Ross et al., 2017). Exposure to these four HM has been acknowledged by the World Health Organization (WHO) as a major public-health concern with negative impacts, and acceptable intakes for each have been well-defined by the FAO (Food and Agricultural Organization)/WHO-Committee (WHO, 2007, 2010a, 2010b, 2019; WHO/FAO, 2011).

While HM research has been conducted throughout the Mediterranean Sea, more emphasis has been placed on the western and central basins, leaving many sections in the Eastern Mediterranean Sea (EMS) lacking in data (Cinnirella et al., 2013). Until now, research on seafood in the south-eastern section of the EMS has been briefly conducted in commercially-available seafood from Egypt (Ghani, 2015; Shreadah et al., 2015), Gaza (Palestine) (Elnabris et al., 2013), Lebanon (Micheline et al., 2019), and Israel (Herut et al., 2012; Krom et al., 1990; Roth & Hornung, 1977). In the coastal marine waters of Israel, past HM inputs had been mostly attributed to industrial wastewater discharge, while current inputs are primarily associated with agricultural runoff (Herut et al., 2003). Locally, long-term monitoring of HM in the marine system has been conducted since 1978 by the Israel Oceanographic and Limnological Research (IOLR) station through the National Monitoring Program (Herut et al., 2012; Roth & Hornung, 1977; Shoham-Frider et al., 2017). While certain areas have been identified as hotspots for anthropogenic pollution, a decreasing trend has been observed since the 1980s due to the reduction of HM discharge following the implementation of environmental restrictions (Israel's National Action Plan (NAP), 2015). With increased national enforcement, HM release into the Mediterranean Sea from land-based sources in Israel has decreased by over 99% from

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Table 1–Characteristics and sampling size of target species.

| Seafood category | Species | Common name | Habitat | Prey | Biological niche | Average length (cm) | Average weight (g) | Sample size |
|---|---|---|---|---|---|---|---|---|
| Fish | *Lithognathus mormyrus* | Striped seabream | Demersal | Invertebrates | Nectobenthic carnivorous | 17.54 ± 1.29 | 73.7 ± 20.33 | 34 |
| | *Mullus barbatus* | Red mullet | Demersal | Benthic invertebrates | Demersal omnivorous | 20.25 ± 2.67 | 89.27 ± 37.39 | 8 |
| | *Mullus surmuletus* | Striped red mullet | Demersal | Benthic invertebrates | Demersal omnivorous | 17.35 ± 1.34 | 62.7 ± 15.42 | 27 |
| | *Nemipterus randalli* | Randall's threadfin bream | Demersal | Benthic invertebrates | Benthopelagic carnivorous | 19.73 ± 3.1 | 88.53 ± 28.43 | 26 |
| | *Sardinella aurita* | Round sardinella | Pelagic | Zooplankton | Pelagic zooplanktivorous | 17.68 ± 2.58 | 47.17 ± 18.9 | 21 |
| | *Saurida lessepsianus* | Brushtooth lizardfish | Benthopelagic | Fish | Demersal piscivorous | 27.89 ± 5.09 | 109.84 ± 59.82 | 41 |
| | *Upeneus moluccensis* | Goldband goatfish | Demersal | Invertebrates | Demersal omnivorous | 14.57 ± 1.26 | 34.49 ± 10.06 | 23 |
| Crustacean | *Marsupenaeus japonicus* | Kuruma shrimp | Benthic | Benthic invertebrates | Benthic omnivorous | 36 ± 48.84 | 37.74 ± 12.2 | 19 |
| | *Portunus pelagicus* | Blue swimming crab | Benthic | Benthic invertebrates | Benthic omnivorous | 12.92 ± 1.33 | 165.35 ± 50.14 | 39 |
| Cephalopod | *Loligo vulgaris* | European squid | Benthopelagic | Fish | Neritic carnivorous | 14.52 ± 2.52 | 63.27 ± 19.1 | 35 |
| | *Sepia officinalis* | Common cuttlefish | Demersal | Invertebrates and fish | Neritic carnivorous | 12.15 ± 2.34 | 252.98 ± 140.05 | 23 |

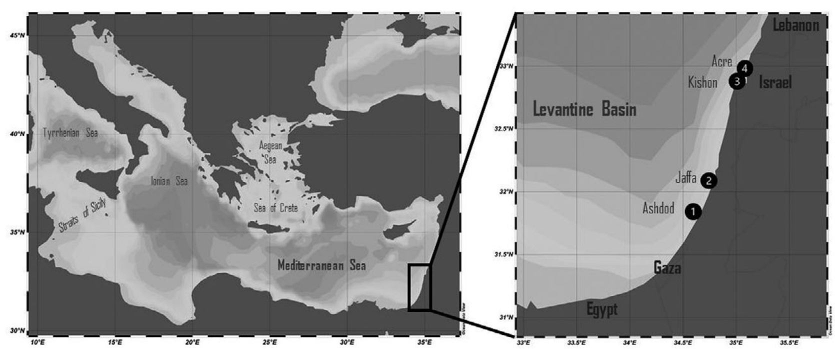


Figure 1–The sampling locations along the Israeli coastline: 1 Ashdod, 2 Jaffa, 3 Kishon, and 4 Acre. Map originated using ODV software (https://odv.awi.de/).

1998 to 2017 (207,588 to 2,017 kg yr$^{-1}$, respectively) (Malster, 2019).

Despite this reduction, HM have been reported in commonly caught commercial fish species from Israeli waters (Roth & Hornung, 1977), though these studies are limited and require further investigation. In 2003, the FAO released guidelines defining the permissible concentrations of Hg, Cd, and Pb in select fish species (FAO, 2003) and have been adopted internationally including the European Commission (2006), the Australia–New-Zealand Food Standards Code (2015), and the Israeli Veterinary Services (IVS) Guidelines (2020). To date, no in-depth biological assessment has been conducted to determine the level of contamination in Israeli local seafood. Our study aims to address this knowledge gap by conducting a comprehensive field study of seafood consumed by the local population and caught in local Israeli-waters. Here, we assess the bioaccumulation of the HM As, Hg, Cd, and Pb in seven fish species, two crustacean species, and two cephalopod species. This extensive survey acts as an initial investigation for most of these species in Israeli waters and can serve as a baseline for further HM research in Israel.

## 2. MATERIALS AND METHODS

### 2.1 Sampling sites and seafood sampling

Three different categories of seafood including fish, crustaceans and cephalopods were sampled for the aim of this study (Table 1). Seafood included fish species: striped seabream (*Lithognathus mormyrus*), red-mullet (*Mullus barbatus*), striped red-mullet (*Mullus surmuletus*), Randall's threadfin-bream (*Nemipterus randalli*), round-sardinella (*Sardinella aurita*), brushtooth-lizardfish (*Saurida lessepsianus*), and goldband-goatfish (*Upeneus moluccensis*); crustacean species: kuruma shrimp (*Marsupenaeus japonicas*), and blue swimming-crab (*Portunus pelagicus*); and cephalopod species: European squid (*Loligo vulgaris*), and common cuttlefish (*Sepia officinalis*). Collection took place between August 2016 to January 2017 from four major landing sites in Acre, Kishon, Jaffa, and Ashdod, all of which have an associated fish market (Figure 1). All specimens were locally caught by fishermen along the Israeli coastline and obtained by artisanal and industrial fishing methods. Specimens from Acre, Kishon, and Jaffa were collected directly from the fish markets, while those from Ashdod were collected through the IOLR's monitoring program via

Table 2–Mean, standard deviation, and range of heavy metals in the target species. Total values are provided for TAs, iAs, Cd, Hg, and Pb (mg/kg w.w.).

| | Mean concentration (Range) mg/kg w.w. | | | | |
|---|---|---|---|---|---|
| Species | Total As | iAs | Cd | Total Hg | Pb |
| *Lithognathus mormyrus* | 17.74 ± 23.39(0.78 to 78.64) | 0.18 ± 0.28(0 to 0.6) | 0 ± 0.02(0–0.1) | 0.11 ± 0.12(0 to 0.37) | 0 ± 0.01(0 to 0.08) |
| *Loligo vulgaris* | 36.63 ± 22.18(9.37 to 81.88) | 0.02 ± 0(0.01 to 0.03) | 0.04 ± 0.06(0 to 0.36) | 0.02 ± 0.05(0 to 0.12) | 0.01 ± 0.03(0 to 0.18) |
| *Marsupenaeus japonicus* | 51.18 ± 65.12(5.06 to 296.48) | 0.06 ± 0.02(0.04 to 0.08) | 0.09 ± 0.19(0 to 0.81) | 0.02 ± 0.05(0 to 0.13) | nd |
| *Mullus barbatus* | 9.14 ± 7.45(1.47 to 18.62) | 0.06 ± 0.03(0.03 to 0.09) | 0 ± 0.01(0 to 0.02) | 0.27 ± 0.17(0.16 to 0.65) | nd |
| *Mullus surmuletus* | 25.49 ± 23.05(4.52 to 74.7) | 0.07 ± 0.08(0 to 0.2) | nd | 0.06 ± 0.06(0 to 0.15) | nd |
| *Nemipterus randalli* | 30.75 ± 33.09(2.05 to 152.64) | 1.01 ± 1.68(0.04 to 3.52) | nd | 0.08 ± 0.07(0 to 0.23) | nd |
| *Portunus pelagicus* | 57.49 ± 54.9(5.2 to 184.6) | 0.41 ± 0.94(0.02 to 2.33) | 0.06 ± 0.11(0 to 0.52) | 0.08 ± 0.09(0 to 0.24) | nd |
| *Sardinella aurita* | 7.76 ± 6.68(0.47 to 17.73) | 0.06 ± 0.05(0.01 to 0.11) | 0 ± 0.01(0 to 0.02) | 0.01 ± 0.04(0 to 0.15) | 0 ± 0.01(0 to 0.05) |
| *Saurida lessepsianus* | 3.01 ± 1.8(0.69 to 10.26) | 0.02 ±0.02(0 to 0.05) | 0(0 to 0.016) | 0.07 ± 0.07(0 to 0.23) | 0 ± 0.01(0 to 0.06) |
| *Sepia officinalis* | 154.82 ± 74.51(77.04 to 333.8) | 0.02 ± 0(0.01 to 0.03) | 0.03 ± 0.03(0 to 0.1) | 0.03 ± 0.06(0 to 0.18) | nd |
| *Upeneus moluccensis* | 13.04 ± 11.9(1.69 to 58.92) | 0.18 ± 0.28(0 to 0.6) | 0(0 to 0.02) | 0.13 ± 0.1(0 to 0.35) | 0.01 ± 0.03(0 to 0.12) |

*MMA and DMA were below LOD (0.02 and 0.01 mg/kg ww, respectively) in all samples.
As, arsenic; iAs, inorganic As; MMA, monomethylarsonic acid; DMA, dimethylarsinic acid; Cd, cadmium; Hg, mercury; Pb, lead; nd, not detected.

trawl fishing. It should, therefore, be emphasized that fish collected from Ashdod have an exact GPS-location (31°49'8.12′′N, 34°30′31.6"E) and were confirmed caught just offshore of Ashdod, whereas no precise catch locations can be verified for the other three sampling locations. The number of specimens collected at each landing is provided in Supporting Information Table S1.

Following collection, all specimens were immediately placed on ice and brought directly to the laboratory, where weight and total length were measured. From each specimen, 50 g of edible sections were collected. Edible tissue of fish and cephalopods included muscle and skin in natural proportions, whereas crustaceans included only muscle without any exoskeleton. When a single specimen could not yield the required 50 g, muscle tissue from multiple specimens of the same species was pooled to produce a single sample. Overall, 492 specimens were collected in this study, with 308 categorized as fish, 94 as crustaceans, and 90 as cephalopods. Of the 296 samples analyzed, 133 were pooled samples, and 163 were single-specimen samples of 492 collected.

## 2.2 HM analysis

Analysis of total As (TAs), Cd, Pb, and total Hg (THg) were performed at the Kimron Veterinary Institute, Israel, with an in-house method, based on a method described earlier by Vieira et al. (2011). Arsenic speciation was performed at the ALS laboratories (ALS Scandinavia AB, Sweden). All methods utilized in this study are ISO-17025-accredited and concentrations are reported according to their wet-weight (w.w.).

**2.2.1 Digestion procedure for Cd, Pb, THg, and TAs determination.** Tissue samples (0.5 g) were digested with 4 mL concentrated nitric acid (TraceSELECT for trace analyses, Fluka, Licestershire, UK), 1 mL of concentrated hydrogen peroxide (26%, for trace analysis, Merck, Darmstadt, Germany) and 2 mL of purified water (type 1) obtained from a MicroPure Water Purification System (Thermo Scientific, Asheville, NC, USA). Digestion was performed in a quartz vessel, utilizing a Discovery SP-D model microwave (CEM Corp., Matthews, NC, USA). Samples were then further diluted with purified water for atomic absorption analysis (final dilution was 1:20 for TAs, Cd, and Pb; 1:200 for Hg).

**2.2.2 Analysis of Cd, Pb, TAs, and THg.** Analysis of Cd, Pb, and TAs was performed on AA600 atomic absorption, graphite furnace spectrometer (Perkin-Elmer, Waltham, MA, USA). The system included Zeeman background correction, and measurements were performed on end-capped graphite tubes with an integrated L'vov platform. Palladium was used as a matrix modifier for the three elements. An electrodeless discharge lamp was used for the analysis of TAs, and hollow cathode lamps were used for Cd and Pb measurements.

Analysis of THg was performed by a flow injection mercury system, FIMS 100 model (Perkin–Elmer, Waltham, MA, USA). The system incorporates a single peristaltic pump and a low-pressure Hg lamp. An automatic baseline offset correction was used before each measurement. Potassium permanganate 5% (20 μL) was added to all samples, including calibrators, as a matrix modifier. Sodium borohydride (0.2% w/v in 0.05% NaOH solution) was used as a reductant and 1% (v/v) hydrochloric acid solution was used as a carrier (all reagents purchased from Sigma-Aldrich, Saint Louis, MO, USA).

A calibration curve for each element was prepared in a blank solution containing acid percentage similar to the diluted samples and with taking sample dilution factor into consideration. The ranges of calibration curves were 10 to 100, 1.25 to 15, 5 to 40, and 0.5 to 7.5 ng/mL, for TAs, Cd, Pb, and Hg, respectively. These are equivalent to 0.2 to 2, 0.025 to 0.3, 0.1 to 0.8, and 0.1 to 1.5 mg/kg of TAs, Cd, Pb, and Hg, respectively, in sample. The certified reference material for canned fish purchased from FAPAS proficiency testing (FERA Science, York, UK) was utilized as a quality control (QC) sample for TAs, THg, and Cd measurement. Accuracy of QC samples was 93 ± 7%, 102 ± 6%, 96 ± 8%, and 95 ± 10%, for TAs, Cd, THg, and Pb, respectively. The detection limit (DL) refers to the concentrations in sample and were defined at 0.01, 0.05, 0.05, and 0.1 mg/kg for Cd, Pb, THg, and TAs, respectively.

**2.2.3 Arsenic speciation.** Following TAs determination, 50 samples (Supporting Information Table S2) were sent to ALS laboratories (ALS Scandinavia AB, Sweden) for As speciation by YL911N anion chromatography system (Young Lin, Anyang-si, Gyeonggi-do, Korea), connected to Element2 inductively coupled plasma sector field mass spectrometry (ICP/SFMS) (Thermo Fisher Scientific, San Jose, CA, USA). Samples were analyzed for inorganic As (iAs) as As(III) and As(V), monomethylarsonic acid (MMA), and dimethylarsenic acid (DMA). The DL were 0.01, 0.01, and 0.02 mg/kg for iAs, DMA, and MMA, respectively.

### 2.3 Statistical analysis

Statistical analysis was conducted using SPSS v20. After determining a lack of normality with the data (Shapiro–Wilk's test), and nonsuccessful transformations were conducted, differences in metal concentrations between species and groupings were determined using the nonparametric Kruskal–Wallis test combined with Dunn's *post hoc* comparison. Statistical significance was considered when $P < 0.05$. Correlation tests were determined using Spearman's rank-correlation test. Data output falling below the DL were replaced with a zero in order to allow statistical analysis to be conducted (Analytical Methods Committee Analyst, 2001). Visual aids were created using R-3.6.2 (R-Core-Team, 2013) and modified in Inkscape-0.92 (Inkscape-Project, 2019).

## 3. RESULTS AND DISCUSSION

TAs, THg, Cd, and Pb were analyzed in 296 samples from 11 different species: seven fishes, two crustaceans, and two cephalopods (Table 1). The mean concentrations and ranges for each HM from all species are summarized in Table 2.

### 3.1 Arsenic

Unlike other HM assessed in the present study, TAs were above the DL across all samples (Figure 2), with mean concentrations and ranges varying between species (Table 2). Mean concentrations significantly differed among the three organism groups ($H = 116.096$, 2 d.f., $P < 0.001$), with the highest concentrations measured in crustaceans, followed by cephalopods, and then fish (Figure 2). Significant differences in TAs concentrations are observed between species ($H = 175.705$, 10 d.f., $P < 0.001$), with significantly higher concentrations in the crustacean species *Portunus pelagicus* and cephalopod species *S. officinalis* compared to others (Figure 3A). Such differences in As levels between seafood groups in the Mediterranean Sea have been previously reported by Ferrante et al. (2019), whose review of fresh seafood found higher As levels in molluscs compared to fish. Particularly, crustaceans and cephalopods have been reported to bioaccumulate greater As concentrations compared to other marine groups (Amlund & Sloth, 2011; Anacleto et al., 2009; Bonsignore et al., 2018; Filippini et al., 2018; Traina et al., 2019). While the typical upper limit for these two groups is defined at 49 mg/kg (Amlund, Sele & Sloth, 2011), the mean values observed for crustaceans and cephalopods in our study are an order of magnitude higher than this limit (Table 2). *Sepia officinalis* levels in our study were particularly high, 16 times more than that of the reported averages for the same species in Portugal (Atlantic Ocean) (Anacleto et al., 2009). This is comparable with an Italian study which revealed a similar pattern with cephalopods having elevated concentrations (Cirillo et al., 2010). With regards to human safety, crustacean shells may play an important role in As accumulation. While shells are not considered an edible part of seafood, shellfish is often prepared for consumption with shells intact, and should be considered as some studies suggest the potential conversion of organic arsenic into iAs following thermal processing or gastrointestinal digestion (Ho & Redan, 2020; Liao et al., 2018) thus leading to a potentially higher exposure.

Of the 296 samples, 50 were further subjected to As speciation of iAs (including As(III) and As(V)), DMA, and MMA, as summarized in Supporting Information Table S2. From this, 48 were found to contain iAs concentrations below 1 mg/kg, ranging between 0.01 to 0.6 mg/kg, while two samples exceeded this value: *N. randalli* at 2.52 mg/kg and *P. pelagicus* at 2.3 mg/kg. Within the different chemical forms of As, toxic iAs has been previously reported to have a greater bioavailability in the Mediterranean Sea (Ferrante et al., 2019). In the current study, DMA and MMA were below DL in all samples, whereas iAs concentrations ranged between 0.01 to 3.52 mg/kg (Table 2). The toxic species, iAs, has a lower detected presence in fish and are reported to contribute less than 10% to the TAs composition (Storelli & Marcotrigiano, 2001) and are often found in lower ranges of 0.5% to 3% (Storelli & Marcotrigiano, 2000; Traina et al., 2019; Zhang et al., 2012). In the current study, iAs contribution ranged between 0.01% to 7.4% of the TAs (Table 2). The majority of TAs may be attributed to the nontoxic organic form arsenobetaine (AsB), which is the most commonly observed form of As in marine organisms and recognized commonly as "fish arsenic" (Edmonds et al., 1997; Francesconi, 2010; Kalia & Khambholja, 2015). AsB in marine organisms has been reported to be the dominating chemical fraction, often exceeding 90% of TAs (Kalantzi et al., 2017; Ruttens et al., 2012; Zhang et al., 2017). In the Mediterranean Sea, AsB has been described within a wide range, such as 67% to 97% from Grecian waters (Kalantzi, Mylona, Sofoulaki, Tsapakis, & Pergantis, 2017), and 89% to 97% in Italian waters (Storelli & Marcotrigiano, 2001). According to the WHO, consumption of small quantities of seafood that contains the less toxic forms of As does not pose a threat to human health (WHO, 2019). However, as the marine arsenic cycle is not clearly understood, further research is required to understand the full toxicity of its chemical forms (EFSA, 2014). This is important due to the lack of accumulation predictability, with only three organism species from our study adhering to textbook bioaccumulation with size increase (Figure 4). While there were some significant correlations, this may be an artifact of grouping, as different size classes were collected at different landing site. Therefore, to better assess the local bioaccumulation patterns, more extensive studies will be needed in the future.

While it is possible that anthropogenic inputs are responsible for elevated As levels in the local seafood, it may actually be the unique set of environmental conditions in the EMS that is driving this accumulation. The environmental conditions of the EMS are characterized by low phosphate (Krom et al., 2010) and high salinity, potentially requiring marine organisms to up-

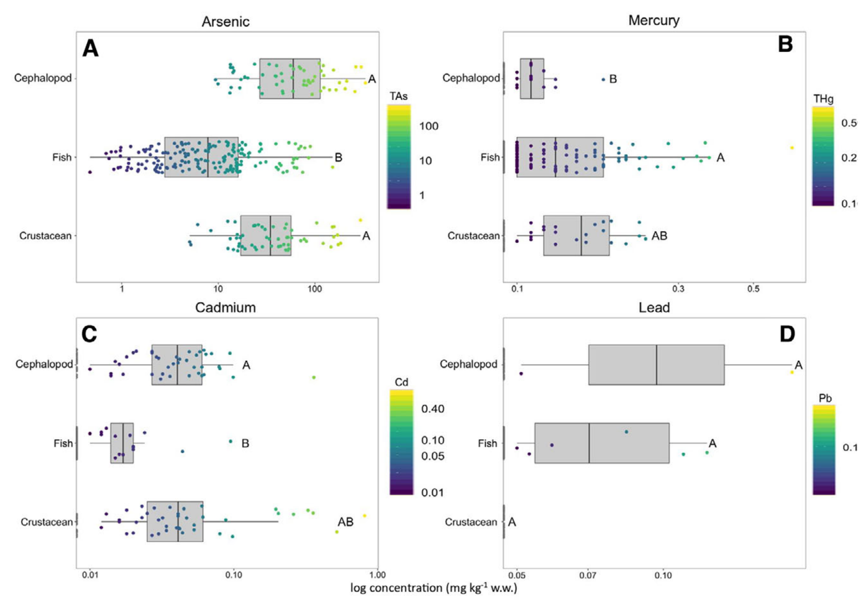


Figure 2–Box plot showing the differences in HM concentrations (mg $kg^{-1}$ wet weight) between cephalopods, fish, and crustaceans. (A) total As, (B) total Hg, (C) Cd, and (D) Pb. Note that data is presented in logarithmic scale. Capitalized lettering denotes significant differences between groups.

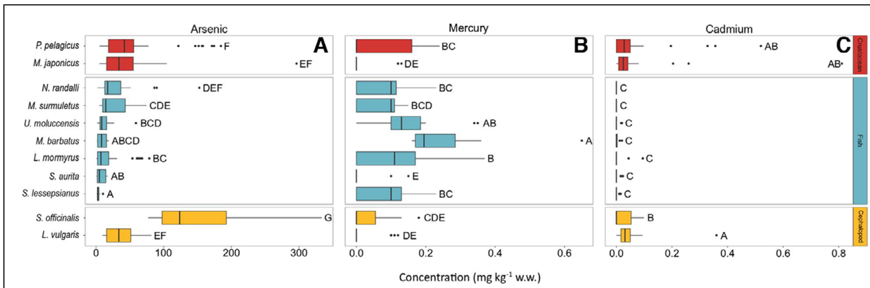


Figure 3–Box plot of heavy metal concentrations per species. Concentrations of (A) TAs, (B) THg, and (C) Cd per species. Significant differences between species are indicated by different uppercase letters ($P < 0.05$). Capitalized lettering denotes significant differences between groups.

take As via the phosphate pathway as an osmoregulatory substitute for phosphate, as supported by Wang et al. (2013). Therefore, this may have regional implications with seafood from the EMS possibly expected to have naturally higher As levels than corresponding species in the Western Mediterranean Sea and Atlantic Ocean.

## 3.2 Mercury

THg was detected in all species and measured above 0.1 mg/kg in 139 out of the 296 samples. Significant differences were observed between organism groupings ($H = 21.571$, 2 d.f., $P < 0.001$), with pairwise comparisons showing significantly higher concentrations in fish than in cephalopods ($P < 0.001$) (Figure 2B). However, while average crustacean concentrations were lower than those of fish, but higher than those of cephalopods, no significant differences between the organism categories were observed (Figure 2B).

Unlike As, Hg distribution and speciation in the marine environment has been generally well documented, with an adequate understanding of its accumulation patterns and ecological impacts. In Israel, Hg is one of the only metals with long term monitoring data, with assessments since the 1970s via the monitoring program of IOLR (Herut et al., 2012) (mostly within Haifa Bay). Generally, differences in THg bioaccumulation can be attributed to diet and exposure (Trudel & Rasmussen, 2006). Increasing trophic level and size (age dependent) have been shown to be positively correlated with Hg accumulation in fish muscle (de Almeida Rodrigues et al., 2019; Trudel & Rasmussen, 2006). In our study, species occupying a biological niche with a higher trophic level (such as *S. lessepsianus*) did not exhibit elevated concentrations of Hg in their muscle tissues compared to others (Figure 3B). While significant positive correlations between THg and body length were observed in *S. lessepsianus* ($r_s = 0.809$, 21 d.f., $P < 0.001$) and *P. pelagicus* ($r_s = 0.505$, 19 d.f., $P = 0.006$), for most species in this study, no significance to size and bioaccumulation were observed. This contrasts to Yannai and Sachs (1978), where trophic position and size did impact the THg concentrations, and carnivorous fish had higher levels than that of herbivorous and omnivorous fish.

Instead, our study shows that *M. barbatus*, an omnivorous fish strongly associated with bottom sediments and uses barbs to search for buried crustacean and annelid prey (Cresson et al., 2015), were found to have the highest concentrations (Figure 3B). Higher Hg levels in *M. barbatus* may be due to its habitat of coastal sediments, which are considered accumulation points for Hg originating from atmospheric and watershed inputs (Dijkstra et al., 2013). Sediments act as a target site for Hg methylation due to organic matter and microbial activity (Blum et al., 2013; Chouvelon et al., 2018; Spada et al., 2012), which is encouraged by resuspension of the sediments (de Almeida Rodrigues et al., 2019). As *M. barbatus* searches for prey, it suspends large amounts of sediments and exposes them to methylated Hg. Mullets have, therefore, been adopted as potential bioindicators of Hg pollution in the Mediterranean Sea (Cresson

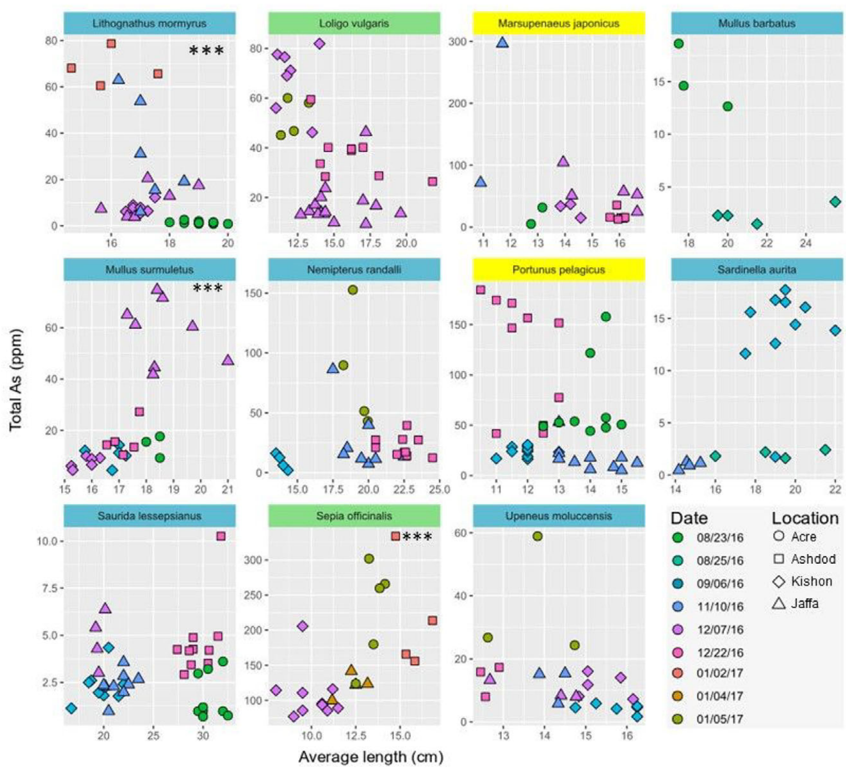


**Figure 4–Correlation of TAs concentration and fish length. Shapes indicate the sampling location, and its color fill indicates the sampling date.**

et al., 2015) and can be used to monitor human exposure from seafood reaching the local markets. While the chemical speciation of Hg is of great interest and can provide deeper insight, this was beyond the scope of our study.

When comparing this study to Israel's national monitoring program, two commercial fish species are common between them, *M. barbatus* and *L. mormyrus*. Results from the present study indicate higher concentrations than those recorded by the program (Herut et al., 2012). Average concentrations of THg in *M. barbatus* in this study are comparable to the higher concentrations observed from the monitoring program in 1980, a year of high Hg loading (approximately 0.25 μg/g w.w.). This loading was one order of magnitude higher following the environmental relaxation in 1991 (approximately 0.08 μg/g w.w.) (Herut et al., 2003), and two orders of magnitude higher than 2011 levels (0.004 μg/g w.w.) (Herut et al., 2012). This trend is similar in *L. mormyrus*, whose THg concentrations in our study (0.114 mg/kg) were two orders of magnitude higher than the IOLR's 2011 measurements (0.001 μg/g w.w.) (Herut et al., 2012). With *M. barbatus* utilized as a bioindicator for the entire Mediterranean Sea, these values are in relative agreement with concentrations observed in reports from other areas (Llull et al., 2017) such as the Sicily Channel (0.31 mg/kg w.w.) (Copat et al., 2012). In other areas along Israel's coastline, assessment of sediment samples revealed relatively low Hg concentrations except for key locations associated with waste water-release points (Herut et al., 2012).

Haifa Bay, where much of the seafood reaching the Kishon and Acre markets is caught (Figure 1), has undergone rapid industrialization since the 1950s and is now a major port and area of intense industrial development. The structure of the area surrounding the bay provides an ideal habitat for many fish species and is currently well fished by artesian fishermen. Between 1956 and 2003, effluents containing Hg were directly released by a chlor-alkali plant, resulting in a corresponding chemical signature observed in the bay's fish populations (Herut et al., 1996; Shoham-Frider et al., 2020). This raised concerns with respect to human health, and sales of the commercial fish white seabream (*Diplodus sargus*) from the bay were reduced between 1979 and 1981 (Krom et al., 1990). The discharge load has since decreased following enforced regulation by Israel, resulting in a relaxation in the Hg signature and environmental levels in the harbor have been deemed acceptable since 1991 (Herut et al., 1996, 2012). However, monitoring efforts by the national monitoring program have since discovered that current inactive chlor-alkali plants are still passively releasing Hg into the bay, resulting in sudden spikes of the chemical signature in marine biota caught from Haifa Bay (Shoham-Frider et al., 2020). With the potential of sudden acute exposure, this emphasizes the importance of consistent evaluations of seafood reaching the public from local fisheries.

## 3.3 Cadmium

Cd was detected in only one-third of the samples tested in this study ($n = 97$), with a general decreasing trend in crustaceans, molluscs, and finally fish (Figure 2C). Nine species contained Cd above the DL with averages and ranges displayed in Table 2. The highest concentration was measured in *Marsupenaeus japonicus* (Table 2). Significant differences between organism groups were observed ($H = 129.557$, 2 d.f., $P < 0.001$), with pairwise comparisons showing significant differences between cephalopods and fish ($P < 0.001$) (Figure 2C). Significant differences were observed between the different species ($H = 138.309$, 10 d.f., $P < 0.001$), with crustacean and cephalopod species displaying higher concentrations than fish species (Figure 3C). A single significant correlation between Cd and body length was observed for *S. officinalis* ($r_s = -0.405$, 11 d.f., $P = 0.027$).

Only a small hand full of surveys have been conducted for this region of the EMS (Duran et al., 2014; Elnabris, 2013; Micheline et al., 2019). However, it has been reported that coastal contamination is higher in some areas of the eastern basin compared to the central and western basin (Copat et al., 2015). Our study finds the contrary, with samples from this study showing lower concentrations with means below 0.1 mg/kg (Table 2). Fish caught off of Sicily, Italy, have been reported to have relatively high concentrations, averaging 0.37 mg/kg, with 60% of the specimens exceeding European Commission (EC) regulations (Copat et al., 2012). These high Cd concentrations were explained by a significant presence of industrial and agricultural activities in most of the studied sites (Copat et al., 2012). However, Cd concentrations in the marine environment appear to show an overall decreasing trend, with reported decreasing concentrations in specimens caught in Turkey, and it was concluded that Cd poses little threat to the health of the human population (Korkmaz et al., 2019). In Israel, marine Cd input has been associated with industrial emission via river discharge (NAP, 2015; Shefer et al., 2015). Similar to Turkey, IOLR's monitoring program has also reported a local decrease in Cd along the coastline, translating to decreasing concentrations of Cd in sediments, suspended material, and molluscs (Herut et al., 2012; Shefer et al., 2015). Therefore, an observed relaxation of Cd in marine biota could be expected as well.

### 3.4 Lead

Of all HM assessed in this study, Pb was the least prevalent, with only eight samples having concentrations above the DL (Figure 2). Concentrations were measured in (highest to lowest): *L. vulgaris*, *U. moluccensis, L. mormyrus, S. lessepsianus*, and *S. aurita* (Table 2). No significant differences were observed between organism groupings ($H = 1.999$, 2 d.f., $P = 0.368$) (Figure 2) or between species ($H = 9.425$, 10 d.f., $P = 0.492$), and no correlation assessments could be conducted between Pb and body length due to statistical limitations. The low Pb presence observed in our study is comparable to that of a fish survey conducted in Lebanon which found that Pb was lower compared to other areas of the Mediterranean Sea (Micheline et al., 2019), yet contrasts to fishes assessed in Gaza which were found to have levels of Pb exceeding acceptable levels by the EC (Elnabris, 2013). Over the past few decades, Pb emissions have dramatically decreased with the reduction in Pb-based gasoline and paint, resulting in significant declines in human blood Pb levels (WHO, 2010b). Similar to global trends, Israel has also seen a reduction in Pb emissions due to the ban on leaded gasolines, as well as the enforcement of nationwide standards of permissible concentrations in effluent discharge, industry, and irrigation, permitted discharge to seawater, and air emissions (United-Nations, 2010). Another major anthropogenic activity contributing to elevated Pb concentration in the surroundings is mining, which is not conducted in Israel. Overall, a decreasing trend in Pb concentrations has been observed in Israeli marine waters since 1996 (NAP, 2015). Turkish waters have also seen decreasing trends of Pb compared to previous years, with mean concentrations ranging between 0.16 and 0.91 mg/kg w.w. (Korkmaz et al., 2019), at least two orders of magnitude higher than our values (Table 2). Of the four HM assessed in this study, it appears that Pb is of the least concern regarding its accumulation in the local marine biota.

### 3.5 Human health

Standards for maximum levels (ML) of HM in consumed seafood have been established at both international and national levels (Supporting Information Table S3). Both WHO/FAO and the EC have defined ML for three of the HM: Hg, Cd, and Pb, yet no standards have been established for As (European Commission, 2006; WHO/FAO, 2011). The revised guidelines of the IVS have set ML for Cd, Hg, and Pb in seafood, yet exclude As (IVS, 2020). This comes as a concern since marine organisms have been well documented to accumulate high concentrations of As in their tissues (Azizur Rahman et al., 2012; Copat et al., 2015; Ferrante et al., 2019), with seafood recognized to contain higher levels compared to other consumed foodstuffs (Brandon et al., 2014; Francesconi & Edmonds, 1996; Miklavčič et al., 2013; Traina et al., 2019). With lacking guidelines on As, whether the levels seen in this study are indeed safe for human consumption remains open for debate. Regarding the other metals, only one sample of *M. barbatus* exceeded Hg ML, one sample of *M. japonicus* exceeded Cd ML, and no samples exceed the Pb ML. Therefore, with a contamination rate of only 0.6% exceeding ML, the local seafood appears to abide by national standards.

The FAO has listed consumption of fish in Israel as the third-highest among countries bordering the Mediterranean Sea, at a consumption rate of 50 g capita$^{-1}$ day$^{-1}$ (Copat et al., 2015). However, according to the Ministry of Agriculture, while in 2017 Israel supplied a total of 161,000 tons of fish to the public, only 1% of the supply originated from local fisheries, equating to 2.7 kg year$^{-1}$ individual$^{-1}$ (Herskovich, 2018). Looking at the fish supply between 2007 and 2017, there has been a decrease in the supply of locally-fished seafood, while local marine aquaculture and imports have increased (Herskovich, 2018). With the local fisheries being so small, there are no existing exports of seafood from Israel. Nevertheless, certain populations, especially those from local coastal fishing communities, may be consuming higher quantities of marine-based proteins which would directly expose them to higher quantities of seafood-based HM.

The JECFA has set provisional tolerable weekly intake levels for methylmercury (1.6 μg kg$^{-1}$ body weight) (WHO, 2007) and Cd (25 μg kg$^{-1}$ body weight) (WHO, 2010a). However, the once-recommended intake values for Pb and As are no longer applicable, with no new levels established (WHO, 2010b, 2019). The concentrations of HM in the marine environment are unique to each country, with an individual natural background signature as well as local influence of anthropogenic activity contributing to external inputs. Therefore, seafood needs to be constantly monitored on a local scale to ensure estimation of intake values for each local population. In addition, pursuant to the WHO recommendations, as well as increasing collected data, this information should be made available to the local citizens to ensure that proper actions are taken to minimize the negative impacts of HM and their associated diseases (Millward et al., 2019; WHO, 2007, 2010b).

## 4. CONCLUSIONS

According to the national health standards, most of the seafood tested in this study abide by the required acceptable levels of HM in consumable seafood. While seafood caught locally does not seem to be the major seafood source in Israel, as citizens opt for either imported or aquaculture-based fish, an active fishing industry still exists, providing the local population with fresh seafood. As with any food item reaching the public, locally caught seafood should be continuously monitored to ensure public health. This is especially true as HM in the environment are not in a steady state and are influenced by environmental conditions and shifts in anthropogenic activity. Additionally, while acceptable standards regarding human health are well established, the environmental implications remain unclear. To date, no national environmental standards exist for acceptable contamination levels in the marine space, whether it be sediment, water, or biota. While our study is more comprehensive compared to those priorly conducted for this area, it still provides a relatively small sampling of marine biota. We recommend that future research on seafood incorporates wider surveys to include other commonly consumed fish species, including higher trophic level fish caught in the local waters.

## AUTHOR CONTRIBUTIONS

D. Ramon, D. Morick, P. Croot, R. Berzak, A. Scheinin and D. Tchernov collected test data, supervised the project, drafted the manuscript, and critically revised the manuscript. D. Morick, N. Davidovich and M. Britzi conceived the original idea, contributed to the details of the experimental design, and analyzed and interpreted the data. D. Ramon, D. Morick, P. Croot, N. Davidovich and M. Britzi contributed to designing of the study, analyzed data, and wrote and revised the manuscript.

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## CONFLICTS OF INTEREST

The authors declare no conflicts of interest.

## ABBREVIATIONS

| | |
|---|---|
| As | arsenic |
| AsB | arsenobetaine |
| Cd | cadmium |
| DL | detection limit |
| DMA | dimethylarsenic |
| EC | European Commission |
| EMS | Eastern Mediterranean Sea |
| FAO | Food and Agriculture Organization |
| Hg | mercury |
| HM | heavy metals |
| iAs | inorganic As |
| IOLR | Israel Oceanographic and Limnological Research Station |
| IVS | Israeli Veterinary Services |
| ML | maximum levels |
| MMA | monomethylarsonic acid |
| Pb | lead |
| TAs | total arsenic |
| THg | total mercury |
| WHO | World Health Organization |

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## Supporting Information

Additional supporting information may be found online in the Supporting Information section at the end of the article.

**Table S1**. Specimen number per species collected at each fish landing.

**Table S2**. Seafood used for arsenic speciation.

**Table S3**. Summary of the acceptable heavy metal concentrations in different types of seafood as established by the European Commission (EC), Australia New Zealand Food Standards Code (AZ), and Israel standards (Is).

Supplement Tables

**Supplement Table 1**

Specimen number per species collected at each fish landing.

| | Species | Acre | Ashdod | Kishon | Jaffa |
|---|---|---|---|---|---|
| Fish | *Lithognathus mormyrus* | 10 | 4 | 8 | 12 |
| | *Mullus barbatus* | 4 | | 4 | |
| | *Mullus surmuletus* | 3 | 5 | 11 | 8 |
| | *Nemipterus randalli* | 4 | 10 | 4 | 8 |
| | *Sardinella aurita* | 3 | | 14 | 4 |
| | *Saurida lessepsianus* | 9 | 10 | 9 | 13 |
| | *Upeneus moluccensis* | 3 | 3 | 11 | 6 |
| Crustacean | *Marsupenaeus japonicus* | 2 | 6 | 3 | 8 |
| | *Portunus pelagicus* | 9 | 10 | 9 | 13 |
| Cephalopod | *Loligo vulgaris* | 4 | 9 | 7 | 15 |
| | *Sepia officinalis* | 5 | 4 | 10 | 4 |

**Supplement Table 2**
Seafood used for arsenic speciation.

| | Species | Average Length (cm) | Average Weight (gr) | Sample Size |
|---|---|---|---|---|
| Fish | *Lithognathus mormyrus* | 16.72 ± 1.67 | 61.58 ± 21.98 | 4 |
| | *Mullus barbatus* | 20.83 ± 4.16 | 106.17 ± 61.46 | 3 |
| | *Mullus surmuletus* | 16.94 ± 1.05 | 58.65 ± 11.4 | 5 |
| | *Nemipterus randalli* | 17.78 ± 3.01 | 67.72 ± 26.19 | 4 |
| | *Sardinella aurita* | 17.78 ± 3.74 | 49.92 ± 25.81 | 4 |
| | *Saurida lessepsianus* | 26.11 ± 6.68 | 136.40 ± 92.42 | 4 |
| | *Upeneus moluccensis* | 14.42 ± 1.41 | 33.08 ± 11.43 | 5 |
| Crustacean | *Marsupenaeus japonicus* | 45.77 ± 64.18 | 30.72 ± 11.88 | 4 |
| | *Portunus pelagicus* | 13.04 ± 1.6 | 174.32 ± 65.53 | 6 |
| Cephalopod | *Loligo vulgaris* | 14.20 ± 2.31 | 60.53 ± 17.73 | 4 |
| | *Sepia officinalis* | 13.25 ± 2.12 | 315.74 ± 166.27 | 7 |

**Supplement Table 3**

Summary of the acceptable heavy metal concentrations in different types of seafood as established by the European Commission (EC), Australia New Zealand Food Standards Code (AZ), and Israel standards (Is).

| Sample type | Standard concentration [ppm] wet weight | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | As | | | Hg | | | Cd | | | Pb | | |
| | EC | AZ | Is | EC | AZ | Is | EC | AZ | Is | EC | AZ | Is |
| **Fishery products & muscle** | – | 2 | – | 0.5 | 0.5 | 0.5 | 0.05 | – | 0.05 | 0.3 | 0.5 | 0.3 |
| **Crustaceans** | – | 2 | – | 1 | 0.5 | 0.5 | 0.5 | – | 0.5 | 0.5 | – | 0.5 |
| **Cephalopods** | – | – | – | – | – | 0.5 | 1 | – | 1 | 1 | – | 0.3 |
| **Bivalve molluscs** | – | 1 | – | – | – | 0.5 | 1 | 2 | 1 | 1.5 | 1 | 1.5 |

"–", no standards.

# Chapter 3: Metal accumulation in marine fish of the Eastern Mediterranean Sea: behavior and driving factors

# Statement of Authorship

## Principal Author

| | |
|---|---|
| Title of Paper | Metal accumulation in marine fish of the Eastern Mediterranean Sea: behavior and driving factors |
| Publication Status | Ready for submission |
| Publication Details | This paper investigates the accumulation of metals in locally caught fishes of economic and ecologic importance, by taking account species-specific interaction, trophic position, location, size, life stages, and migratory habits. |
| Name of Principal Author (Candidate) | Debra Ramon |
| Contribution to the Paper | Conceptualization, formal analysis, investigation, data curation, writing – original draft, visualization |
| Certification: | This paper reports on original research I conducted during the period of my Higher Degree by Research candidature and is not subject to any obligations or contractual agreements with a third party that would constrain its inclusion in this thesis. I am the primary author of this paper. |
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By signing the Statement of Authorship, each author certifies that:

I. the candidate's stated contribution to the publication is accurate (as detailed above);
II. permission is granted for the candidate in include the publication in the dissertation

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# Metal accumulation in marine fish of the Eastern Mediterranean Sea: behavior and driving factors


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## Abstract

Chemical pollutants such as heavy metals are a major threat to the health of the marine systems. While much research has been placed on bioaccumulation of metals and human exposure via consumed seafood, there are still large knowledge gaps regarding the impacts of metals to the health of the marine environment. This study aims to address this knowledge gap by assessing the accumulation of mercury, arsenic, cadmium, and lead in fish of ecological and economic importance collected along the Israeli coastline, by taking into consideration species, location, length, body mass index (BMI), trophic position, age group (juvenile/adult), compound specific amino acid cluster, migratory status, and reserve status (within or outside marine protected areas (MPA)). The results of this study show the significant differences between metals, with arsenic and mercury with high prevalence in fish, while cadmium and lead were marginally present. Additionally, it emphasizes the species-specific differences. Through the application of a

Generalized Additive Mixed Model (GAMM), BMI and age group were isolated as the driving factors for arsenic accumulation, while mercury was influenced by a combination of parameters, with mature fish with higher BMIs characterized by higher mercury levels within an MPA. The data generated in this study not only provides essential baseline information regarding metal accumulation in various fish species concerning health standards but also offers valuable ecological insights into the underlying mechanisms driving accumulation patterns. It also provides a logistically accessible approach to fisheries sampling to obtain environmentally relevant information. Furthermore, by examining the efficacy of MPAs in mitigating the impacts of chemical pollutants on fish populations, this research contributes to our understanding of marine conservation strategies and their implications for ecosystem health and human well-being.

**Keywords**

Marine Protected Area (MPA), Arsenic, Mercury, Cadmium, Lead, GAMM

## Introduction

The accumulation of metals in marine biota has gathered significant attention due to their profound impacts on both the marine environment and human health. Four metals in particular - arsenic, mercury, cadmium, and lead - have been subject to intense investigation owing to their high association with human poisoning. Chemical pollutants, like metals, are particularly concerning due to their extended residence time in marine ecosystems and their inability to degrade into less toxic compounds. Additionally, their specific speciation in the ocean can amplify their toxicity. Given that dietary intake, especially from marine products, is a primary pathway for these metals to enter the human food chain (Chen et al., 2012), extensive research has focused on their presence in the edible tissues of seafood (e.g. Esposito et al., 2018; García-Hernández et al., 2007; Gobert et al., 2017; Ruttens et al., 2012; Sinkus et al., 2017). Consequently, a significant portion of research on this subject is dedicated to assessing seafood safety under local or international food safety regulations, with a primary focus on metal prevalence. However, despite efforts to standardize assessments and facilitate comparisons between studies by referencing health standards, these standards often lack environmental context. Moreover, ecological aspects of metal exposure and bioaccumulation are frequently overlooked in such studies, leading to limited ecotoxicological insight.

To generalize metal behavior, as metals enter the marine environment, they can undergo chemical transformations as a function of environmental conditions or be assimilated biologically into the marine food web. This assimilation can occur through various pathways, including photosynthetic activity by algae and phytoplankton, leading to subsequent transfer to other organisms through predator-prey interactions, or direct contact through respiratory pathways via the gills of marine biota. These pollutants can then bioaccumulate within the organisms over time as well as redistribute throughout the trophic system. While metals share categorical similarities, their behaviors vary greatly in the marine environment, showcasing distinct distributions, chemical speciation, biological interactions, and environmental impacts. Among the four metals, mercury's marine biogeochemical cycle is the most well-understood, characterized by classic bioaccumulation and biomagnification behavior in marine biota, and is established as having negative neurological impacts in humans (Chen et al., 2012). Both cadmium and lead are assimilated biologically through phytoplankton or gills (respiration), with liver tissues in fish exhibiting accumulation patterns within the trophic system (Rohonczy et al., 2024), though neither are described to have biomagnifying characteristics (Shah, 2021). Meanwhile, arsenic, does not conform to a textbook accumulation pattern like mercury, and its speciation and behavior in the marine environment is not well defined (Azizur Rahman et al., 2012). Marine fish are exposed to a cocktail of chemical pollutants which either enter their bodies through environmental exposure via sediment and water, or through ingestion. With their diverse life strategies and habitats, fish have served as sentinels of environmental health for decades, reflecting the state of marine ecosystems and the impact of pollution. Furthermore, fish serve as major vectors for contaminant movement from the environment to the human population through ingestion. This underscores the interconnectedness of marine ecosystems and human health, highlighting the need for comprehensive studies on metal behavior, bioaccumulation, and ecological impacts to ensure both environmental sustainability and public health.

Numerous factors contribute to metal accumulation in the marine environment and biota, necessitating a comprehensive understanding that includes both external (environmental conditions) and internal (fish-specific characteristics) influences. One of the main external factors is metal enrichment from anthropogenic sources, greatly impacting metal presence and availability. Additionally, the metal type plays a crucial role, with each metal exhibiting unique properties and behaviors once released into the environment (Shah, 2021). Abiotic factors also play a pivotal role in metal accumulation, affecting the chemical speciation of metals in water and sediment fractions. These factors include pH, salinity, nutrients, oxygen levels, and temperature (Solan & Whitely, 2016). Microbial activity is another factor, as it plays an important role for the initial entry point into the marine food web by both concentrating metals at levels higher than ambient conditions as well as transforming biologically unavailable metal speciation into those that are available (Solan & Whitely, 2016). Seasonal variations are another significant factor to consider, as weather events can impact environmental conditions and reintroduce secondary contaminants into the system (Bareket et al., 2016), further affecting metal dynamics. Fish habitats are crucial considerations as well, encompassing differences such as benthic/pelagic, coastal/oceanic, and rocky/sandy habitats. Although less explored, differences between habitats within marine protected areas (MPAs) compared to those outside may also influence metal accumulation patterns. Life traits of marine organisms are highly influential and contribute to significant variations in metal concentrations within and between studies. These traits include species-specific interactions, age groups (juvenile/adult), sex (male/female/hermaphrodites), reproductive stage (spawning season), diet (prey, trophic position), and size (weight/length), all of which can impact the bioaccumulation and bioavailability of metals in marine biota. Integrating these various factors is essential for a holistic understanding of metal accumulation processes in the marine environment and their implications for ecosystem health and human well-being.

Israel's coastline expands for 273 km of continuous shoreline, with a marine space of 26,000 $km^2$. Despite the harsh environmental conditions of this highly oligotrophic sea with high temperatures, it fosters a thriving marine ecosystem, though its true richness and diversity of which are just coming to light with more research. The local Israeli population highly benefits from these healthy seas, with the Mediterranean offering a variety of critical ecological services, including a modest fishery compared to other areas of the Mediterranean Sea. There are numerous MPAs in both territorial waters and beyond, with the no-take Rosh HaNikra MPA holding special significance due to its richness and local contribution to both ecological health and fisheries through reserve overspill. Historically, major sources of metals from anthropogenic sources in Israel have been release of effluents directly into the sea as well as industrial activities, especially around high industrial areas such as the Haifa Bay - Kishon estuary, which still today has significant petrochemical infrastructure. Research on metal pollution in Israel's marine environment has largely been conducted through the monitoring program of Israel's National Institute of Oceanography at the Israel Oceanographic and Limnological Research (IOLR) center, which has been monitoring sediments since 1978 (Bareket et al., 2016; Herut et al., 1993; Hornung et al., 1989) and biota since 1981 (Shefer et al., 2015a). A significant portion of their research has centered on the Kishon Estuary – Haifa Bay (Bareket et al., 2016; Hornung et al., 1989; Shoham-

Frider et al., 2020), recognized as a major pollution hotspot due to intense anthropogenic activities characterized by urban development, a major harbor, multiple industries discharging into the water, and a river collecting water and runoff from its entire basin, making it a focal point for pollution. For decades, it was regarded as one of Israel's most polluted waterways, with detrimental effects on the local biota as well as human health (Richter et al., 2003). While some research beyond the monitoring program has been conducted, there are major knowledge gaps in the behavior of the different metals in the local marine biota, and the driving factors for their accumulation. In a previous study, Ramon et al., 2021 explored the local seafood, and observed arsenic levels amongst the highest reported in the literature, mercury in a fish species highly associated with bottom sediments, and a low prevalence of both cadmium and lead. However, sampling was limited and did not represent fish catch considered as highly prized or keystone species.

Generally speaking, metal research in the marine environment typically falls into two main categories; 1) metal concentration in seafood with respect to health standards or 2) investigating the accumulation behavior of specific metals. To broaden ecological understanding, we have utilized a fish survey originally designed for health assessments in local waters. This study focuses on arsenic, mercury, lead, and cadmium levels in mostly carnivorous fish within the Eastern Mediterranean Sea off the coast of Israel, integrating lifestyle traits to explore accumulation patterns. A key aspect of this study is its incorporation of fish species that hold both economic and ecological significance and sampling from specific areas of interest such as highly polluted industrial areas and designated MPAs. Also, by distinguishing between local and migratory fish species, we aim to account for both external environmental influences and internal biological factors impacting metal accumulation. Through this approach, we can explore the following questions with regards to arsenic, mercury, lead, and cadmium accumulation; 1) What is the prevalence of these metals in local fish populations?; 2) What are the species-specific accumulation behavior?; 3) What are the primary drivers of metal accumulation, considering factors such as species characteristics, geographical location, fish size, trophic position within the food web, and lifestyle traits?; and 4) What is the potential human exposure to these metals through fish consumption? The data generated from this study not only provides essential baseline information regarding metal accumulation in various fish species concerning health standards but also offers valuable ecological insights into the underlying mechanisms driving accumulation patterns. Furthermore, by examining the efficacy of MPAs in mitigating the impacts of chemical pollutants on fish populations, this research contributes to our understanding of marine conservation strategies and their implications for ecosystem health and human well-being.

## Materials and Methods

### Site description

The marine coastal area of Israel is characterized by a predominant sandy habitat with 12% of the seabed of territorial waters defined as rocky reefs, becoming more frequent in a north gradient (Action Plan for Protecting the Biodiversity of the Rocky Habitat along the Mediterranean Coast of Israel, 2014). From the southern border north until Haifa, occasional rocky structures are found within the sandy habitats, while from Haifa north until Rosh Hanikra (Achziv) there are longer stretches of rock (Golani et al., 2007). Much of these rocky habitats are calcareous sandstone and the nearshore areas affected by waves have formed unique Vermetid Reefs (abrasion platforms), which provide habitual complexity compared to sandy bottoms (Action Plan for Protecting the Biodiversity of the Rocky Habitat along the Mediterranean Coast of Israel, 2014; Golani et al., 2007). There are two major ports in Israel with intense industrial activities and include the Ashdod Port in the south and the Haifa Port in the north (Ramon et al., 2023). There are numerous rivers and streams that flow into the Mediterranean Sea with the major ones being the (from south to north) Yarkon River, Alexander River (transboundary), and Kishon River (Ramon et al., 2023). Though there has been an improvement in river health, these rivers are still considered highly polluted with a cocktail of anthropogenic inputs including fertilizers, herbicides, pesticides, agricultural runoff, sewage, and industrial releases (both local and transboundary).

While fish collection took place along the entire coastline of Israel, five generalized locations were appointed based on unifying environmental characteristics and are as follows; 1) the northern MPA named as ‘Achziv’, 2) the area of Haifa Bay and the Kishon Estuary jointly named ‘Haifa Bay’, 3) the area south of Haifa Bay named as ‘Haifa South’, 4) the central area in proximity to Tel Aviv named ‘Center’, and 5) the southern area of Ashdod and Ashkelon named ‘South’ (Figure 1).

### Fish sampling

Fish sampling took place all along the Israeli coastline between 2019 – 2023. Species in the sampling include: *Argyrosomus regius* (meagre), *Coryphaena hippurus* (Common dolphinfish), *Dicentrarchus labrax* (European seabass), *Epinephelus aeneus* (White grouper), *Epinephelus costae* (Goldblotch grouper), *Epinephelus marginatus* (Dusky grouper), *Euthynnus alletteratus* (Little tunny), *Mugil cephalus* (Flathead grey mullet), *Mycteroperca rubra* (Mottled grouper), *Pagrus caeruleostictus* (Bluespotted seabream), *Pterois miles* (Lionfish), *Scomber colias* (Atlantic chub mackerel), *Scomberomorus commerson* (Narrow-barred Spanish mackerel), *Seriola dumerili* (Greater amberjack), *Thunnus alalunga* (Albacore), *Thunnus thynnus* (Atlantic bluefin tuna), *Xiphias gladius* (Swordfish) and an unidentified species of the phylogenetic tribe decided as *Thunnini spp*.

The fish sampling was based on opportunistic accessibility to local catch, with fish caught from reliable sources, thus ensuring all fish were locally caught in Israeli Mediterranean waters. To do this, we incorporated five different strategies for collecting specimens; 1) sampling directly by the researchers, 2) buying from artisanal fishermen, 3) sampling from local sport fishermen, 4) collection from IOLR monitoring survey through commercial trawling, and 5) confiscation of illegal catch in the Achziv MPA by Israel's Nature and Parks Authority (INPA). Fishing by researchers was conducted by boat using a fishing pole and jigging technique. All fishing was conducted in areas allocated to fishing and under fishing permit as granted by Israel's Ministry of Agriculture and Rural Development. Some specimen were bought directly from commercial artisanal fishermen prior to being sold at distribution centers. Two approaches were used when acquiring fish from fishermen. The first, fishermen were requested to catch specific species and upon landing keep whole and place on ice. The second, we approached fishermen either on the water or immediately after landing and requested to purchase the specimen directly from them. By purchasing fish directly from the fishermen, we were able to provide reliable information on catch location, which would have been lost upon reaching distribution centers. Enlisting the help from local sport fishermen was initiated through social media (Facebook), where we reached out to local fishermen through major fishing groups in Israel (6,400 community members as of February 2024). A poster was distributed with the target fish list and researcher contact information. Fishermen were instructed via telephone on the sampling process and what information was required to use as a sample. Lastly, all fish illegally caught in the Rosh HaNikra MPA and confiscated by INPA were given to the researchers whole and frozen.

Laboratory processing

Following sample collection, specimen were either brought back into the lab for processing or immediately processed in the field. Specimen that were brought back to the lab fully intact were transferred on ice, and placed in -20 ℃ until processing. Processing included measuring weight and total length. Fish were filleted comprising both muscle and skin. Specimen processed in the field were measured, filleted, and transferred to the laboratory on ice. Following initial processing, from all samples, a subsample of clean muscle weighing 0.5 gr was taken for metal analysis and approximately 1 gr was taken for isotope analysis. The remaining sample was stored in -20 ℃. When samples were collected from fishermen, they were requested to save a sample from the caught fish containing 50 gr muscle. Information including catch location, weight, length, and photos of specimen were recorded from the fishermen.

Metal analysis

Analysis of HM was performed as described earlier (Ramon et al., 2021) with a validated, ISO 17025- accredited method. Briefly, 0.5g tissue samples were digested with 4mL HNO3 (TraceSELECT for trace analyses, Fluka, Licestershire, UK) and 1mL hydrogen peroxide (26%, for trace analysis, Merck, Darmstadt, Germany) and diluted with purified water (type 1, MicroPure Water Purification System, Thermo Scientific, Asheville, NC, USA). Concentrations of Cd, Pb, TAs were determined using graphite furnace atomic absorption (AA600 atomic absorption, graphite furnace spectrometer, Perkin-Elmer, Waltham, MA, USA), and THg was measured with a flow injection mercury system (FIMS 100 model, Perkin-Elmer, Waltham, MA, USA). Canned fish quality control sample (FAPAS, FERA Science, York, UK)) was utilized as a quality control sample. Detection limits (DL) were 0.01 mg $kg^{-1}$, 0.05 mg $kg^{-1}$, 0.05 mg $kg^{-1}$, and 0.1 mg $kg^{-1}$ for Cd, Pb, THg, and TAs, respectively.

Amino Acid Compound Specific Stable Isotope Analysis

All work with amino acid preparation, analysis, and corrections were done according to the recommended method per Martinez et al., 2020 and detailed by Tsadok et al., 2023 under sections ‘Compound-specific stable isotope analysis’ and ‘Data analysis and corrections’. In brief, freeze dried muscle tissue underwent acid hydrolyzation with Hydrochloric Acid (HCl). An EZ:faast amino acid analysis kit (Phenomenex Inc, Torrance, California, USA) was used for the derivatization, where reagent 6 was replaced by dichloromethane (DCM) as the solvent. The prepared sample was then analyzed using a Thermo Scientific Trace 1300 Gas Chromatographer (Waltham, MA, USA). The amino acids underwent a two-way split on a MicroChannel Device, with one split undergoing amino acid identification on a Thermo Scientific SQ quadruple (Waltham, MA, USA), and the other split for carbon and nitrogen isotope analysis on a Thermo

Scientific Delta V advantage (Waltham, MA, USA). In order to provide the carbon and nitrogen isotopic ratio, amino acids were combusted in a Thermo scientific GC isolink II (Waltham, MA, USA) for $CO_2$ and $N_2$. For each sample, triplicates were injected for both carbon and nitrogen analysis. Trophic position was calculated according to the equation $TP_{Glu/Phe} = \left(\frac{\delta^{15}N_{Glu} - \delta^{15}N_{Phe} - \beta}{TDF_{AA}}\right) + 1$ where $\beta = -0.36$ and $TDF_{AA} = 4.54$ presented in Martinez et al., 2020.

Statistical analysis

Statistical analysis was conducted using R version 4.3.3 (R Core Team, 2019) and the 'Tidyverse' package (Wickham et al., 2019). Data was assessed for normality using the Shapiro–Wilk's test. The non-parametric test Kruskall-Wallis test combined with Dunn's post hoc was used to assess metal difference between species and location. ANOVA and Tukey post hoc was used to assess differences in trophic positions between feeding strategy groups. Statistical significance was considered when $P < 0.05$. Metal concentration output below LOD was reported as zero in order to allow statistical analysis to be conducted while metal values below LOQ were reported as half the LOQ value (Analytical Methods Committee Analyst, 2001). Base visual aids were created using either R version 4.3.3 or Microsoft Excel (Microsoft Corporation, 2018), while base maps were created using Ocean Data View 4 (Schlitzer, 2015). Visual aids were modified in Inkscape-0.92 (Inkscape Project, 2020).

Generalized additive mixed effect model

A generalized additive mixed effect model (GAMM) was developed for arsenic and mercury due to their high prevalence in the sampling, allowing for the identifying of driving factors for accumulation. For the development of the model, in order to supplement missing data, a few different strategies were incorporated by utilizing the 'simputation' package (van der Loo, 2022). Missing length values were imputed using the EM-base imputation. kNN imputation was applied to trophic positions and amino acids using the weights and groupings of species, location, and age. For further principal component analysis (PCA) and generalized linear modeling (GLM), any observation with further missing values was dropped. Observation with additional missing values was removed from analysis for PCA and GLM.

Differences in categorial parameters and its contribution to numerical features were explored using PCA. Collinearity was assessed between independent variables and transformed accordingly. Due to high correlation between weight and length, body mass index (BMI) was calculated using the equation $\frac{weight_{kg}}{length_m^2}$. For amino acid composition, a k-means clustering was applied following an ordered quantile normalization transformation. It was determined that the ideal number of clusters to be two following assessment of both silhouette (average silhouette width) and total within sum of square (WSS) methods combined with visual inspection of the data.

Possible grouping-specific effects regarding catch location and species was identified. Though the validation of the assumption of linearity between the dependent and independent variables (predictors and response), a mixed effect generalized additive model (GAMM) was applied, using the Tweedie family and log link to compensate for zero inflation in the "mgcv" package. A global model was designed to compare mercury and arsenic concentration with the following parameters defined as fixed parameters; length, BMI, trophic position, age group, amino acid cluster, migratory status, and reserve (MPA) status. Species used for the model include *E. aeneus*, *E. costae*, *E. marginatus*, *E. alletteratus*, *M. cephalus*, *P. caeruleostictus*, *P. miles*, *S. colias*, *S. commerson*, *S. dumerili*, and *T. thynnus*. The interaction between species and sampling location was defined as random effects for the model. Based on the results of the global model, additional models were constructed using variations of the significant variables. The most appropriate model was selected using the small samples corrected Akaike Information Criterion (AICc).

## Results

### Target Species and Sampling effort

A total of 332 specimen were collected from 18 species, nine local species and nine highly migratory species (Table 1). Local species include *Argyrosomus regius* (meagre), *Dicentrarchus labrax* (European seabass), *Epinephelus aeneus* (white grouper), *Epinephelus costae* (goldblotch grouper), *Epinephelus marginatus* (dusky grouper), *Mugil cephalus* (flathead grey mullet), *Mycteroperca rubra* (mottled grouper), *Pagrus caeruleostictus* (bluespotted seabream), and *Pterois miles* (lionfish). Migratory species included *Coryphaena hippurus* (common dolphinfish), *Euthynnus alletteratus* (little tunny), *Scomber colias* (Atlantic chub mackerel), *Scomberomorus commerson* (narrow-barred Spanish mackerel), *Seriola dumerili* (greater amberjack), *Thunnus alalunga* (albacore), *Thunnus thynnus* (Atlantic bluefin tuna), *Xiphias gladius* (swordfish), and one tuna specimen categorized as unidentifiable on the species level but belonging to the tribe *Thunnini*. Sampling effort through the five collection strategies used in this study included 1) 30 specimen by researchers, 2) 156 specimen from artisanal fishermen where 24 were opportunistic and 132 were requested species, 3) 17 specimen from sport fishers, 4) 79 specimen from the monitoring program, and 5) 50 species from illegal confiscation by the INPA (Supplement Figure 1).

<u>Compound specific stable isotope analysis</u>

Due to logistical limitations, isotopic analysis analyzed on a third of the total collected specimen (34% n=114) (Supplement Table 1) and is summarized in Figure 2. The frequencies of trophic level groups amongst all measured specimen are presented in Figure 2C. Calculated averages for most specimen were calculated as either trophic positions 2-3 (39% n=45) or between trophic position 3-4 (52% n=59), while just a few specimen were calculated as trophic positions 4-5 (6% n=7) or as trophic positions 5-6 (2% n=2) (Figure 2A). Only one specimen was calculated below trophic position 2, at 1.9, placing it as the only specimen defined as an herbivorous consumer. When fish were categorized according to feeding strategy (local carnivore, migratory carnivore, planktivore, and detritivore) (Figure 2B), local and migratory carnivores were characterized by higher frequencies at trophic positions 3-4 (Figure 2A), with no significant differences in the average trophic position were found between them (3.2±0.6 and 3.4±0.6 respectively), though both significantly higher than the planktivores and detritivores ($F(3,110) = 8.67, p < 0.0001$) (Figure 2B). Planktivores and detrivores were similar with averages of 2.7±0.5 and 2.5±0.5 respectively, with highest frequency between trophic positions 2-3, and no significant differences from each other.

Trophic position was highly variable between and within species (Figure 1C). When comparing the average trophic position calculated in this study with those provided for these species on FishBase, FishBase values were higher (except for *D. labrax*) and with an average difference of 0.88 (Supplementary Table 6). Average values of the local carnivores and migratory carnivores were very similar at 3.4 and 3.2 respectively, placing them between level 3 (secondary consumers) and level 4 (tertiary consumers). Notably lower trophic levels were observed for the only dentrivorous species *M. cephalus* at an average of 2.5 and the only planktivorous fish *S. colias* at an average of 2.7, placing them between primary consumers and secondary consumers. There was high variance of trophic position based on size.

Metal Results

**Metal Prevalence** Metal prevalence in this study are as follows; arsenic > mercury > lead > cadmium. Arsenic was detected in 329 (99.1%) specimens, mercury in 309 (93.1%), lead in 46 (13.9%), and cadmium in 27 (8.13%).

**Health Standards** When comparing to the respective health standards for each metal, arsenic had 254 (76.5%) specimen exceed 1 mg $kg^{-1}$ (former health standard), mercury with 26 (7.8%) exceeding 0.5 mg $kg^{-1}$, lead with 22 (6.6%) exceeding 0.3 mg $kg^{-1}$, and 1 (0.3%) exceeding 0.05 mg $kg^{-1}$ (Supplement Table 2). Mercury and arsenic was observed in all species (n=17), lead in most species (n=12) from both migratory (n=5) and local species (n=7), and cadmium in six species from mostly migratory species (n=5) (Supplement Table 2).

**Migratory/Local** Comparisons between location was done for both migratory and local species (Figure 3). For migratory species, significant differences between locations were observed for arsenic $(x^2(3) = 64.49, p < 0.0001, n = 104)$, mercury $(x^2(3) = 30.41, p < 0.0001, n = 104)$, cadmium $(x^2(3) = 42.39, p < 0.0001, n = 104)$, and lead $(x^2(3) = 13.91, p = 0.003, n = 104)$ (Figure 3). For local species, significant differences between locations were observed for arsenic $(x^2(4) = 75.93, p < 0.0001, n = 228)$, mercury $(x^2(4) = 62.16, p < 0.0001, n = 228)$, and lead $x^2(4) = 34.67, p < 0.0001, n = 228)$ (Figure 3). No significant difference was observed for cadmium between locations $(x^2(4) = 2.51, p = 0.644, n = 228)$ (Figure 3). Post-hoc rankings for both migratory and local species, arsenic was significantly higher in fish from Haifa South, compared to other locations. For mercury, higher concentration found in migratory fish in the south, compared to local fish were levels were higher in Haifa South. The post hoc rankings of each location per metal are presented in figure 3.

**Species comparison**

Due to small sample sizes of some species, when comparing between species, only species with a sampling of n>10 were considered. Species comparisons are shown in Figure 4, with all species displayed while statistics and post hoc was conducted on species with the appropriate sample size. A significant difference was found in species comparisons for each metal (Figure 4). Distributions of arsenic and mercury as a factor of weight for each species is shown in Figure 5.

GAMM Model

A base global model was developed for each metal as well as two alternative models for arsenic and five for mercury. Assumptions for the model can be found in Supplementary Figure 3. Comparisons between model parameters for arsenic and mercury can be found in Supplementary Table 3 and Supplementary Table 4 respectively, with their AICc values in Supplementary Table 5. Visualizations of the best fit models for both arsenic and mercury are shown in Figure 6.

The arsenic global model (M1 model) significantly explained 84.5% of the deviance, with significant variables being age as a factor of mature fish (Figure 6). Based on the AICc values, the M2 which was significantly influenced by BMI and location, and with no interaction between parameters, was determined as the best fit for arsenic behavior. M2 was found to be a better fit compared to M3, which significantly explained 83.7% of the deviance, with the interaction between BMI as a function of the juvenile age grouping was found to be significant while BMI as a function of the adult age grouping was not (Supplementary Table 3).

The mercury global model (M1 model) significantly explained 92.3% of the deviance, with significant variables being age as a factor of mature fish and reserves (MPA) (Supplementary Table 4). M3 was determined as the best fit model based on the AICc values (Supplementary Table 5). Here, age as a factor of mature fish and reserves were determined as significant factors, with the interaction of BMI and age group showing being significant with the mature fish and non-significant with juvenile fish (Figure 6).

**Discussion**

Trophic Position

For many of the species sampled in this study, stable isotope based trophic position calculations are a first report in this region of the Eastern Mediterranean Sea. Fish species in this study constitute a very small component of the trophic food web, focusing mainly on carnivorous fish, and, thus, is limiting when assessing differences in accumulation between functional groups. This allowed for comparisons either within or between species. To demonstrate the importance of study specific TP, when comparing values calculated in this study to that reported in FishBase, values in FishBase (Froese & Pauly, 2024) were often higher, with an average difference of ΔTP 0.7 in local carnivores and ΔTP 1.2 in migratory carnivores (Supplementary Table 6). These differences can be due to regional differences, where fish from the highly oligotrophic

Mediterranean Sea exhibit different trophic behavior compared to either the same species or functionally parallel species from other regions of the Ocean. Another reason may be due to a large variability within species, as individuals of different age groups and location impact trophic levels differently. As not all specimen caught and assessed for isotopes were fully mature individuals, the comparability is highly limiting. To compare, Romero et al., 2021 observed similar TP values to those reported in this study. So, while trophic positions can be a beneficial tool when assessing metal accumulation, without improved baseline data, incorporating trophic levels into our future assessments is challenging. Therefore, in order to better understand trophic connectivity in local waters, regional specific calculations for trophic levels are required with consideration to differences with age groupings.

Arsenic

Of the four metals evaluated in this study, arsenic was the most prevalent metal, consistent with a previous study performed in this area on the local marine biota which showed a similarly high prevalence (Ramon et al., 2021). Arsenic is particularly interesting as its environmental behavior is not well established and does not follow bioaccumulation characteristics. Generally, dominating factors of arsenic bioaccumulation in biota can be summarized as a function of the following three dynamics: 1) environmental conditions, specifically the arsenic-phosphate dynamic, 2) diet, and 3) physiology. By assessing these dynamics for each component of this study, we can provide better context to the accumulation of arsenic.

When assessing the impacts of location, dynamics of migratory fish and location become less relevant, as migratory fish can be assumed to be incorporating external sources of metals, with catch location being a chance affair (Figure 3). Local fish, however, can provide context to the local drivers of arsenic accumulation in marine biota. The accumulation of arsenic as a factor of locations is as follows; Haifa South> South=Nahariya>Haifa (Figure 3). A notable difference can be observed between Haifa with low arsenic concentrations compared to Haifa South with high concentrations. This difference is possibly due to the difference in water quality from nutrient loading, in relation to arsenic's phosphate dynamics. Haifa South is considered relatively pristine as there are no major industries or land-based input of nutrients. This compares to Haifa, which is influenced by the Kishon Estuary and the runoff from intense agricultural areas, with the water quality characterized by high nutrient loading and a resulting change in primary producer biomass (Herut, Gertner, et al., 2023). Phosphate in pelagic surface waters along the coast have been measured to be 6 nM (Ben Ezra et al., 2021); compared to Kishon concentrations at 3900 nM (Herut, Gertner, et al., 2023). Therefore, the two sites may possibly be inversely correlated, with Haifa Bay's high phosphate and lower salinity levels (Herut, Gertner, et al., 2023) might reduce the arsenic uptake by the local marine organisms, while the pristine area of Haifa South with low phosphates and high salinity may be driving for higher uptake. This influence might be signaled in the cosmopolitan indicator species *M. cephelus*, which was caught in the Kishon Harbor area, and showed significantly lower concentrations than other compared species (Figure 4). However, both species specific diet (detritivore) and physiological processes (i.e. detoxification) for *M. cephalus* cannot be ruled out.

Concentrations in this study are generally lower than a previous study conducted in local waters which reported high arsenic levels in fish reaching 60 ppm (Ramon et al., 2021). However, the concentrations observed in this study are in consensus with the concentration ranges of fish from other areas of the Mediterranean Sea which observed a maximum level of 20 ppm in demersal fish and 52 ppm in pelagic fish (Ferrante et al., 2019). Of the migratory species, *S. dumerili* had significantly higher concentrations compared to other species in the grouping (Figure 4). The diet of adult *S. dumerili* in the Central Mediterranean Sea was dependent on demersal prey, with frequent prey items including *Loligo spp.* and *Sepia officianlis* (Andaloro & Pipitone, 1997), species that were reported in our first survey with high concentrations of arsenic (Ramon et al., 2021). From local species, *P. caeruleostictus* and *E. marginatus* showed significantly higher concentrations, while the remaining migratory and local species have relatively low and similar arsenic accumulation (Figure 4). Similar to *S. dumerili*, diet may explain the higher concentrations with *P. caeruleostictus* and *E. marginatus* consuming mostly molluscs and crustacea as juveniles and shifting to a higher piscivorous diet with age (Hamida et al., 2010; Harmelin & Harmelin-Vivien, 1999). Based on the GAMM model for arsenic, the influencing factors for arsenic were BMI and fish age (juvenile/adult). The various aspects of a fish's lifestyle in addition to the environmental parameters play an important role in influencing arsenic accumulation in fish.

<u>Mercury</u>

Mercury was the second most prevalent metal in this study and is characterized by expectedly high accumulation in certain large pelagic species like tunas (*T. alalunga*, *T. thynnus*) (Moura Reis Manhães et al., 2020) and relatively low concentrations in tuna like fish and local species (Figure 4). Accumulation in tunas have been well established as they are a favored fish for consumption and are considered sentinels of large pelagic species. These species are characterized by a high metabolism as they are continuously active (Graham & Laurs, 1982), especially in juveniles and those in the midst of seasonal migrations (Goñi & Arrizabalaga, 2010; Harden Jones, 1984). Interestingly, despite its significant size difference, smaller *T. alalunga* (albacore tuna) exhibited higher concentrations than that of the larger species *T. thynnus* (bluefin tuna). These species are often thought to swim together, with overlapping prey. However, it is important to note that fish reaching Israel are in the process of a seasonal migration, which results in physiological changes, especially in fat content of fish (Goñi & Arrizabalaga, 2010). As mercury has a strong affinity to the lipid fraction, the changes in fat content can potentially lead to increased levels within muscle as mercury is released from the fats as it is used for energy or result in biodilution as fish increases their fat storages, thus reducing muscle mercury level. Low concentrations in *C. hippurus* observed in this study are comparable with the literature (Adams, 2009) and can be explained by their different lifestyle traits, characterized by a quick growth rate and short life span of just a few years (Sacco et al., 2017). Their quick growth rate may result in biodilution of mercury, combined with their short lifespan which limits accumulation with time.

When comparing mercury accumulation in different locations, notable differences emerged between Haifa, known for its high pollution levels, and pristine areas like Haifa South and the Nahariya MPA (Figure 3). The mercury levels at both pristine sites were significantly higher than those found in the 'contaminated' area of Haifa. While the mercury signature in the Haifa Bay has shown a decreasing trend in monitoring surveys (Herut, Segel, et al., 2023) with stronger mitigation as well as restoration projects of the Kishon River, we had originally hypothesized that the signal in the fish would still remain higher compared to other locations. Contrary, fish in Haifa Bay exhibited the lowest concentrations of mercury among the studied locations, with all specimens well below the health limit standard of 0.5 ppm. Impacts of the MPA on mercury accumulation is supported by our GAMM model, which shows that the Nahariya MPA plays a significant role in higher accumulation, with mature fish accumulating higher concentrations as a function of BMI. While MPAs would be expected to provide protection against chemical pollutants, the topic has been rarely investigated, and little information exists on this issue (Abessa et al., 2018). Establishment of MPAs predominantly focus on the protection of marine habitats and biodiversity. Beyond the ecological benefits of MPAs, they also contribute to ecosystem services used by mankind. They particularly benefit fisheries, as it can help fish stocks by supporting key habitats for sensitive life stages, act as a sink/source for dispersal, and result in a spillover effect where the surrounding areas beyond the boundaries of the MPA with potential catch (Commonwealth of Australia, 2003). While the management infrastructure of an MPA can allow a certain level control, pollution remains a major component impacting Ocean health, with chemical pollution not respecting the boundaries of MPAs (Mazaris et al., 2019) thus affecting the wildlife within. When assessing the success of an MPA, parameters such as fish health or contamination are not often considered. When examining specific pollution point sources influencing the Nahariya MPA, the heightened mercury levels observed could stem from the legacy release of mercury from a chlor-alkali plant in the northern section of Haifa bay, with possible transportation via the north bound current along Israel. Studies have indicated that this release has led to elevated mercury levels in sediments, particulate matter, plankton, algae, and biota, with transport northwards from Haifa Bay (Shoham-Frider et al., 2020). This transport mechanism could potentially introduce mercury into the area encompassing the MPA. Alternatively, the structure of a MPA may play a crucial role in mercury accumulation, although whether it facilitates accumulation or dilution remains uncertain. A richer MPA structure, characterized by more trophic connections, biodiversity, and size ranges, could potentially dilute mercury by dispersing it across a larger biomass. However, it's also plausible that a more connected ecosystem within the MPA could provide better entry points for mercury into the food web, leading to higher accumulation levels. The specific impact of MPA structure on mercury dynamics requires further investigation to clarify its role definitively.

Lead

Overall, lead exhibits a low prevalence within the sampling. This observation is consistent with a previous fish survey conducted in local waters which also reported similarly low numbers of lead contaminated fishes and concentrations (Ramon et al., 2021). Though low prevalence is a positive outcome when conducting such environmental surveys, as it indicates that the pollutant is not a cause of alarm, it highly limits the obtainable insight of metal accumulation behavior throughout the marine ecosystem. Despite the low prevalence, some unique points stand out in this sampling.

One specimen of *P. miles* caught from the MPA had surprisingly high lead concentration of 1.36 ppm w.w. When reviewing all the possible parameters involved, it is unclear what the driving force behind such a high lead level. When assessing whether this is related to species specific accumulation, no other specimen of the same species exhibited similarly high lead levels, indicating that the accumulation behavior does not appear to be species specific. Location, and its associated environmental conditions, also doesn't seem a likely reason, as the next highest concentration for Nahariya (MPA) is at levels of the LOQ (0.02 ppm), indicating that no unique exposure to lead is taking place at this site. As the size of the fish was small, its accumulation does not appear to be a factor of increasing size. However, as its small size limits prey size, it is possible that this particular individual was exposed to higher levels of lead through a particular food source.

*M. cephelus* was also observed to have high species prevalence of lead, as over half (n=16, 53%) of specimen were found characterized by measurable levels, though concentrations were low with a range of 0.02-0.1 (average 0.03±0.02). Though most specimen were at the quantification limit, it is the only species with such high prevalence for lead. *M. cephelus* is commonly found along the coastline and well observed in areas of high anthropogenic activity like marinas and harbors. It is considered a highly tolerant species that can survive in brackish waters and has been reported to survive in Haifa Harbor waters at the height of its pollution in the 50s – 70s (Richter et al., 2003). The specimens in our study were caught close to the opening of the Kishon within Haifa Harbor, considered a pollution hotspot. With the removal of lead-based fuels, Israel has witnessed an overall decreasing trend in the local inputs of lead entering the marine environment (Chien et al., 2019; Harlavan et al., 2010). While the national monitoring program through the IOLR has reported a general decreasing trend of lead in the sediments of the harbor since 1996, with a small recent increase in the trend between 2014-2022 (Herut, Segel, et al., 2023), thus indicating that lead is still present and continues to be enriched within the system.

Both *P. miles* and *M. cephelus* are important local fish as they are consumed by the local population, especially sport and artisanal fishers. *M. cephelus* is a common species both locally and worldwide and is considered a relatively easy catch, thus making it highly accessible. Local villages in particular enjoy mullet as a food source and it is often observed being brought in as the daily catch. Additionally, it is one of the major fisheries of the local aquaculture. *P. miles,* an invasive species from the Red Sea, has recently emerged as a sought-after fish by local fishermen, especially spearfishermen. This is due to a unique combination of its successful settling in local waters, prized quality meat, and encouragement of local authorities to remove them from the water as a management strategy to mitigate their established negative impacts on reefs worldwide. While muscle is the tissue that is most often analyzed as it has relevance to human risk assessments, environmental assessments have indicated that other organs such as gills absorb higher concentrations of lead compared to muscle (Fazio et al., 2020). Mercury is one of the only metals with a high affinity for muscle and is the exception rather than the normal. Other metals, lead included, appear to show affinity for other tissues, which needs to be taken into account from an ecotoxicological perspective.

Cadmium

Cadmium was the least prevalent metal in this sampling. However, despite low prevalence and low concentrations, there was a notable presence in migratory fish compared to local species. Particularly, a high prevalence was observed in S. *commerson* (~25% of samples), *E. alletteratus* (~25% of samples), and *T. thynnus*. Highest concentrations were reported at 0.05 ppm, beyond the established health standard. It is possible that differences in migratory and local species are due to the difference in lifestyles between the two groupings, with the highly migratory fish characterized as high-performance fish, equating to a higher metabolism, increased food intake, and higher metal load on the consumer (Ansel & Benamar, 2018). Similar habitat differences have been previously shown, with pelagic fish characterized by higher accumulation than demersal fish (Vetsis et al., 2021). Looking at our sampling, as migratory fish are constantly on the move, their accumulation may be dominated by open ocean cadmium processes. In open waters, cadmium distribution aligns with phytoplankton nutrient profiles, mirroring the vertical distribution patterns of phosphate in the water column (Baars et al., 2014). Specifically, phytoplankton is responsible for the accumulation of cadmium from the water column via either the Mn or the Zn transport system (Xu & Morel, 2013). The bioavailability of cadmium diminishes with increasing salinity, impacting the availability of toxic ionic cadmium species (Neff, 2002). Similar to arsenic, the accumulation behavior of cadmium is unclear, with past studies indicating bioaccumulation potential while current studies highlighting its complexities as it is transferred though the food web (Saidon et al., 2024). Marine organisms are exposed to cadmium through either dissolved ionic cadmium via their in their gills (Neff, 2002) or with their diet. Studies have shown that cadmium does not necessarily biomagnify in marine food webs from the bottom trophic levels to the top. Within a system, different trophodynamics have been observed based on the organism category with invertebrates exhibiting biomagnification while fishes displaying biodilution (Espejo et al., 2018). Size (age) associated accumulation of cadmium has been shown for *E. alletteratus* (Ansel & Benamar, 2018). Additionally, when liver tissues were assessed bioaccumulation patterns did emerge (Ansel & Benamar, 2018; Rohonczy et al., 2024; Vetsis et al., 2021), indicating that muscle may not be an appropriate representation of accumulation. With liver showing such significant differences than muscle, fish may be constantly detoxifying cadmium from their systems (Ansel &

Benamar, 2018). Diet wise, cadmium may be brought to surface waters through diurnal migration of marine species, which come to the surfaces at night to feed, thus reintroducing cadmium back into the surface through trophic dynamics. Alternatively, though large pelagic tunas have been shown to prefer the upper mixed layer waters (Fenton et al., 2015), they also utilize the deeper waters of 200 -1000 m (Block et al., 2001; Fenton et al., 2015) which is where they may be exposed to more cadmium compared to other shallow swimming species. While such highly migratory fish does not act as indicators for local cadmium dynamics, with improved ecological information of these species in the Eastern Mediterranean Sea, they can provide better insight to general cadmium behaviors throughout the open waters of this area. Locally, when assessing cadmium inputs in sediments from highly polluted areas like the Kishon, overall concentrations remain low (Herut, Segel, et al., 2023), and may explain their lack of prevalence in the local fishes.

Human health

The sampling strategy utilized in this study can be viewed as a constraint due to the resulting high bias toward certain species and sizes, which can influence the ecological context of the data. However, this strategy also offers crucial insights into human health considerations, as all sampled species are catchable and consumed by the local population. As marine fisheries in Israel are modest compared to other countries in the Mediterranean Sea, locally caught fish are not a uniform protein source in all of the local population. However, there are certain sub-groups in the population that are more susceptible and include those whose communities have stronger ties to artisanal fishing as well as sport fishers who provide both themselves and their families with fresh fish. A study conducted by Taylor & Williamson, 2017 in New England showed that from a survey of anglers and their families, who self-reported higher fish intake, half were found to have mercury concentrations higher than the acceptable United States Environmental Protection Agency (US EPA) reference dose. They also noted that elevated exposure was attributed to key target species characterized by higher mercury levels (Taylor & Williamson, 2017). Unfortunately, local marine fish do not undergo the same level of health scrutiny as other protein sources do, highlighting a knowledge gap that this study partially aimed to address.

## Conclusions

This study presents a comprehensive collection of species that provides valuable insights into the behavior of metal pollution in local waters. While conducting such surveys can be logistically challenging due to species diversity, making it difficult to ensure appropriate sample sizes for accurate representation of location and size distribution, leveraging fisheries as an available sampling source can offer crucial context for assessing ecological impacts. Moreover, this approach is highly representative of the fish caught by local fisheries and anglers, consumed by citizens. Taking a holistic approach by considering biological, environmental, and lifestyle factors, and using tools like compound-specific stable isotopes and a GLMM model, enables us to provide essential ecological context. Although the resolution of analysis may be limited, this study establishes important baseline information, highlighting intriguing dynamics and potential avenues for future research. As this study captures only a moment in time, it underscores the need for consistent monitoring of metals in the marine environment. Understanding species-specific dynamics and establishing locally specific indicator species, coupled with ongoing monitoring, can enhance our assessment of local waters and the well-being of communities relying on them.

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Table 1: List of target species, characterizing traits and sampling size

| | Species | Adult Habitat | Prey Simplified | Trophic Level (Fishbase) | TL AA CSSI average (this study) | Trophic Level Category | Origin | IUCN Status | Weight [gr] (avg ± SD, range) | Length [cm] (avg ± SD, range) | n |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Local | *Argyrosomus regius* | Benthopelagic | Carnivore | 4.3 | 3.4 | Third Level Carnivore | Atlantic-Mediterranean | Least Concern | 62±5<br>56 - 68 | 3048±905<br>2020-4180 | 5 |
| | *Dicentrarchus labrax* | Demersal | Carnivore | 3.5 | 3.7 | Second Level Carnivore | Atlantic-Mediterranean | Least Concern | NA<br>1000 | NA<br>30 | 1 |
| | *Epinephelus aeneus* | Demersal | Carnivore | 4 | 3.2 | Third Level Carnivore | Atlantic-Mediterranean | Near Threatened | 3752±5255<br>98-18120 | 50±29<br>17-108 | 27 |
| | *Epinephelus costae* | Demersal | Carnivore | 3.9 | 3.6 | Second Level Carnivore | Atlantic-Mediterranean | Data Deficient | 576±943<br>165-5000 | 28±10<br>20-70 | 32 |
| | *Epinephelus marginatus* | Reef-Associated | Carnivore | 4.4 | 3.6 | Third Level Carnivore | Atlantic-Mediterranean | Vulnerable | 595±524<br>142-2200 | 27±7<br>18-45 | 44 |
| | *Mugil cephalus* | Benthopelagic | Detritivore | 2.5 | 2.5 | First Level Carnivore | Cosmopolitan | Least Concern | 443±137<br>320-1032 | 33±3<br>30-42 | 30 |
| | *Mycteroperca rubra* | Reef-Associated | Carnivore | 4.1 | 2.8 | Third Level Carnivore | Atlantic-Mediterranean | Least Concern | 297±109<br>136-435 | 24±4<br>18-31 | 6 |
| | *Pagrus caeruleostictus* | Benthopelagic | Carnivore | 3.7 | 3.3 | Second Level Carnivore | Atlantic-Mediterranean | Least Concern | 360±492<br>42-2000 | 21±10<br>11-52 | 39 |
| | *Pterois miles* | Reef-Associated | Carnivore | 4.5 | 3.3 | Third Level Carnivore | Indo-Pacific | Least Concern | 256±153<br>124-785 | 20±4<br>15-31 | 17 |
| | *Scomber colias* | Pelagic-Neritic | Planktivore | 3.9 | 2.7 | Second Level Carnivore | Atlantic-Mediterranean | Least Concern | 90±71<br>22-231 | 102±447<br>14-2425 | 29 |
| Highly Migratory | *Coryphaena hippurus* | Pelagic-Oceanic | Carnivore | 4.4 | 2.8 | Third Level Carnivore | Cosmopolitan | Least Concern | 412±79<br>295-473 | 39±6<br>32-45 | 4 |
| | *Euthynnus alletteratus* | Pelagic-Oceanic | Carnivore | 4.5 | 3.8 | Third Level Carnivore | Atlantic-Mediterranean | Least Concern | 615±2609<br>42-12000 | 1297±315<br>79-1730 | 21 |
| | *Scomberomorus commerson* | Pelagic-Neritic | Carnivore | 4.5 | 3.1 | Third Level Carnivore | Indo-Pacific | Near Threatened | 1380±2696<br>95-12450 | 44±24<br>21-115 | 38 |
| | *Seriola dumerili* | Benthopelagic | Carnivore | 4.5 | 3.5 | Third Level Carnivore | Atlantic-Mediterranean | Least Concern | 1443±4420<br>228-22000 | 32±15<br>24-95 | 24 |
| | *Thunnus alalunga* | Pelagic-Oceanic | Carnivore | 4.3 | 3.1 | Third Level Carnivore | Cosmopolitan | Least Concern | 10105±3387<br>7710-12500 | NA<br>72 | 2 |
| | *Thunnus thynnus* | Pelagic-Oceanic | Carnivore | 4.5 | 3.1 | Third Level Carnivore | Atlantic-Mediterranean | Least Concern | 100725±47896<br>33600-175000 | 205±45<br>140-260 | 13 |
| | *Xiphias gladius* | Pelagic-Oceanic | Carnivore | 4.5 | 3.6 | Third Level Carnivore | Cosmopolitan | Near Threatened | NA<br>7000 | NA<br>NA | 1 |

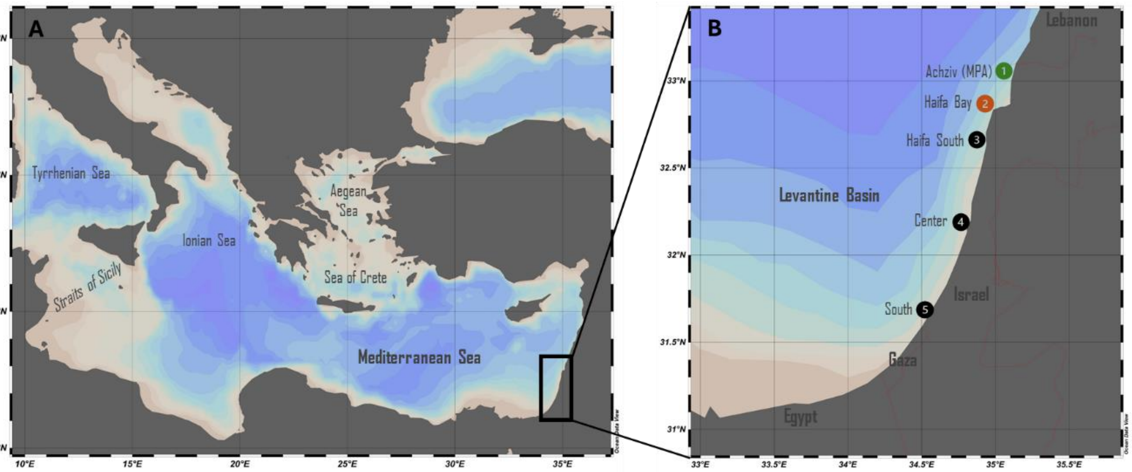



Figure 1: Map of sampling site. The four locations include 1) the MPA Achziv (Nahariya), 2) Haifa Bay – Kishon, 3) Haifa South, 4) Center, and 5) South.

Table 2: Descriptive statistic table of average concentrations (mg $kg^{-1}$ wet weight) (±SD) and range for all metals and species.

| | | Concentration [mg/kg w.w.] | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Arsenic | | Mercury | | Cadmium | | Lead | |
| | Species | Mean ± SD | Range | Mean ± SD | Range | Mean ± SD | Range | Mean ± SD | Range |
| Local | *Argyrosomus regius* | 0.53±0.27 | 0.17-0.92 | 0.3±0.38 | 0.1-0.97 | 0 | 0-0.01 | 0 | 0.02 |
| | *Dicentrarchus labrax* | | 1.81 | 0 | 0.05 | ND | ND | ND | ND |
| | *Epinephelus aeneus* | 1.64±1.68 | 0.2-6.07 | 0.22±0.21 | 0.05-0.8 | ND | ND | 0±0.01 | 0-0.02 |
| | *Epinephelus costae* | 3.45±1.54 | 0.2-7.37 | 0.12±0.04 | 0.05-0.2 | ND | ND | 0±0.01 | 0-0.02 |
| | *Epinephelus marginatus* | 6.15±3.02 | 1.36-16.21 | 0.2±0.13 | 0.05-0.67 | ND | ND | 0±0.01 | 0-0.02 |
| | *Mugil cephalus* | 0.99±0.56 | 0.41-2.84 | 0.04±0.02 | 0-0.05 | ND | ND | 0.02±0.02 | 0-0.1 |
| | *Mycteroperca rubra* | 0.49±0.23 | 0.28-0.8 | 0.06±0.03 | 0.05-0.13 | ND | ND | ND | ND |
| | *Pagrus caeruleostictus* | 6.78±3.63 | 1.61-18.64 | 0.16±0.21 | 0.05-0.78 | ND | ND | 0±0.01 | 0-0.02 |
| | *Pterois miles* | 1.64±1.07 | 0.63-4 | 0.13±0.08 | 0.05-0.33 | ND | ND | 0.09±0.33 | 0-1.36 |
| | *Scomber colias* | 2.51±1.16 | 0.93-4.78 | 0.07±0.04 | 0.05-0.19 | 0 | 0-0.01 | ND | ND |
| Highly Migratory | *Coryphaena hippurus* | 1.2±0.48 | 0.75-1.64 | 0.05±0 | 0.05 | ND | ND | 0 | 0 |
| | *Euthynnus alletteratus* | 1.7±0.5 | 1.1±3.2 | 0.09±0.06 | 0.05-0.26 | 0 | 0-0.01 | 0±0.01 | 0-0.02 |
| | *Scomberomorus commerson* | 1.42±1.09 | 0-4.48 | 0.08±0.1 | 0-0.55 | 0±0.01 | 0-0.05 | 0.01±0.05 | 0-0.27 |
| | *Seriola dumerili* | 11.39±5.51 | 5.21-29.83 | 0.08±0.07 | 0.05-0.31 | ND | ND | 0±0.01 | 0-0.02 |
| | *Thunnus alalunga* | 4.71±1 | 4.01-5.42 | 1.27±0.07 | 1.22-1.32 | 0.02±0 | 0.02 | 0.25±0.35 | 0-0.5 |
| | *Thunnus thynnus* | 3.47±1.54 | 0.85-5.81 | 0.79±0.36 | 0.14-1.41 | 0.01±0.01 | 0-0.03 | 0.03±0.05 | 0-0.14 |
| | *Xiphias gladius* | ND | 0.52 | ND | 0.21 | ND | 0 | ND | 0 |

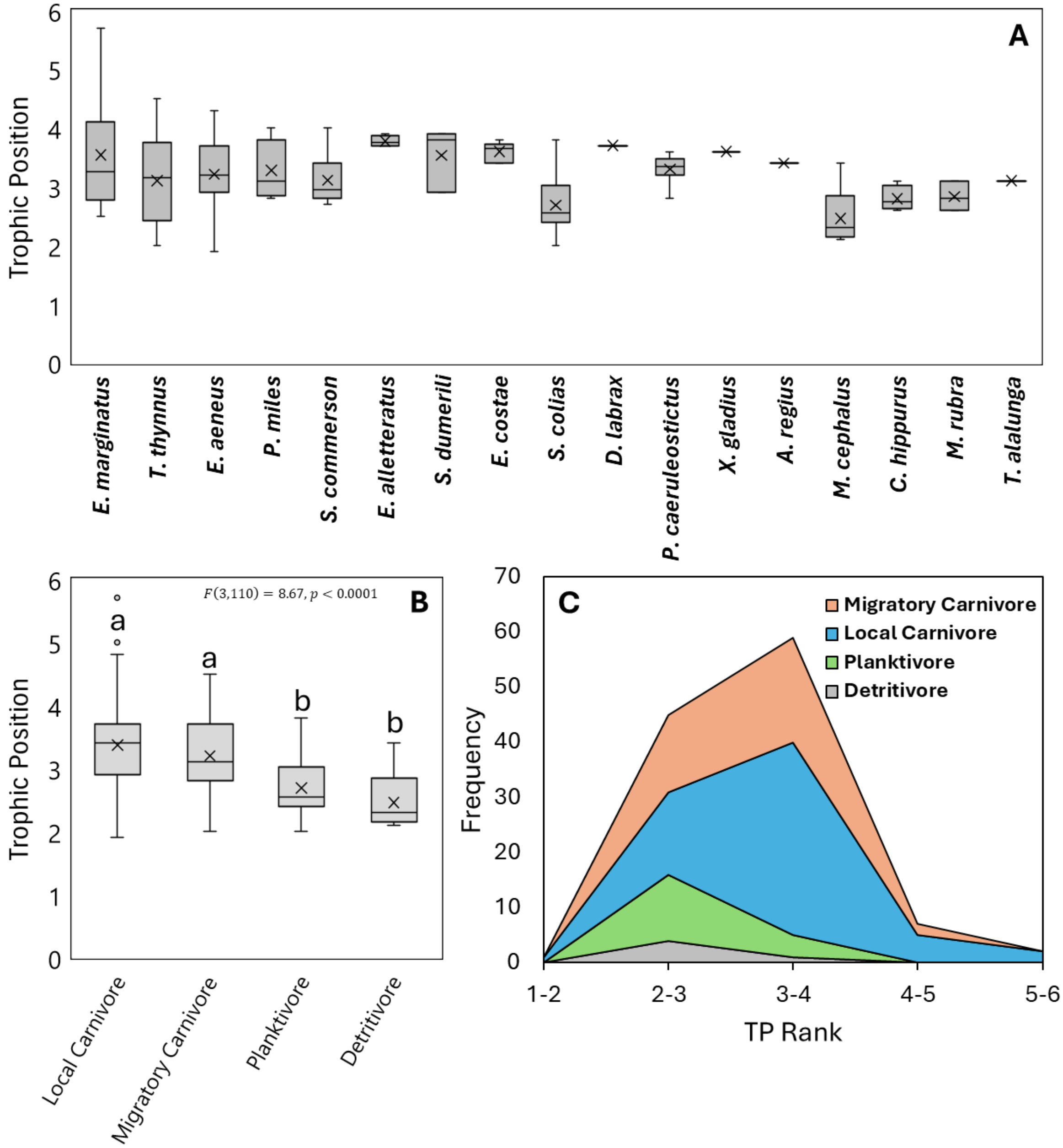



Figure 2: Trophic positions of species (a) and feeding strategies (b and c).

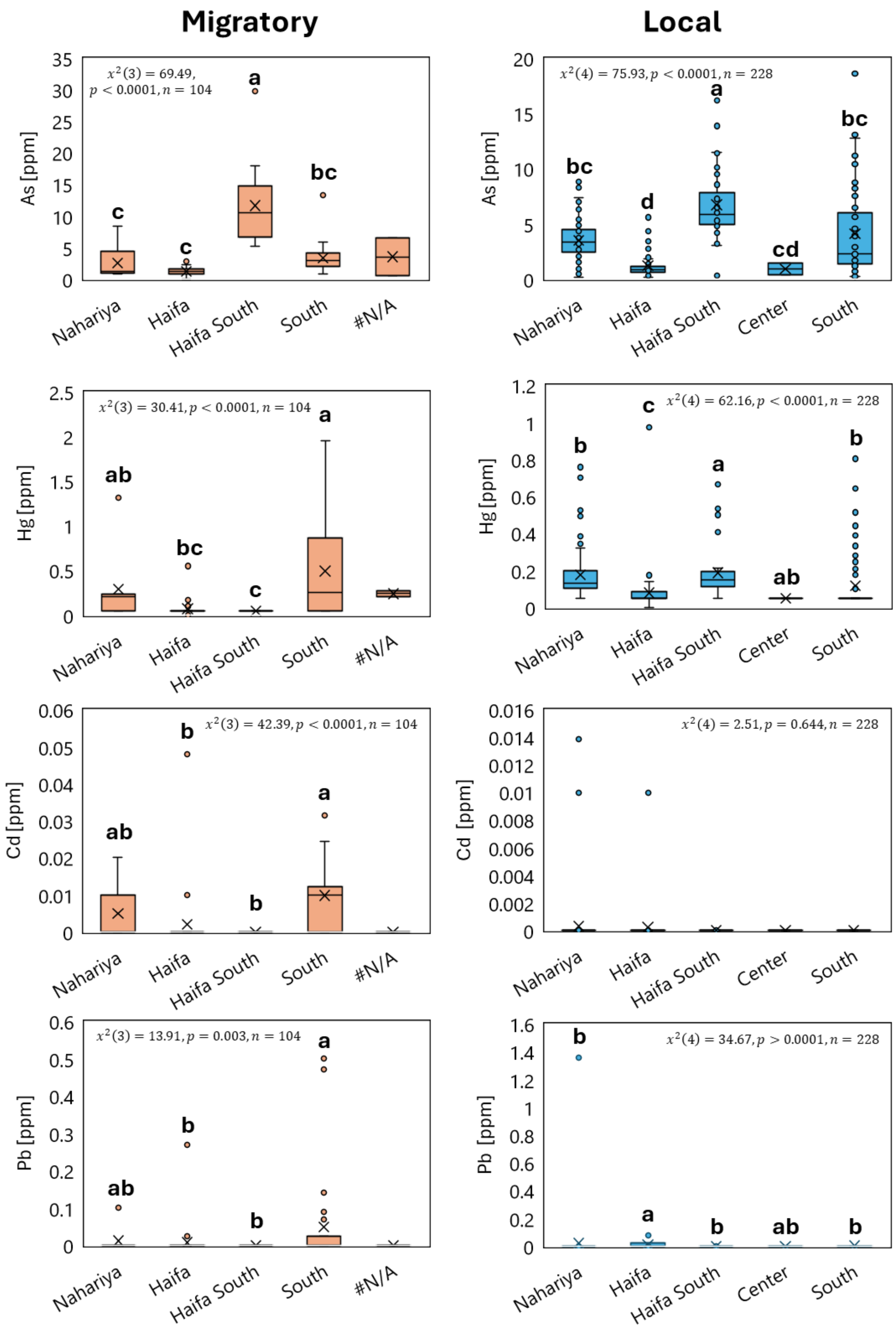



Figure 3: Distribution of metals as a factor of site for both migratory and local fish.

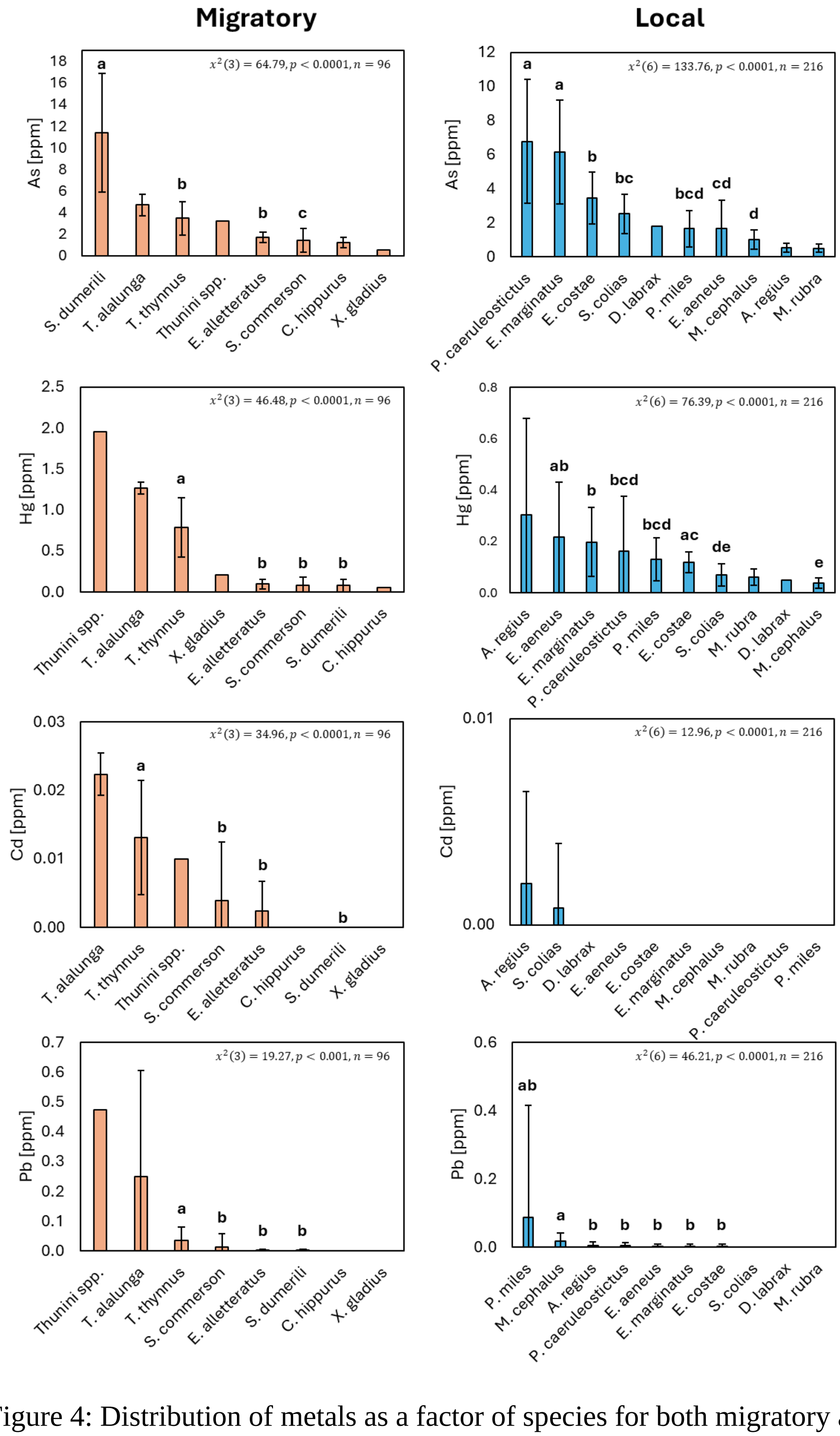



Figure 4: Distribution of metals as a factor of species for both migratory and local fish.

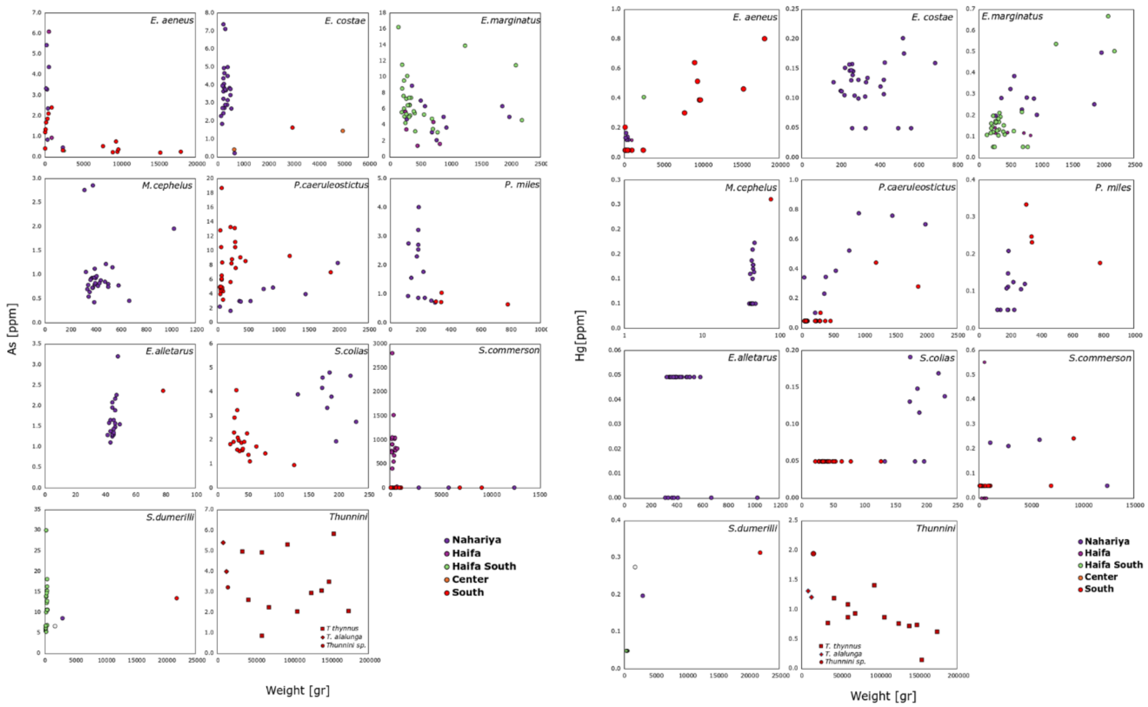
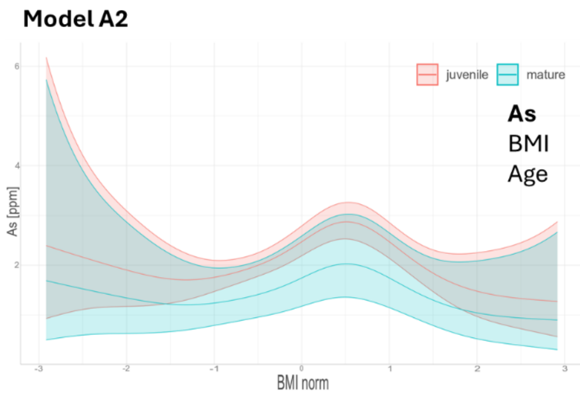
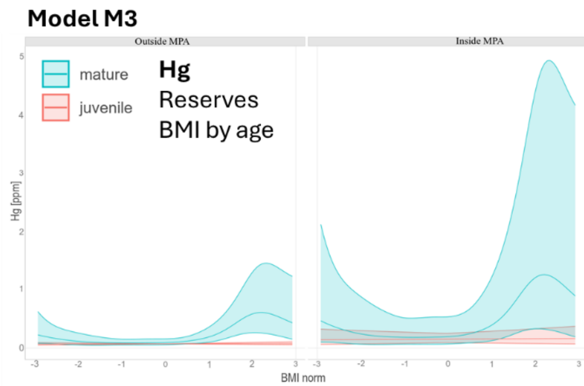



Figure 5: Distribution of arsenic and mercury as a factor of species and weight.



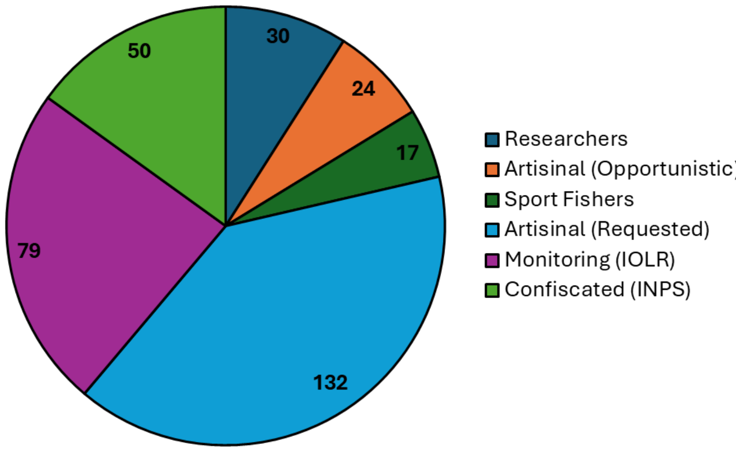

| As M2 Model | R sq (adj)=0.71 Deviance explained 83.9%<br>Scale est.=0.14, n=263 | | | | | | |
|---|---|---|---|---|---|---|---|
| | **Component** | **Term** | **Estimate** | **Std Error** | **T-value** | **P-value** | |
| | A. Parametric coefficients | (intercept) | 0.782 | 0.2495 | 3.135 | 0.00194 | ** |
| | | migrator | 0.417 | 0.364 | 1.144 | 0.254 | |
| | | Age mature | -0.349 | 0.139 | -2.5 | 0.013 | * |
| | | Reserve | 0.4817 | 0.352 | 1.367 | 0.173 | |
| | | Isotope cluster2 | -0.073 | 0.072 | -1.021 | 0.308 | |
| | **Component** | **Term** | **edf** | **Ref. df** | **F-value** | **P-value** | |
| | B. Smooth terms | BMI | 4.954 | 6.052 | 3.594 | 0.002 | ** |




| Hg M3 model | R sq (adj)=0.9 Deviance explained 92.4%<br>Scale est.=0.074, n=255 | | | | | | |
|---|---|---|---|---|---|---|---|
| | **Component** | **Term** | **Estimate** | **Std Error** | **T-value** | **P-value** | |
| | A. Parametric coefficients | (intercept) | -2.596 | 0.18 | -14.45 | <2e-16 | *** |
| | | migrator | -0.104 | 0.261 | -0.398 | 0.691 | |
| | | Age mature | 0.514 | 0.159 | 3.232 | 0.001 | ** |
| | | Reserve | 0.723 | 0.253 | 2.859 | 0.00465 | ** |
| | | Isotope cluster2 | 0.033 | 0.054 | 0.624 | 0.533 | |
| | **Component** | **Term** | **edf** | **Ref. df** | **F-value** | **P-value** | |
| | B. Smooth terms | BMI: age group*juvenile | 1.001 | 1.002 | 0.163 | 0.687 | |
| | | BMI: age group*mature | 5.552 | 6.635 | 7.8 | <2e-16 | *** |

Figure 6: Visual representation of best fit model based on AICc value with model parameters and statistics below each. For arsenic, Model A2 was used, with influencing parameters BMI and age. For mercury, model M3 was used with parameters reserves and the interaction between BMI and age used.

Supplements



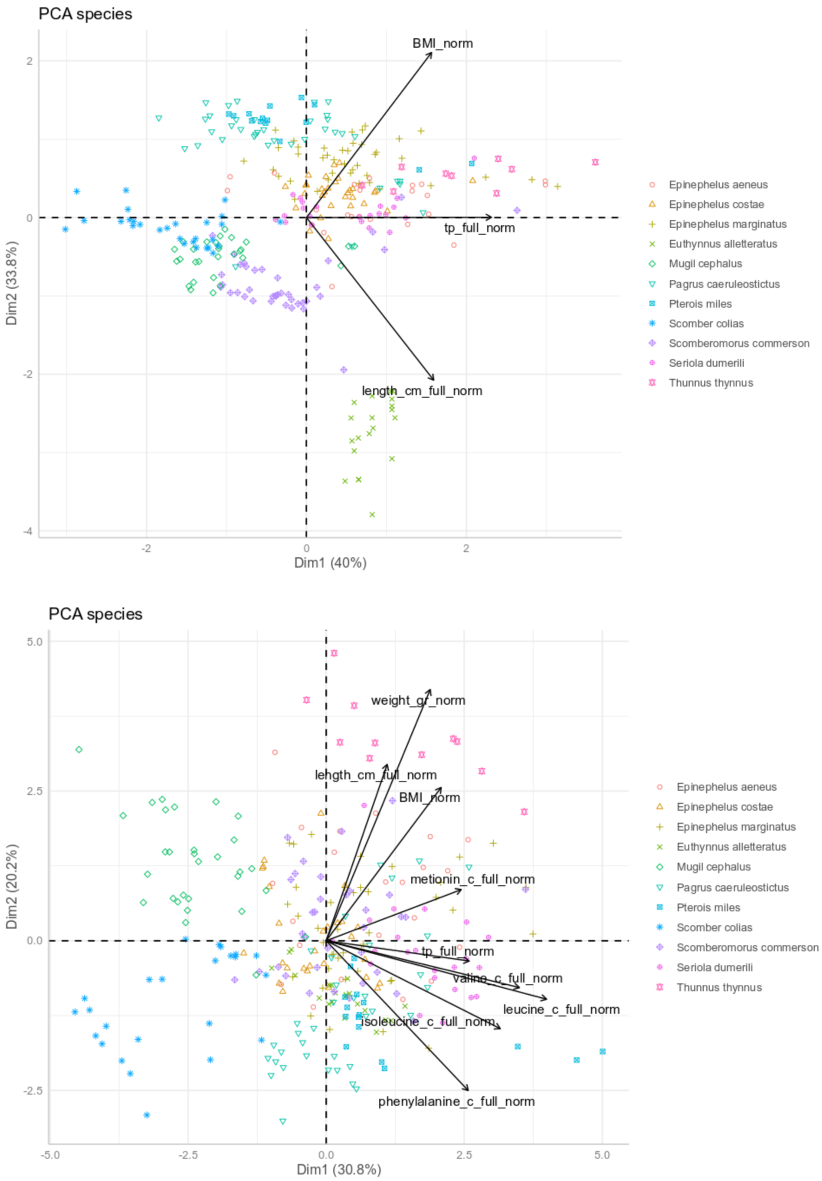

Supplement Figure 1: Division of fish collection sampling effort

Supplement Table 1: Samples list used for stable isotopic analysis.

| | |
|---|---|
| Argyrosomus regius | 2 |
| Coryphaena hippurus | 4 |
| Dicentrarchus labrax | 1 |
| Epinephelus aeneus | 15 |
| Epinephelus costae | 6 |
| Epinephelus marginatus | 17 |
| Euthynnus alletteratus | 4 |
| Mugil cephalus | 5 |
| Mycteroperca rubra | 3 |
| Pagrus caeruleostictus | 8 |
| Pterois miles | 5 |
| Scomber colias | 16 |
| Scomberomorus commerson | 10 |
| Seriola dumerili | 3 |
| Thunnus alalunga | 1 |
| Thunnus thynnus | 12 |
| Xiphias gladius | 1 |

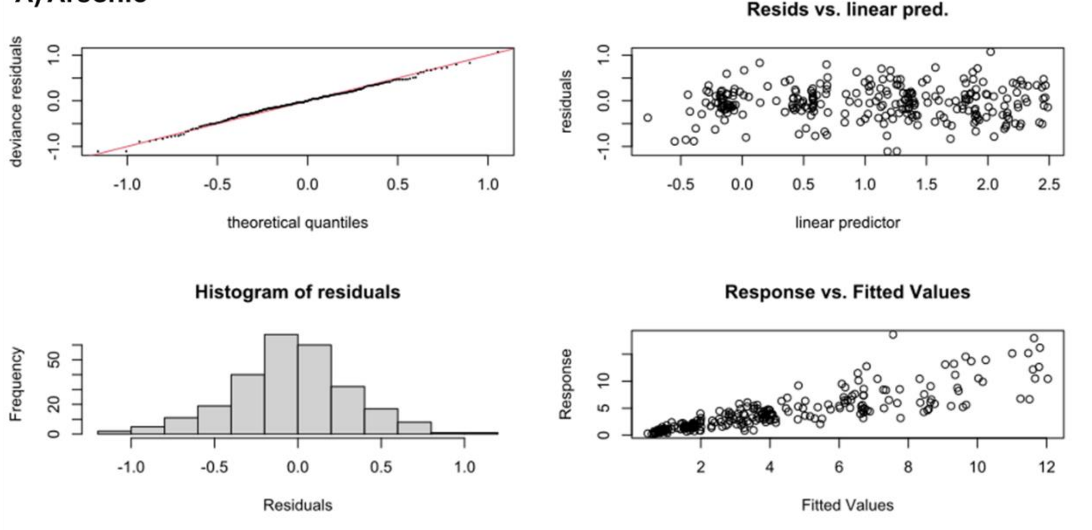
Supplement Table 2: Metal prevalence for each metal per species. Health standards used for comparison are according to the Israeli health standards.

| | | As | | Hg | | Pb | | Cd | |
|---|---|---|---|---|---|---|---|---|---|
| | Species | LOD | Health | LOD | Health | LOD | Health | LOD | Health |
| Local | *Argyrosomus regius* | 5 | | 5 | 1 | 1 | | 1 | |
| | *Dicentrarchus labrax* | 1 | 1 | 1 | | | | | |
| | *Epinephelus aeneus* | 25 | 12 | 25 | 3 | 2 | | | |
| | *Epinephelus costae* | 32 | 30 | 32 | | 2 | | | |
| | *Epinephelus marginatus* | 44 | 44 | 44 | 3 | 3 | | | |
| | *Mugil cephalus* | 30 | 7 | 21 | | 16 | | | |
| | *Mycteroperca rubra* | 6 | | 6 | | | | | |
| | *Pagrus caeruleostictus* | 39 | 39 | 39 | 4 | 6 | | | |
| | *Pterois miles* | 17 | 9 | 17 | | 5 | 1 | | |
| Highly Migratory | *Coryphaena hippurus* | 4 | 2 | 4 | | | | | |
| | *Euthynnus alletteratus* | 21 | 21 | 21 | | 1 | | 5 | |
| | *Scomber colias* | 29 | 28 | 29 | | | | 2 | |
| | *Scomberomorus commerson* | 35 | 22 | 34 | 1 | 6 | | 11 | 1 |
| | *Seriola dumerili* | 24 | 24 | 24 | | 1 | | | |
| | *Thunnus alalunga* | 2 | 2 | 2 | 2 | 1 | 1 | 2 | |
| | *Thunnus thynnus* | 13 | 12 | 13 | 11 | 7 | | 1 | |
| | *Xiphias gladius* | 1 | | 1 | | | | | |

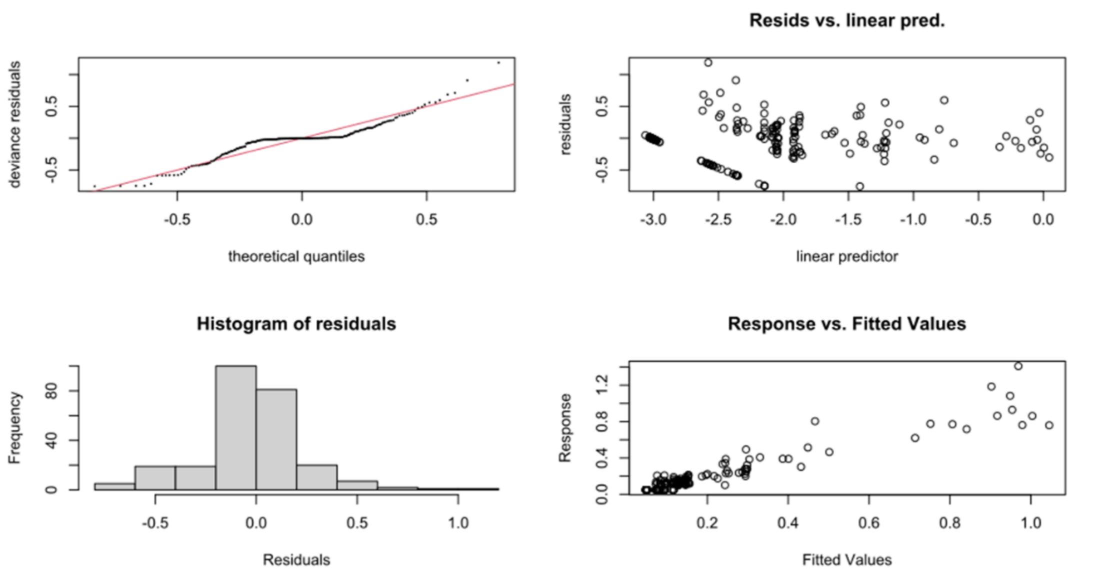



Supplement Figure 2: PCA analysis for all species.

**A) Arsenic**




**B) Mercury**




Supplement Figure 3: assumptions used in model for A) arsenic and B) Mercury

Supplement Table 3: Arsenic output for GAMM model (one global and two interaction models).

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| As M1 Model Global | R sq (adj)=0.708, Deviance explained 84.5% Scale est.=0.137, n=263 | | | | | | |
| | Component | Term | Estimate | Std Error | T-value | P-value | |
| | A. Parametric coefficients | (intercept) | 0.819 | 0.264 | 3.103 | 0.002 | ** |
| | | migrator | 0.319 | 0.3939 | 0.811 | 0.41827 | |
| | | Age mature | -0.388 | 0.154 | -2.526 | 0.0122 | * |
| | | Reserve | 0.483 | 0.369 | 1.306 | 0.193 | |
| | | Isotope cluster 2 | -0.076 | 0.071 | -1.058 | 0.291 | |
| | Component | Term | edf | Ref. df | F-value | P-value | |
| | B. Smooth terms | BMI | 5.257 | 6.688 | 0 | 1 | |
| | | Length | 2.08 | 2.649 | 0 | 1 | |
| | | TP | 1 | 1 | 0.192 | 0.661 | |
| As M2 Model | R sq (adj)=0.71 Deviance explained 83.9% Scale est.=0.14, n=263 | | | | | | |
| | Component | Term | Estimate | Std Error | T-value | P-value | |
| | A. Parametric coefficients | (intercept) | 0.782 | 0.2495 | 3.135 | 0.00194 | ** |
| | | migrator | 0.417 | 0.364 | 1.144 | 0.254 | |
| | | Age mature | -0.349 | 0.139 | -2.5 | 0.013 | * |
| | | Reserve | 0.4817 | 0.352 | 1.367 | 0.173 | |
| | | Isotope cluster2 | -0.073 | 0.072 | -1.021 | 0.308 | |
| | Component | Term | edf | Ref. df | F-value | P-value | |
| | B. Smooth terms | BMI | 4.954 | 6.052 | 3.594 | 0.002 | ** |
| | | Location | 19.171 | 21 | 37.85 | <2e-16 | *** |
| As M3 model | R sq (adj)=0.71 Deviance explained 83.7% Scale est.=0.14, n=263 | | | | | | |
| | Component | Term | Estimate | Std Error | T-value | P-value | |
| | A. Parametric coefficients | (intercept) | 0.775 | 0.249 | 3.107 | 0.002 | ** |
| | | migrator | 0.337 | 0.357 | 0.943 | 0.346 | |
| | | Age mature | -0.268 | 0.185 | -1.447 | 0.149 | |
| | | Reserve | 0.407 | 0.348 | 1.169 | 0.244 | |
| | | Isotope cluster2 | -0.059 | 0.073 | -0.812 | 0.417 | |
| | Component | Term | edf | Ref. df | F-value | P-value | |
| | B. Smooth terms | BMI: age group*juvenile | 3.425 | 4.192 | 4.024 | 0.008 | ** |
| | | BMI: age group*mature | 2.837 | 3.564 | 0.833 | 0.414 | |
| | | Location | 18.779 | 21 | 29.92 | <2e-16 | *** |

Supplement Table 4: Table summarizing the mercury output for the model for one global (M1) and two interaction models (M2 and M3).

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Hg M1 Model (Global) | R sq (adj)=0.901, Deviance explained 92.3%<br>Scale est.=-505.86, n=255 | | | | | | |
| | **Component** | **Term** | **Estimate** | **Std Error** | **T-value** | **P-value** | |
| | A. Parametric coefficients | (intercept) | -2.583 | 0.194 | -13.322 | <2e-16 | *** |
| | | migrator | -0.265 | 0.289 | -0.918 | 0.36 | |
| | | Age mature | 0.867 | 0.129 | 6.73 | 1.43e-10 | *** |
| | | Reserve | 0.542 | 0.267 | 2.031 | 0.043 | * |
| | | Isotope cluster 2 | 0.035 | 0.056 | 0.62 | 0.536 | |
| | **Component** | **Term** | **edf** | **Ref. df** | **F-value** | **P-value** | |
| | B. Smooth terms | BMI | 7.194 | 8.171 | 4.067 | 0.0001 | *** |
| | | Length | 1 | 1 | 0.001 | 0.983 | |
| | | TP | 1 | 1 | 0.001 | 0.973 | |
| | | Location | 18.881 | 21 | 17.405 | <2e-16 | *** |
| Hg M2 Model | R sq (adj)=0.71 Deviance explained 83.9%<br>Scale est.=0.14, n=263 | | | | | | |
| | **Component** | **Term** | **Estimate** | **Std Error** | **T-value** | **P-value** | |
| | A. Parametric coefficients | (intercept) | -2.582 | 0.19 | -13.558 | <2E-16 | *** |
| | | migrator | -0.268 | 0.246 | -0.969 | 0.333 | |
| | | Age mature | 0.866 | 0.122 | 7.087 | 1.76e-11 | *** |
| | | Reserve | 0.542 | 0.266 | 2.039 | 0.0426 | *** |
| | | Isotope cluster2 | 0.035 | 0.056 | 0.623 | 0.534 | |
| | **Component** | **Term** | **Edf** | **Ref. df** | **F-value** | **P-value** | |
| | B. Smooth terms | BMI | 7.223 | 8.19 | 4.727 | 2.25e-5 | *** |
| | | Location | 18.994 | 21 | 19.269 | <2e-16 | *** |
| Hg M3 model | R sq (adj)=0.9 Deviance explained 92.4%<br>Scale est.=0.074, n=255 | | | | | | |
| | **Component** | **Term** | **Estimate** | **Std Error** | **T-value** | **P-value** | |
| | A. Parametric coefficients | (intercept) | -2.596 | 0.18 | -14.45 | <2e-16 | *** |
| | | migrator | -0.104 | 0.261 | -0.398 | 0.691 | |
| | | Age mature | 0.514 | 0.159 | 3.232 | 0.001 | ** |
| | | Reserve | 0.723 | 0.253 | 2.859 | 0.00465 | ** |
| | | Isotope cluster2 | 0.033 | 0.054 | 0.624 | 0.533 | |
| | **Component** | **Term** | **edf** | **Ref. df** | **F-value** | **P-value** | |
| | B. Smooth terms | BMI: age group*juvenile | 1.001 | 1.002 | 0.163 | 0.687 | |
| | | BMI: age group*mature | 5.552 | 6.635 | 7.8 | <2e-16 | *** |
| | | Location | 18.593 | 21 | 16.742 | <2e-16 | *** |

Cont. Table 4

| Model | Component | Term | Estimate | Std Error | T-value | P-value | |
|---|---|---|---|---|---|---|---|
| Hg M4 Model | R sq (adj)=0.9, Deviance explained 92.2%<br>Scale est.=-0.07, n=255 | | | | | | |
| | **Component** | **Term** | **Estimate** | **Std Error** | **T-value** | **P-value** | |
| | A. Parametric coefficients | (intercept) | -2.607 | 0.191 | -13.647 | <2e-16 | *** |
| | | migrator | -0.176 | 0.276 | -0.64 | 0.523 | |
| | | Age mature | 0.827 | 0.126 | 6.544 | 4e-10 | *** |
| | | Reserve | 0.597 | 0.271 | 2.207 | 0.028 | * |
| | | Isotope cluster 2 | 0.02 | 0.056 | 0.402 | 0.688 | |
| | **Component** | **Term** | **edf** | **Ref. df** | **F-value** | **P-value** | |
| | B. Smooth terms | BMI: reserve No | 7.138 | 8.141 | 4.687 | 3e-5 | *** |
| | | BMI: reserve Yes | 1 | 1.001 | 0.939 | 0.33 | |
| | | Location | 18.827 | 21 | 17.725 | 2e-16 | *** |
| Hg M5 Model | R sq (adj)=0.907 Deviance explained 92.5%<br>Scale est.=0.075, n=255 | | | | | | |
| | **Component** | **Term** | **Estimate** | **Std Error** | **T-value** | **P-value** | |
| | A. Parametric coefficients | (intercept) | -2.628 | 0.179 | -14.657 | 2e-16 | *** |
| | | migrator | -0.103 | 0.264 | -0.392 | 0.696 | |
| | | Age mature | 0.576 | 0.16 | 3.602 | 0.0004 | *** |
| | | Reserve | 0.687 | 0.259 | 2.656 | 0.008 | ** |
| | | Isotope cluster2 | 0.035 | 0.055 | 0.634 | 0.527 | |
| | **Component** | **Term** | **Edf** | **Ref. df** | **F-value** | **P-value** | |
| | B. Smooth terms | BMI: age*reserve_juvenile No | 1 | 1 | 0.147 | 0.702 | |
| | | BMI: age*reserve_mature No | 4.878 | 5.7 | 8.496 | 2e-16 | *** |
| | | BMI: age*reserve_juvenile Yes | 1 | 1 | 0.593 | 280.442 | |
| | | BMI: age*reserve_mature No | 1.968 | 2.392 | 1.491 | 0.179 | |
| | | location | 18.211 | 21 | 16.185 | 2e-16 | *** |
| Hg M6 model | R sq (adj)=0.9 04Deviance explained 92.5%<br>Scale est.=0.074, n=255 | | | | | | |
| | **Component** | **Term** | **Estimate** | **Std Error** | **T-value** | **P-value** | |
| | A. Parametric coefficients | (intercept) | -2.771 | 0.169 | -16.440 | 2e-16 | *** |
| | | Reserve | 1.276 | 0.291 | 4.38 | 1.83e-5 | *** |
| | | Isotope cluster2 | 0.037 | 0.055 | 0.672 | 0.502 | |
| | | Age*Reserve Mature No | 0.91 | 0.255 | 3.57 | 0.0004 | *** |
| | | Age*Reserve Juvenile Yes | -0.388 | 0.201 | -1.925 | 0.0556 | |
| | | Age*ReserveMature Yes | 0 | 0 | NA | Na | |
| | **Component** | **Term** | **edf** | **Ref. df** | **F-value** | **P-value** | |
| | B. Smooth terms | BMI: age reserve juvenile no | 1.054 | 1 | 0.136 | 0.713 | |
| | | BMI: age reserve mature no | 4.378 | 5.123 | 3.413 | 0.004 | ** |
| | | Age reserve juvenile yes | 1 | 1 | 0.231 | 0.632 | |
| | | Age reserve mature yes | 1.908 | 2.322 | 2.128 | 0.093 | |
| | | location | 18.661 | 22 | 16 | 2e-16 | *** |

Supplement Table 5: Reported AICc values per model.

| | Model | AICc |
|---|---|---|
| As | M1 | 802 |
| | M2 | 796 |
| | M3 | 807 |
| Hg | M1 | -1076 |
| | M2 | -1081 |
| | M3 | -1091 |
| | M4 | -1078 |
| | M5 | -1084 |

Supplementary Table 6: Comparison of trophic positions from FishBase to values calculated in this study.

| | Species | TP (This Study) | average | TP (Fishbase) | Difference | Average difference |
|---|---|---|---|---|---|---|
| Detritivore | *Mugil cephalus* | 2.5 | | 2.5 | 0 | |
| Plantktivore | *Scomber colias* | 2.7 | | 3.9 | 1.2 | |
| Local Carnivores | *Argyrosomus regius* | 3.4 | 3.4 | 4.3 | 0.9 | 0.7 |
| | *Dicentrarchus labrax* | 3.7 | | 3.5 | -0.2 | |
| | *Epinephelus aeneus* | 3.2 | | 4 | 0.8 | |
| | *Epinephelus costae* | 3.6 | | 3.9 | 0.3 | |
| | *Epinephelus marginatus* | 3.6 | | 4.4 | 0.8 | |
| | *Mycteroperca rubra* | 2.8 | | 4.1 | 1.3 | |
| | *Pagrus caeruleostictus* | 3.3 | | 3.7 | 0.4 | |
| | *Pterois miles* | 3.3 | | 4.5 | 1.2 | |
| Migratory carnivores | *Coryphaena hippurus* | 2.8 | 3.3 | 4.4 | 1.6 | 1.2 |
| | *Euthynnus alletteratus* | 3.8 | | 4.5 | 0.7 | |
| | *Scomberomorus commerson* | 3.1 | | 4.5 | 1.4 | |
| | *Seriola dumerili* | 3.5 | | 4.5 | 1 | |
| | *Thunnus alalunga* | 3.1 | | 4.3 | 1.2 | |
| | *Thunnus thynnus* | 3.1 | | 4.5 | 1.4 | |
| | *Xiphias gladius* | 3.6 | | 4.5 | 0.9 | |
| | Average Difference | | | | 0.88 | |

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# General Discussion

Though marine metal pollution has been extensively studied for decades, it is a complex category of pollutants and there are many basic principles to its behavior that research still has not provided answers to. This thesis presents some answers to part of those research gaps, specifically on the local scale, while highlighting the intricacies of each individual metal behavior in the understudied Eastern Mediterranean Sea region.

## Behavior of Metals in Israeli Coastal Waters

For cadmium and lead, this thesis shows that there is low prevalence within the local marine biota of Israel (shown in chapter two and three). This is encouraging to observe, especially samples collected from areas of historically high contamination like the Kishon Estuary – Haifa Harbor (Richter et al., 2003). Not only were levels below those defined by Israeli health standards, but they were also below the limits of detection, a sign of improvement for both human and animal health. On the other hand, the low prevalence within specimen limits our ability to assess cadmium and lead behavior in the local marine environment. There are a few explanations for their low prevalence, one being the evident reduction in their release due to mitigation efforts on both a national and international level. Prior to the phaseout of lead from fuels, fuel combustion used to be the major local contributor to atmospheric release in Israel (Erel et al., 2002). Chien 2019 showed the observable decrease in lead in seawater and particulate matter following the removal of leaded fuels in the Red Sea. However, the question remains how the foreign input of lead, which may be the dominating fraction, continues to influence the biogeochemical cycle of lead in the local marine environment. Whether a release to the atmosphere or into the water, this emphasizes the importance of considering areas beyond national boundaries and incorporating a more regional approach, which I show in chapter 1. A similar reduction in cadmium release into the environment has also been reported in monitoring programs, especially around Kishon Estuary – Haifa Bay (Shefer et al., 2015b). However, mollusc bioindicator species show an increase in concentrations while surrounding sediments decrease (Shefer et al., 2015b). This discrepancy potentially indicates that while the release in the environment may be changing, there may be changes in biological availability of cadmium to biota, with differences in chemical functioning within the aquatic and sediment fractions and between different organism groupings. Indeed, I show in chapter two that crustaceans and cephalopods display higher behavior than their fish counterparts, thus, the use of fish as a bioindicators of marine health for cadmium may not be appropriate. It is possible that the bioaccumulation strategies for the two differ from one another, and that there is no trophic biomagnification. Physiological differences between the two might also be a factor with differences in detoxification mechanisms. Additionally, assessing muscle may be limiting, as muscle is not always the target tissue/organ for accumulation (Gray, 2002). Lastly, as shown in chapter 3, there may be an impact of life strategies, with highly migratory fish characterized by high metabolism and utilizing the habitats of open Ocean differ from locally caught species. Therefore, without taking these numerous considerations into account when conducting such metal research, identifying the accumulation mechanism is not possible.

These considerations also apply to the behavior of mercury and arsenic, however, as seen in chapters two and three, these metals differ from cadmium and lead as they are characterized by a high prevalence throughout. This higher prevalence allows for a better assessment of metal behavior. Arsenic concentrations are high throughout the sampling, with some of the highest concentrations reported in the Mediterranean Sea, as shown in chapter two with cephalopods. Of the four metals assessed here, arsenic is the least understood of the four, with major knowledge gaps in its biogeochemical cycle, especially in the eastern Mediterranean Sea. With the high variability within each species, no clear accumulation patterns are observed that could indicate that accumulation mechanisms are in play. While metals are often described to bioaccumulate and biomagnify with trophic position and size (Gray, 2002), these findings provide support that mercury is an exception to that behavior rather than being the standard. While further investigation is needed, we hypothesize that the dominating factors of arsenic accumulation for this region are associated with the abiotic conditions of the highly oligotrophic waters, specifically salinity levels and phosphate concentration. Unfortunately, though chapter 2 provides a respectable sampling collection with the same species collected from four landings uniformly, landings do not always equate to catch location. Adjusting the sampling strategy by ensuring catch location (chapter 3) allows for the use of indicator species, like *M. cephalus*, to provide insight into the impacts of abiotic conditions on arsenic accumulation. Though *M. cephalus* is characterized as a species with higher tolerance to polluted waters, its presence in the Haifa Harbor, richer in nutrients than the open waters due to a constant input from the Kishon Estuary, may explain their lower arsenic levels compared to other locations and species. Here, the higher phosphate availability in the water and the lower salinity due to freshwater input may reduce the uptake of arsenic. Alternatively, it's worth considering that *M. cephelus* may possess physiological properties enabling it to detoxify more efficiently compared to other fish species. This highlights the need for caution when using them as an indicator species, emphasizing the importance of understanding these physiological mechanisms. Along the same lines, seasonal conditions may contribute to the variance, with winter storms highly influencing nutrient inputs to the water column. However, in order to address seasonality, long-term monitoring data is required. Open questions still remain regarding the influence of such high concentration on both fish and human health.

## Human Health

The combined insights from all three chapters offer a critical foundation for understanding metal accumulation in local marine organisms, underlining the importance of ongoing monitoring to detect potential threats to environmental and human health. This becomes particularly crucial in the context of climate change, which can alter environmental conditions and increase the availability of metals in marine ecosystems (Hauser-Davis & Wosnick, 2022). These environmental shifts can impact ecosystem services such as biodiversity and fisheries along the Israeli coastline.

Although Israeli marine fisheries do not play a significant role as a protein source for the majority of the population or contribute to the economy through exports, certain local communities are more exposed to metal contamination through the consumption of local marine fish. According to the Israel Environmental Protection Agency's Blue Half program, in 2015, the local Israeli catch was reported at 2,700 tons (The Fishing Reform for Mediterranean Sea Management (Hebrew), 2015). A reported 70,000 sport fishermen were responsible for 18% of the local catch and 1,000 beach pole fishermen were responsible for 14% of the local catch (The Fishing Reform for Mediterranean Sea Management (Hebrew), 2015). Certain communities that rely on locally sourced marine fish for protein may be more susceptible to dietary metal exposure from seafood. Such communities include Israeli-Arab villages/communities of Jiser-al-Zarka, Furodis, Jaffa, and Akko. Additionally, citizens who actively participate in sport and recreational fishing, and bring home seafood to their families which include more vulnerable individuals such as women and children, are possibly exposed to higher quantities of dietary metals compared to those who do not consume local seafood.

Despite the existence of health standards in Israel for assessing metals in food products, including seafood, the local seafood is not routinely evaluated for human health safety. This signifies a significant gap between established health standards aimed at protecting the public and their actual implementation. Addressing this disconnect is crucial to ensure the safety and well-being of communities relying on marine resources for sustenance and recreation. Working with local fishermen provided invaluable insight into the extensive knowledge that this community possesses regarding the sea. Furthermore, it offered fishermen the chance to voice their concerns about fish quality, with many expressing a keen interest in understanding the prevalence of marine chemicals in local fish, their impacts, and the potential exposure to these chemicals through consumption, whether by the fishermen themselves or their families. Continued research, monitoring, regulatory actions, and outreach are all essential to safeguard both environmental integrity and human health in the face of metal pollution in marine environments.

# Conclusion

The findings of this thesis shows the intricate nature of metals in the marine environment and emphasize the ongoing impacts of metal pollution on Israel's marine ecosystems. Despite successful mitigation efforts that have reduced metal releases, these pollutants remain a persistent and enduring part of the marine system due to their stability. While metal pollution might seem like a well-known issue, this research highlights the necessity of continuous monitoring and research in the marine environment to safeguard both human and environmental health. Although there are existing national programs for monitoring sediments and using bioindicator species, there is a need for a more comprehensive approach that includes a wider range of species and encompasses diverse geographical locations. Furthermore, there is a crucial need to ensure that scientific knowledge derived from such studies is effectively communicated to the general public. Public awareness and understanding of metal pollution impacts can foster greater support for conservation efforts and encourage responsible practices that minimize further harm to marine ecosystems. By prioritizing ongoing research, comprehensive monitoring, and effective public outreach, we can work towards a healthier and more sustainable marine environment for current and future generations.

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הצטברות של מתכות כבדות במזרח ים התיכון, ישראל: בריאות הסביבה הימית ואדם

דבורה רמון

תקציר

הצטברותן של מתכות כמו ארסן, כספית, קדמיום ועופרת ביצורים ימיים עוררה זה מכבר דאגות בנוגע לבריאות הסביבה והציבור, עקב השפעותיהן האקולוגיות והבריאותיות הפוטנציאליות. מתכות המגיעות למערכת הימית, בין אם באופן טבעי ובין אם בעקבות פעילות אנתרופוגנית, נאגרות בתוך יצורים ימיים מסביבתם, כתלות בתנאי הסביבה כמו גם במאפייני האגירה הספציפיים לכל מין. בפרט, מאכלי ים משמשים כווקטור המעביר מתכות מהסביבה הימית אל אוכלוסיית האדם. מאכלי ים מהווים מקור חיוני לחלבון ומספקים יתרונות בריאותיים מסוימים לאדם. לפיכך, סיכונים בריאותיים הקשורים למתכות מדגישים את חשיבות ניטורם של מוצרי מזון מן הים אשר משווקים לצריכה על ידי האדם, על מנת להפחית את החשיפה אליהן. על אף ההשלכות המשמעותיות, המחקר על הצטברות מתכות במי החופים של ישראל והערכה מינימלית של חשיפת האדם למתכות דרך מאכלי ים הנדוגים מקומית נותר מוגבל. מטרת מחקר זה אפוא היא לספק מידע בסיסי על תפוצתן של כספית, קדמיום, עופרת וארסן במזון מן הים הזמין באופן מקומי, כולל מאכלי ים ודגים בעלי חשיבות כלכלית ואקולוגית, ולחקור את הגורמים האפשריים המניעים את הצטברותן. לצורך כך, נערכו שני סקרים נרחבים, האחד התמקד במאכלי ים הנפוצים לצריכה והשני במיני דגים חיוניים מבחינה אקולוגית וכלכלית. תוצאות הסקרים הצביעו על כךשלארסן השכיחות הגבוהה ביותר ואחריו כספית, עופרת וקדמיום. בישראל, ריכוזי ארסן הם בין הגבוהים ביותר שדווחו בספרות, יתכן כי בשל תנאי הסביבה הייחודים למזרח הים התיכון. אזור זה מאופיין במליחות גבוהה וריכוזי פוספט נמוכים, תנאים אשר מעודדים את קליטתה על ידי יצורים ימיים. התנהגותה של כספית היתה יחסית צפויה, עם רמות גבוהות יותר בדגים סדימנטריים או בבוגרים, ולמרבה העניין עם רמות גבוהות יותר באזורי שמורות ימיות בהשוואה למוקדי זיהום. שכיחותן הנמוכה יחסית של עופרת וקדמיום מצביעה ככל הנראה על יעילותם של מאמצי ההפחתה בישראל. תכונות חיים ספציפיות למין, דוגמת בית גידול ושלב חיים, זוהו כגורמים מובהקים בהשפעתם על צבירת מתכות ביצורים ימיים. בעוד שהשוואה בין משתנים בודדים סיפקה תובנות לגבי הגורמים המניעים הצטברות, ניתוח כלל המשתנים בו-זמנית התבצע באמצעות פיתוח מודל משולב מצטבר כללי (GAM general additive mixed model) להצטברות כספית וארסן. מודל ה-GAM הראה הצטברות מוגברת של כספית בתוך אזור השמורה הימית בהתאם לבגרות הדג. המחקר אף מדגיש את תפקידם של מאכלי ים הנדוגים מקומית כנתיב לחשיפת האוכלוסייה המקומית למתכות, כאשר קהילות מסוימות פגיעות יותר. באופן כללי, מחקר זה מספק הערכה נרחבת, המאפשרת התבוננות בקנה מידה גדול יותר, ומצביע על אזורים למחקר נוסף. יחד עם זאת, בשל התנהגותה המובחנת של כל מתכת בסביבה הימית והשונות הניכרת בין המינים, יש צורך במחקר מעמיק יותר לשיפור הבנתנו את התנהגות המתכות המקומיות ביצורים ימיים וסביבתם. לסיכום, עבודה זו תורמת תובנות משמעותיות למורכבות של הימצאות מתכות בסביבה הימית, בדגש על השפעותיהן המתמשכות על המערכות האקולוגיות בישראל ועל כיווני מחקר עתידיים.

**הצטברות של מתכות כבדות במזרח ים התיכון, ישראל:**

**בריאות הסביבה הימית ואדם**

מאת: דבורה רמון

בהנחיית: פרופ' דן צ'רנוב ופרופ' פיטר קרוט

חיבור לשם קבלת התואר "דוקטור לפילוסופיה"

דוקטורט פרסומים

אוניברסיטת חיפה

בית ספר למדעי הים ע"ש לאון צ'רני

החוג לביולוגיה ימית

ינואר 2025

# הצטברות של מתכות כבדות במזרח ים התיכון, ישראל:

# בריאות הסביבה הימית ואדם

דבורה רמון

חיבור לשם קבלת התואר "דוקטור לפילוסופיה"

דוקטורט פרסומים

אוניברסיטת חיפה

בית ספר למדעי הים ע"ש לאון צ'רני

החוג לביולוגיה ימית

ינואר 2025