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Regression of the Level of Different Heavy Metals to Size of Marine Organisms Harvested from the "Jiyeh" Oil Spill Zone of the Eastern Mediterranean Sea

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Abstract This study aimed to establish a baseline data on regression of the levels of Lead (Pb), Nickel (Ni) and Vanadium (V) to specific size dimensions of selected marine organisms harvested from an oil spill zone of the Eastern Mediterranean Sea. Twenty samples of each of *Siganus rivulatus,* Mullets and oysters were collected from each of six harvest sites. A total of 1, 3, and 3 respective significant regression equations ($p < 0.01$) were established between Pb, Ni, V and specific size dimensions of the selected marine organisms. The significant correlation associated with the highest R^2 value was obtained between the Pb (y) level and the width (x) of the *Siganus rivulatus* ($y = -86.833x + 417.72$). The other six statistically significant correlations were associated with lower values of R^2 ranging between 0.338 and 0.380. This baseline data will be used in the future to evaluate the self-purification process of pollutants in different sizes of indicator-marine organisms in this part of the Mediterranean Sea.

Keywords Oil spill · Heavy metals · Fish · Oysters

The huge oil spill from "Jiyeh" power plant, located at 30.3 km south of the capital Beirut, affected around 150 km of the coastline (UNEP 2007). A volume of 15,000 tons of number 6-heavy fuel oil spilled into the Eastern Mediterranean Sea, and was driven by South to North winds. A previous search, accomplished 3 years before the oil spill, revealed already a scarce presence of copepods density due to a high contamination of the Eastern Mediterranean artesian water zones (Barbour et al. 2004). The spilled heavy fuel oil is among the most difficult to combat due to its high viscous nature, low volatility, high specific gravity and tendency to sink to the seabed which could lead to prolonged persistence in the marine environment, and the need of decades to rehabilitate the marine ecosystems (UNEP 2007). Previous incidents of oil spills around the world including, the Exxon Valdez oil spill in Alaska in 1989, the Apex Barge oil spill in Galveston Bay in 1990, and the Erika oil spill in Atlantic coast of France in 1999 have resulted in significant contamination of the marine life (SAEB 1989; Budzinki et al. 2004); such contaminations could need decades for self purification processes to remidify (Barbour et al. 1986; Budzinki et al. 2004).

The major contaminants, originating from the oil spill and known to cause serious damages to the marine life and to human consumers include heavy metals such as Lead (Pb), Nickel (Ni) and Vanadium (V) (ATSDR 1993, 1999, 2006). Only one previous study related to metal concentrations in certain coastal organisms of the Eastern Mediterranean Sea was cited (Shiber 1981), showing that Lead and Nickel levels were the highest in polychaete *Hermodice carunculata*, a carnivorous scavenger. Regarding these metals, the fish *Thalassoma pavo*, locally known as Araysi, was the only specie to have higher levels in comparison to twelve other species of fish harvested from the Eastern Mediterranean coast of Israel (Shiber 1981). The purpose of this work was to establish the first

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base-line data of the regression of the level of three heavy metals, following an oil spill in the Eastern Mediterranean sea, to specific size parameters of three selected organisms.

Materials and Methods

Six locations across the Eastern Mediterranean were included in the sampling design. Two of the six locations were expected control negatives located 24 km South of the Jiyeh Power Plant (source of oil spill), namely at 24.1 and 47.8 km South of the plant. The other four locations were situated at the following distances north of the plant namely, 30.3, 57.9, 72.4, and 78.3 km. The direction of the sea currents at the time of the oil spill was South to North. The coordinates of the 6 sites, according to the Global Positioning System (GPS) data provided by the Greenpeace divers of the Rainbow Warrior ship, were: two South sites (N 33° 17.548′, E 035° 12.741′ and N 33° 28.388′, E 035° 16.749′), and four North sites (N 33° 53.579′, E 035° 27.855′; N 34° 01.089′, E 035° 37.264′; N 34° 07.729′, E 035° 38.209′; N 34° 12.181′; E 035° 38.060′).

Two major fish species, (*Siganus rivulatus* and Mullets of the Mugilidae family) and oysters, predominant in artisanal fishing activity of this part of the Eastern Mediterranean, were sampled from the six locations mentioned above. The total number of samples was 360 individuals, including 20 individual samples of each species per location. Sampling of fish and oysters from the six designated sites was accomplished at 117 and 72 days post the oil spill, respectively. The oysters were transported and kept at −80°C at the Animal Science Laboratory of the American University of Beirut. Dorsal muscles of the freshly caught fish were collected and also kept at −80°C. Individual organism dimensions of fish were recorded namely, length, maximum width, and weight, while the measured oyster's parameters included the shell length, width, and weight. The sampling, cleaning and storage were done according to previously reported standard methods (Lasrado et al. 2003).

Thawed dorsal muscle parts of the two fish species and the whole oyster were individually homogenized, lyophilized at −50°C and 0.22 m Bar pressure for 48 h, and then re-homogenized (NIST 2001). The twenty freeze dried and homogenized individual samples of each specie, collected in a specific location, and at the specified times, were pooled in equal weights into 4 replicates for fish and 5 replicates for oysters, computing the average of each size parameter in a pooled sample.

The level of the three inorganic chemical contaminants in the digested samples was detected using the Inductively Coupled Plasma Mass Spectrophotometer (ICP-MS 4500, Agilent, Japan) equipped with a Cetac – ASX 520 – Auto Sampler. The minimum detection limit (MDL), known as the sensitivity of the machine, is 0.002 µg/g. Dry weight of each heavy metals. Briefly, the procedure included the mixing of 0.5 g of each lyophilized pooled sample with 7 mL of Nitric acid 65% (HNO_3) and 1 mL of Hydrogen Peroxide 30% (H_2O_2). The acid digestion was performed at 200°C for 20 min. The digested material was diluted up to 20 mL with double distilled water and filtered through a 0.45 µm Millipore filters. The filtered solution was analyzed for Lead, Nickel, and Vanadium using an Inductively Coupled Plasma Mass Spectrophotometer. Standard curves were prepared, and routine quality assurance/quality control procedures were conducted.

The computed number of interactions resulting in a study of 63 regression equations for each heavy metal is shown in Table 1. Significant linear regression equations were selected, relating the level of the heavy metal (y) to specific size parameter (x) at $p < 0.01$ (Steel et al. 1997). These regression equations were established for each marine organism at each harvest site. Moreover, the regression equations of the level of these chemical contaminants to size parameters were determined for the same organism when data are pooled of the six sites (SPSS 15.0, SPSS Inc., Chicago, USA).

Results and Discussion

The collected individual *Siganus rivulatus* had a mean of length equivalent to 15.4 cm, an indicator of maturity in the examined organisms of this specie; in addition, the collected individual Mullets had a mean of length equivalent to 31.2 cm, an indication also of the maturity of these organisms. Moreover, the mean of size parameter of mature oysters were 142.04 g for weight, 7.2 cm for length, and 5.6 cm for width.

The regression equations of the linear standard curves for Lead, Nickel, and Vanadium were significant at $p < 0.05$; more specifically, the regression of Lead concentration (ppb) (x) to Ratio (y) was $y = 0.465x + 0.133$ with $R^2 = 0.9989$.

Table 1 Number of interactions resulting in 63 regression equations for each studied heavy metal

Number of organisms	Number of size parameters[a]	Number of harvest sites	Number of total interaction[b]
3	3	6	54
3	3	1 pool of 6 sites	9
		Total	63

[a] Measured dimensions of an organism were three namely, width, length, and weight

[b] Total interaction is deduced from multiplication of the number of organisms × the number of size parameters × the number of harvest sites

Table 2 Significant correlations of three heavy metals levels (y) in different selected marine organisms to the size parameters (x)

Heavy metal-y (Marine organism[a])	Locations (km)[b]	Size parameter-x	Regression equation	R^2	$p < 0.01$
Lead (Pb)					
(Siganus rivulatus)	Tyr (47.8, S)	Width	$y = -86.833x + 417.72$	0.995	0.003
Nickel (Ni)					
(Oysters)	All locations (pooled data)	Weight	$y = 0.0431x + 0.5111$	0.339	0.001
		Length	$y = 2.0643x - 8.2299$	0.367	0.000
		Width	$y = 2.6908x - 8.5315$	0.338	0.001
Vanadium (V)					
(Oysters)	All locations (pooled data)	Weight	$y = 0.0164x - 0.5156$	0.373	0.000
		Length	$y = 0.757x - 3.6377$	0.376	0.000
		Width	$y = 1.033x - 4.012$	0.380	0.000

[a] Harvests of oysters and the two fish specie were accomplished in the year 2006 in September (72 days post the oil spill) and November (117 days post the oil spill), respectively

[b] Distance from source could be to North (N) or South (S) of the oil spill source, and is reported in km. The direction of sea current at the time of the oil spill was South to North

The regression of Nickel (x) to Ratio (y) was $y = 0.237x-0.136$ with $R^2 = 0.9988$; however, the regression of Vanadium (x) to Ratio (y) was $y = 0.820x + 0.424$ with $R^2 = 0.9991$. Moreover, results of the quality assurance/quality control were within the normal range.

Sixty-three regression equations were studied relating the level of each heavy metal in the three organisms to the different size parameters (Table 1). The studied 63 regressions for Lead resulted in one highly statistical significant regression ($p < 0.01$) (Table 2). This highest significant correlation of Lead level was seen in *Siganus rivulatus* harvested at 47.8 km South of the oil spill source in relation to the width parameter ($R^2 = 0.995$ and $p = 0.003$).

Sixty-three regressions, similar to regressions studied for Lead, resulted in three highly statistical significant correlations ($p < 0.01$) (Table 2), relating Ni levels in oysters to weight, length and width.

Sixty-three regressions were also studied for V levels resulting in three significant correlations ($p < 0.01$) (Table 2), to weight, length, and width of oysters.

All the seven highly significant regression equations had positive slopes, except for one negative correlation resulting in a decrease of the Lead level with the width of *Siganus rivulatus* organisms, which could be due to the growth dilution effect (Otchere 2003).

There was a consistent pattern in the 3 significant regressions of Ni level in oysters to size parameters resulting only in positive slopes. Nickel is clearly correlated positively to size dimensions and most likely to age. This data is in agreement with previous reports pointing to the positive relationship between Nickel and age or dimension (Casas and Bacher 2006).

The same pattern seen for Nickel is also repeating in the studied regressions of Vanadium to size parameters in oysters, with presence of only positive slopes (Table 2). It is worth noting that Nickel and Vanadium are present in heavy fuel oil in higher values compared to lead (Chiffoleau et al. 2004), which could be the reason for obtaining this similar pattern in regressions of Nickel and Vanadium to size parameters.

Future investigations will study the fate in time of the studied heavy metals in correlation to the size parameters of the selected indicator-marine organisms present at the same six sites, to evaluate the impact of self-purification of these heavy metals and the nature of the expected change in the regression equations.

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