Middle East Journal of Applied Sciences 4(2): 326-335, 2014
ISSN 2077-4613

Analysis of Six Trace Elements (Cd, Cr, Cu, Ni, Pb And Zn) In *Diplodus Sargus* And *Siganus Rivulatus* Fish In Three Sites Along The Lebanese Coast

[1,2]W. Skaff, [1]N. Estephan, [3]A.H. Mouneimne, [1]N. Ouaini, [2]V. Camel

[1]Department of Chemistry and Life Sciences, Faculty of Sciences, Holy Spirit University of Kaslik, B.P. 446 Jounieh, Lebanon.
[2]Analytical Chemistry Laboratory, AgroParisTech, 16 rue Claude-Bernard, 75005 Paris, France.
[3]Faculty of Agriculture, Lebanese University, Dekwaneh, El Metn, Lebanon.

ABSTRACT

The Lebanese coast is subjected to a strong urban, touristic and industrial pressure. The wastewater of the littoral zone eventually reaches the sea without undergoing, in general, any pretreatment. This precarious situation escalates with the absence of laws that address the "food security" and "environmental" aspects throughout the Lebanese coast or the non-application of the existing ones. The fisheries sector in particular, suffered the consequences. Indeed, in Lebanon, the consumer's interest for fish is growing. For them the sea products in particularly fish are considered as a healthy food, or even as a luxury food. The sea food restaurants lining the coast are among the most expensive and the most prestigious in the country. But consumer confidence has been eroded by media reports evoking the maritime pollution in the country. It is in this context that we chose to study the metal pollution of two species of fish (*Diplodus sargus* and *Siganus rivulatus*) in a region particularly affected by pollution which run from Tabarja to the north of Beirut and end at Ouzaï located at the south of the capital. The captured fishes was completely grounded, lyophilized and mineralized. The mineralization was conducted in a microwave digester. After that, the six trace elements were analyzed by atomic absorption spectroscopy: Cd, Cr, Cu, Ni, Pb and Zn. The obtained results are in general, consistent within international studies: the fish accumulation for the metal contaminants (with exception of Hg) is low. The recorded values are less or equal than the maximum limits in food set by international bodies. Considering the season factor, we note a seasonal fluctuation in the concentration of the studied metals. By comparing the metal level for the three sites, we note that the Ouzaï site is in general, the most polluted one.

Key words: Trace elements, cadmium, chromium, copper, nickel, lead, zinc, fishes, *Diplodus sargus*, *Siganus rivulatus*, Lebanese coast

Introduction

The Lebanese coastal waters are the final receptacle of panoply of organic and metallic contaminants emanating from the anthropogenic activity.

In Lebanon, the Lebanese fishing sector plays an important role in economic and social planning (MoA/FAO, 2004). The yearly fished quantities do not exceed 8000 tons (MoA/FAO, 2009).These amounts cover only 25% of local need (MoA/FAO, 2007). The so-called "valuable species" of fish are in sharp decline due to the constant pressure by fishermen who often operate far from the legal framework established by the relevant authorities (MoA/FAO, 2007).

The geographic, climatic and hydrographic frames of Lebanon are so particular. They affect the accumulation of chemical contaminants by various marine organisms, including fish.

Trace metals are found naturally in the environment (BENAMAR *et al.*, 2010). They were behind the development of industrial societies (INERIS, 2006a). According to MIQUEL, (2001), the human activity is causing the change in their geographical distribution and their chemical forms as well as their anthropogenic inputs in various ecosystems.

For a better understanding to the chemical contamination in the marine environment, IFREMER, (2003) point to conduct analyzes of sedentary species. This choice allows linking the observed contamination to a specific geographic area. Thus the choice of species was made taking into account the widespread endemic species on the Lebanese coast and especially their mobility. These species are: *Siganus rivulatus* and *Diplodus sargus*.

Therefore, the aim of this study is to determine the contamination of the two endemic species of fish (*Diplodus sargus and Siganus rivulatus*) by six trace elements (Cd, Cr, Cu, Ni, Pb and Zn) around Beirut area.

Corresponding Author: W. Skaff, Department of Chemistry and Life Sciences, Faculty of Sciences, Holy Spirit University of Kaslik, B.P. 446 Jounieh, Lebanon
E-mail: skafwad@hotmail.com

Methodology:

Sampling:

The sampling of fish is carried out on three selected sites around Beirut area (Figure1): Tabarja (red), Dora (blue) and Ouzaï (green). These sites are particularly affected by various anthropogenic and industrial discharges.

At each site, depending on the availability of the species studied, a seasonal collection of two kilograms of each selected species was recovered from fish products.

To ensure the reliability of the raw material, we used to wait each fisherman in early morning at the fishing port before their arrival. Once purchased, and to reduce the risk of contamination, fish were packed in polyethylene bags in a refrigerated container and transferred to the laboratory.

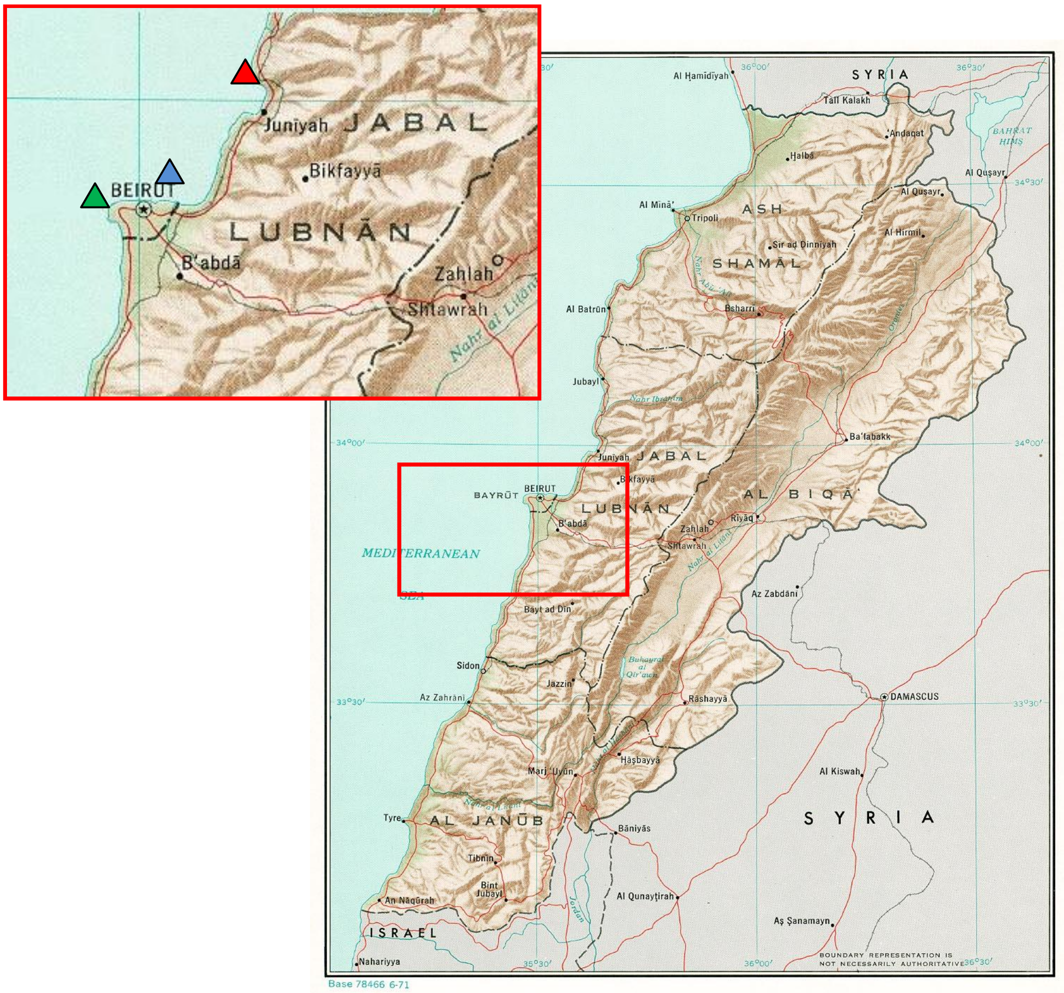


Fig. 1: Map of Lebanon which included the study area (red box) and the three sampling sites of fish: Tabarja(red), Dora(blue) and Ouzaï(green)

Sample preparation:

Once in the laboratory, every fish was individually washed with distilled water, the size and weight of each was individually recorded. Then the samples were placed in a cold room waiting for the grinding.

Each sampled fish was cut on a polyethylene plate with a molybdenum-vanadium coated knife to avoid sample contamination. The pieces were then ground in a meat grinder, brand type "Moulinex HV8", having a stainless steel blade. After that, the obtained mash was placed in a freeze-drying flask previously washed and calibrated.

The freeze dryer used in our work is of type "VirTis, 40666." The adopted–drying protocol was as follows:

- Freezing the grounded fish at a temperature of-80°C for a period of 18h.
- Vacuum evaporation for a period of 120h under a pressure fixed at 100mTorr(Mt).
- Capture of the produced steam with a condenser at a-86^{o}C temperature.

Once the process ended, the freeze-dried fishes were then introduced, for a better homogenization, into a mixerchopperbrand "Keenwood BL745", with a stainless steel blade. Once mixed, the samples were kept cold in a sealed glass jars prior to analysis.

The mineralization was carried out using a microwave digester type Milestone "ETHOS 1Pro". An experimental design was used to optimize the digestion method for the freeze-dried fish. The obtained optimal method consist to add for a 0.5g of freeze-dried fish, placed in a Poly-Tetra-Fluoro-Ethylene (PTFE) bombs, 10 ml of nitric acid (HNO_3 65%) and 2ml of hydrogen peroxide (H_2O_2 30%). After that, the closed bombs were placed in the digester and the temperature is raised in steps to 210°C (rise time of 10min to 200^{o}C, temperature level of 200^{o}C for 5min, rise time of 5min to 210^{o}C, temperature level of 200^{o}C for 5min).

For analysis we used an ultrapure nitric acid for analysis ($HNO_3$65%) type "Merck" (Darmstadt, Germany) and a hydrogen peroxide (H_2O_2 30%) type "Sigma-Aldrich" (Steinheim, Germany).

Atomic absorption analysis:

An atomic absorption spectrometer "ZEEnit700" produced by the German company "Analytic jena" was used to measure cadmium, chromium, copper, lead, nickel and zinc content in the samples.

Analyses of Cd, Cr, Cu, Ni and Pb were carried out systematically in electrothermal atomic absorption spectrometry with a correction system by Zeeman Effect, while the analysis of zinc was performed in flame mode.

These analyzes were based on calibration curves using standard additions to reduce the matrix effect. The table below shows the nature and content of the solutions used for the analysis of trace metals (standards and zero).

Table 1: Nature and content of the solutions used for AAS analysis

Metal	Cd	Cr	Cu	Ni	Pb	Zn
Flame						X
Graphite furnace	X	X	X	X	X	
Stock standard solution	10µg/L	100µg/L	100µg/L	200µg/L	250µg/L	2,5mg/L
Blank solution	HNO_3 (0,5%)	HNO_3 (0,5%)	HNO_3 (0,5%)	HNO_3 (0,5%)	HNO_3 (0,5%)	HCl (0,5%)
Matrix modificator	$NH_4H_2PO_4$ (1%)	$Mg(NO_3)_2$ (0,1%)			$NH_4H_2PO_4$ (1%)	

For each sample, three collects were made. To ensure repeatability of the measurements, the device was programmed to perform three simultaneous readings for each collect. The results mentioned below represent the arithmetic average of the three collects.

Results And Discussion

Analysis of the six trace elements:

The results obtained from the analysis of different trace elements in samples of both species *Diplodus sargus* and *Siganus rivulatus* from Dora, Ouzaï and Tabarja sites are shown in Table 2.

Table 2: Concentrations in trace elements measured in samples (± Standard Deviation)

Samples	Concentrations (in µg/g d.w.)					
Species-Site-Season	Cd	Cr	Cu	Ni	Pb	Zn
DS-O-Sp	0.087±0.055	1.317±0.029	3.270±0.242	0.688±0.493	1.187±0.133	146±2
DS-O-Su	0.187±0.071	1.631±0.100	1.027±0.041	0.261±0.085	0.218±0.114	161±3
DS-O-A	0.079±0.028	0.316±0.012	0.313±0.138	<LD[2]	0.360±0.058	133±1
DS-O-W	0.135±0.064	0.712±0.037	0.447±0.015	0.270±0.087	1.060±0.114	136±4
SR-O-Sp	0.217±0.029	1.887±0.021	1.624±0.052	0.768±0.165	2.427±0.071	132±2
SR-O-Su	0.270±0.034	0.893±0.035	1.776±0.040	0.330±0.152	4.904±0.330	114±2
SR-O-A	0.072±0.017	0.500±0.047	1.232±0.029	0.289±0.058	1.494±0.234	120±1
SR-O-W	0.189±0.031	0.911±0.056	0.968±0.022	0.957±0.075	1.371±0.074	108±4
DS-D-Su	0.010±0.007	0.254±0.033	0.939±0.059	<LD	1.261±0.051	123±5
DS-D-A	0.061±0.034	0.153±0.009	0.169±0.005	<LD	0.914±0.068	112±3
SR-D-Su	0.179±0.050	0.077±0.039	2.815±0.446	0.773±0.073	1.202±0.123	142±2
DS-T-Su	0.010±0.012	<LD[1]	0.130±0.009	<LD	1.609±0.265	102±5
SR-T-Su	0.197±0.035	0.223±0.005	1.727±0.020	0.042±0.014	1.144±0.076	123±5

DS : Diplodus sargus ; SR : Siganus rivulatus / O : Ouzaï ; T : Tabarja ; D : Dora / Su : Summer ; Sp : Spring ; A : Automn ; W : Winter ; LD : limit of detection

1. Limit of detection (LD) for chromium 0.0014µg/g d.w.; 2. Limit of detection (LD) for Nickel 0.0012µg/g d.w.

The results vary depending on the studied metals. The first observed results revealed very low levels of cadmium in *Diplodus sargus* collected at Dora and Tabarja during summer. On the other side, the *Siganus* *rivulatus* of the Ouzaï site, caught during the same season contained the highest level. The same species from Dora and Tabarja sites during summer and from Ouzaï during winter also contained high levels of cadmium. Among *Diplodus sargus*, those of Ouzaï site captured during summer and winter seasons were the busiest with cadmium.

As for the chromium, the busiest *Diplodus sargus* were those collected during spring and summer at the Ouzaï site, while the less charged were those of Tabarja in summer (total absence of chrome).

Concerning the *Siganus rivulatus*, the highest levels of chromium were found in Ouzaï during spring; those collected in the summer at Dora and Ouzaï sites also contained lesser amounts. All samples combined, the *Siganus rivulatus* of Tabarja were the least loaded with cadmium.

Most fish loaded with copper in spring were the *Diplodus sargus* of Ouzaï site and the *Siganus rivulatus* of Dora in summer. By cons, respectively, the *Diplodus sargus* of Tabarja in summer and of Dora in autumn held the lowest levels.

The *Siganus rivulatus* collected during winter at Ouzaï contained the highest concentrations of nickel; following the *Siganus* of Dora as well as the samples of the two species collected at Ouzaï during spring. As against, the absence of nickel was observed in the Dora and Tabarja *Diplodus Sargus*, sampled in summer and those of Dora and Ouzaï sampled in autumn.

The lowest levels of lead were found in the *Diplodus sargus* collected at Ouzaï during summer and autumn. As against the spring and summer *Siganus* of Ouzaï were the most contaminated with lead. The Tabarja fish, compared to the ones of other sites, contained relatively high levels of lead. Finally, we note the presence of zinc in all samples processed and analyzed. However the *Diplodus sargus* sampled in Ouzaï during spring and summer had the largest concentrations of zinc.

The concentrations of the six trace elements analyzed in this framework are generally lower than the maximum concentrations of these contaminants in foodstuffs, set by various international bodies.

These of cadmium varied in the range of 0.01-0.027µg/g of dry weight, that to say (0.002-0.077µg/g of the wet weight); The regulation (EC) N^{o}1881/2006, as amended by the regulation (EC) N^{o}629/2008, set to fish the threshold value of 0.05µg/g of fresh weight. Comparing our results to this value, we found that Ouzaï *Siganus rivulatus*, with the exception of those taken in autumn, exceeded this value.

Regarding the chromium, the observed concentrations ranged between 0.0 and 1.803µg/g of dry weight, that to say, between 0.0 -0.558µg/g of wet weight. These values were much lower than the one of 12-13µg/g brought forward by the U.S. FDA in 2011.

Copper levels vary in the range 0.130-3.270µg/g of dry weight, that to say, between 0.038-1.015µg/g of wet weight; they were much lower than those maximum values set by JECFA for fish and crustaceans.

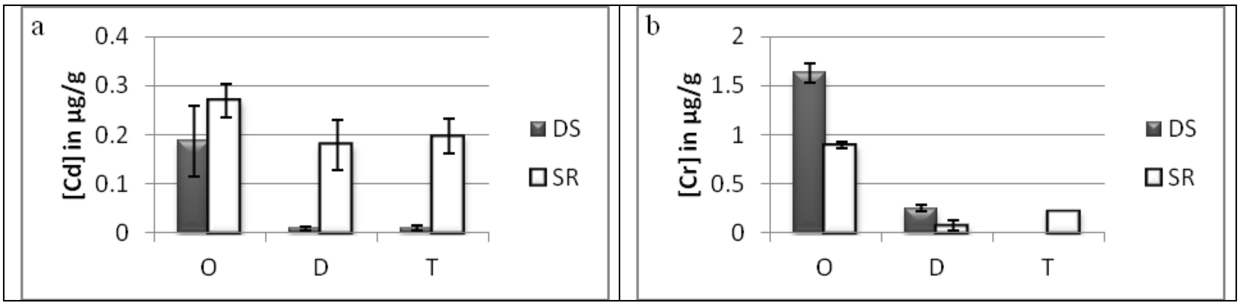
Nickel concentrations varied between 0.0 and 0.957µg/g of dry weight that is between 0.0 and 0.323µg/g of wet weight. Our values were very far from the limit of 70-80mg/kg set by the U.S.FDA, (2011).

As for lead, the contents vary between 0.218 and 4.904µg/g of dry weight that is between 0.064 and 1.401µg/g of wet weight, they were below the limit value of 1.5-1.7µg/g determined by the U.S.FDA, (2011).

As for measured zinc concentrations, they ranged between102 and 161mg/kg of dry weight.

Observed trends:

For both fish species, the Ouzaï site was the most polluted in cadmium and chromium (Figures 2.a and 2.b). The comparison between the two species reveals this site had a higher accumulation of lead in *Siganus rivulatus* (especially in summer) (Figure 2.e); an opposite trend was observed for chromium (Figure 2.b). For copper, the highest content was found in the *Siganus rivulatus* of Dora region.



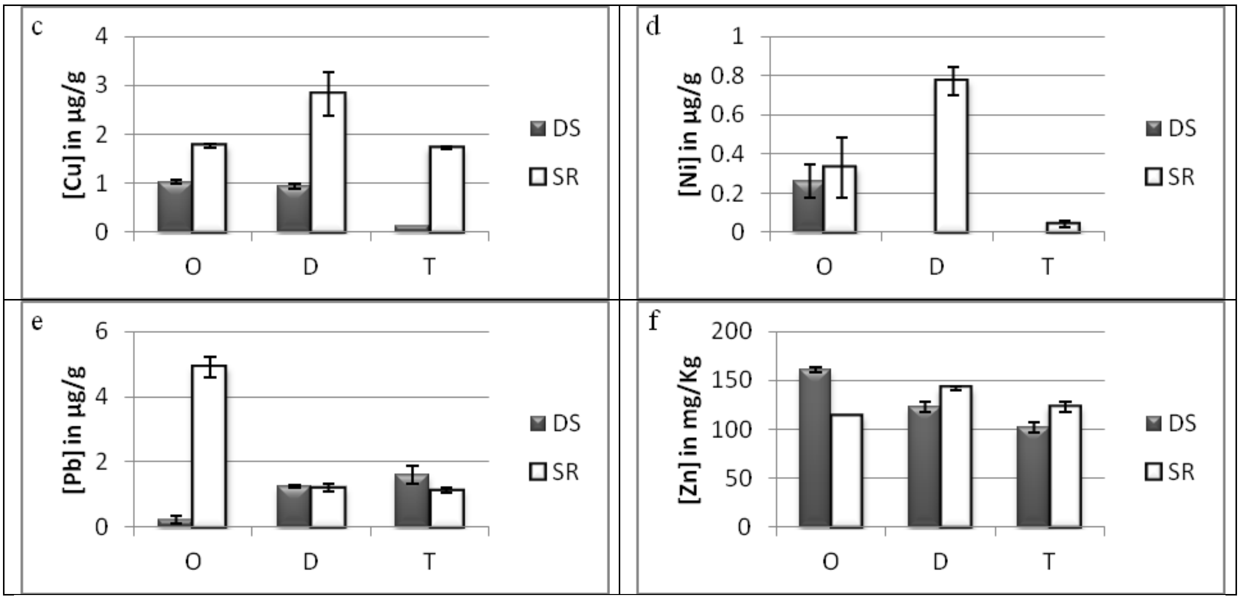


Fig. 2: Cd, Cr, Cu, Ni, Pb and Zn concentrations (µg/g of d.w. and mg/g of d.w.) in Diplodus sargus (black) and Siganus rivulatus (gray) at Ouzaï(O), Dora (D) and Tabarja (T) sites during summer. Error bars are standard deviation.

It is interesting to note that for Dora and Tabarja sites, the levels of cadmium and chromium were higher in *Siganus rivulatus* than in the *Diplodus Sargus*. However, in the case of the lead levels, measures in Dora and Tabarja were relatively close in *Diplodus sargus* and *Siganus rivulatus.*

The highest nickel contents were recorded in the *Siganus rivulatus* of Dora captured during the summer. Fish from Ouzaï also contained nickel, with similar levels in both species.

The Ouzaï site:

Ouzaï is an urban agglomeration, highly populated in the southern suburbs of Beirut. The anarchic, illegal there abound constructions reaching the coast. Waste water from these houses flows directly into the sea. However, cadmium is found in relatively high amounts in sewage and garbage (HEALTH CANADA, 2008), so this may explain the levels of cadmium found in the samples within this area. The lead pipes of some building can also contribute to the release of lead into the marine environment through untreated effluents.

For homes connected to public sewerage, they undergo primary treatment in the "El-Ghadir" WWTP, which treats the wastewater of 250,000 inhabitants (KHALAF *et al.*, 2009) and serves a wide area extremely populated that includes the south-western suburbs of Greater Beirut and southern parts of Aley and Baabda cazas (CDR, 2009; MeHSIP-PPIF, 2010).

There are also various types of industry in this area, among other industries of textiles and paints, plastics industries, printing (ALI, 2011), etc. However, the releases of these industries, connected to the "El-Ghadir" station are sources of trace metals such as cadmium, lead and nickel (HEALTH CANADA, 2008). Indeed nickel, associated to copper and chromium goes into the manufacture of various alloys (INERIS, 2006b); it is also used in the manufacture of nickel-cadmium batteries and kitchen utensils (INERIS 2006b; LAUWERYS, 2007). Therefore, the nickel is in the domestic and industrial effluents flowing without any treatment into all marine waters along the coast. Among the plants in this area are also metal electrical industries as well as canning industries (cans) (ALI, 2011) whose effluents are likely source of copper in the environment (INERIS, 2005b).

Chromium is also found in various industrial and domestic effluents because of its many industrial (stainless steel, textiles, paints, tapes, etc.) and domestic (detergents, etc.) uses. Industrial effluents of Dora and Baabda and Aley cazas may also contribute to zinc levels in the different samples collected from Ouzaï. Indeed, zinc goes into the manufacture of dry cell batteries, rubber, plastics, paints and varnishes (ZnO, ZnS) and is also used in para-pharmaceutical industries (pharmaceuticals, disinfectants, etc.), cosmetics (sunscreens) and wood, as well as in tanneries (INERIS, 2005c; IZA, 2010; LAUWERYS, 2007; MOLL and MOLL, 2000). Finally, the tire wear on the road is also a major source of zinc in the environment (INERIS, 2005c, 2004).

The "El-Ghadir" station casts away theoretically its treated water through a 2.6km long outfall immersed in water at 60m depth (GEARA *et al.*, 2010). However technical problems have prevented its use: the discharge of wastewater is therefore often through an emissary long of only 500m (MeHSIP-PPIF, 2010; CDR, 2009). Thus the fishing area of the region suffers the consequences and is possibly contaminated by metal contaminants from various anthropogenic, which, in our study could explain the fact that Ouzaï is the most polluted site in trace elements (including cadmium).

These observations are consistent with those of ABU-JAWDEH *et al.,* (2000) who noticed an intensification of marine pollution in the vicinity of coastal areas due to multiple uncontrolled and illegal constructions, and the silting of the beaches. In parallel, according to FAOUR *et al.,* (2004), the main pollutant inputs (60%) are concentrated near the capital (among others Ouzaï and Dora); the areas of high population density (Ouzaï) are particularly affected. In addition, "El-Ghadir" receives daily 250 tons of leachate treated with lime from the Naemeh dump; this leachate undergoes practically no treatment and is discharged into the sea (SWEEPNET, 2010, EC 2006).

It is known that heavy metals are among the pollutants found in the leachate (JENSEN *et al.*, 1999; KJELDSEN *et al.*, 2002) particularly young (<5 years) (TRABELSI, 2012). According to the same source, in the leachate, such as that of Naemeh dump, the load of heavy metals (cadmium, among others) can reach 2g/L. However, according to HEALTH CANADA, (2008), the treatment of wastewater with lime can remove up to 98% of the cadmium contained therein.

Although we have not been able to find figures on the rate of Cd removed from the leachate treated with lime and assuming that the rate of cadmium removed is the same, the remaining cadmium that reaches Ouzaï waters is sufficient to contribute to the pollution of the site. The contribution of leachate into the nickel concentration in the Ouzaï fish is not to be neglected.

Finally, in Ouzaï, the fishing port is just next to the sea track of the Rafic Hariri International Airport, with the fishery in its extension. The fishing weights and bowling boats contribute to the pollution of water by lead. In addition, the tetraethyl lead used as an anti-fuse in the kerosene of the civil aircraft, including those who use this airport, may contribute to high levels of lead in the Ouzaï *Siganus rivulatus* especially in summer; the latter being the peak season in airport activity (CAS, 2008). A final observation that may explain the high levels of lead at the Ouzaï site, during the Israeli war against Lebanon in 2006, the Ouzaï port was bombed by the Israeli Air Force. Thus, possible contamination of marine sediments by the lead found in ammunition is not excluded.

The Dora site:

According to KHALAF *et al.*, (2009), the coastline in Beirut, including Dora is under the stress of domestic and industrial effluents; the emissaries of the domestic and industrial effluents flow directly into surface waters of the coast, which promote further contamination of *Siganus rivulatus*. Indeed, the region of Dora packs lots of metal industries, canned food, and textiles (tanneries) (ALI, 2011). Although the number of these is now in decline (MoE, 2012), their negative impact remains on the marine environment as their wastewater is discharged directly into the sea without undergoing any prior treatment. These industrial discharges contain particularly copper (IFREMER, 2011; INERIS, 2005b), nickel (INERIS, 2006b) and zinc, and are most likely to cause levels found in fish from the region. EL-FADEL *et al.,* (2000) found in Dora marine waters, near the industrial area, a nickel and chromium concentrations respectively in the range of 41 and 160µg/L. Note that the region of Dora is known for its tanneries (ALI, 2011; MoE, 2012), that may release chromium and zinc in the environment (INERIS, 2005a).

In addition, in Dora there is a large part of the Lebanese oil companies; the oil tankers empty their cargo in huge reservoirs on the coast and cast their anchors in our study area. The contribution of fishing weights and bowling of the boats that anchor in Dora to the pollution of marine waters is not excluded. In addition, the anti-fouling paintings used for the protection of the tankers and the boats of fishermen contain copper (CHIFFOLEAU, 2001) and they may contribute to the presence of copper in the surrounding seawater. Zinc is also a component of anti-fouling paints used in ports (GUERRA-GARCIA and GARCIA-GOMEZ, 2005); it is likely that the dissolution of zinc attached to the submerged parts of the ship also contributes to the pollution. In addition, a dispersion of metal contaminants, among other zinc, from Beirut port located west of Dora is not excluded.

The marine waters of Dora are remarkably polluted by lead (MoE, 2012). They contain it at various levels reaching 320 ng/L in summer (NAKHLE, 2003). For comparison, KHALAF *et al.*, (2009) reported that the average content of lead in the Mediterranean is about 50ng/L. For COSSA *et al.*, (1993), the lead contamination of coastal sediments is widespread. Marine sediments of Dora don’t make exception and contain high concentrations of lead.

ABI- GHANEM (2008) stated that the lead content in this site is in the range of 70-101µg/g of dry weight. The remobilization of lead found in these sediments and the contamination of marine organisms has been highlighted by NAKHLE, (2003). Lead is used in industry for various purposes: batteries for cars, mobile phones, pipes and insulation in homes, etc. (INERIS, 2003; LAUWERYS, 2007; COSSA *et al.*, 1993), paints and pesticides (ATSDR, 2007). The coating of electrical wires, ammunition, glass and ceramics also contain quantities of lead that are also found in the fishing weights and keels of boats (INERIS, 2003; LAUWERYS, 2007). ABI-GHANEM (2008) also found in the Dora marine sediments cadmium concentrations located in the range from 0.6 to 0.94µg/g knowing that the average cadmium content in marine sediments is 0.2µg/g (COSSA and LASSUS, 1989).

Note that the Dora site is under the influence of two coastal waters of rivers flowing respectively to the north and west of the site: Nahr Antelias and Nahr Beirut. These two rivers are the main ways that transfer domestic and industrial wastewater from the inland to the sea (KHALAF *et al.*, 2009).

At the mouth of Nahr Antelias exists a large urban and industrial agglomeration; due to anthropogenic releases, the quality of drinking water of the river in the 1980s, has significantly deteriorated especially at its mouth. SAAD *et al.* (2004) found at the end of the summer, a lead level of 66.77µg/L while NAKHLE, (2003) reported a lead concentration of 165ng/L in the river; as comparison, the WHO defines a maximum lead content in fresh water equals to10µg/L (WHO, 2011). Note that the river contents in trace elements increase at its mouth (SAAD *et al.*, 2004). Respective cadmium concentrations of up to 3.97µg/L have been reported (SAAD *et al.*, 2004) and nickel concentrations in the range of 52.44-329.11µg/L Note that the Lebanese legislator set at 100µg/L the maximum permissible concentration of nickel in the wastewater discharged into the sea (MoE, 1996). In parallel, NAKHLE, (2003) estimates that the power plant of Zouk generates daily 1100g of cadmium per day which influences the concentrations of cadmium in Dora marine waters Dora (KHALAF *et al.*, 2009).

Regarding Nahr Beirut, RIZK and ADJIZIAN-GERARD, (2001) identified 82 plants in their watershed; among these plants are many mechanical, metallurgical and chemical industries whose effluents are discharged directly into the river without any treatment. In summer, the lower course of the river, which extends to its mouth dries, only the wastewater flows in his bed (KHALAF *et al.,* 2001). However, according to the same authors, another danger threatens the waters of this river; it is reflected by the presence of 30 car repair garages (sheet metal, electricity, drainage, paint) that discharge waste oil, the rest of painting and all kinds of waste into the river without treatment. Faced with this grim situation, the water quality of the river has deteriorated severely (KHALAF *et al.,* 2001).

The industrial and urban pressure is compounded by the Dora dump that is bordering the sea and the fishing port. Closed since 1997 (CDR, 2005) this dump looks like a mountain of junk; it occupies an area of18ha, and is up to 50min the sky (KHALAF *et al*., 2009) and annually dropped at sea 120,000 tons of leachate (EC, 2006). According to ABI-GHANEM, (2008) and NASSIF, (2004), it is a major source of contamination of the marine environment, especially trace metals. In fact it contains various types of solid waste, among other batteries and accumulators containing metal contaminants (such as lead). TRABELSI, (2012) and KJELDSEN *et al.,* (2002) reported the presence of a multitude of trace metals in the leachate, including copper and nickel, these metals migrate for several years in landfills (JENSEN *et al.,* 1999). However, according to KJELDSEN *et al.,* (2002), older leachate over 10 years (as leachate Dora) becomes more stable and contains only very low levels of heavy metals.

The Tabarja site:

Far from industrial pressure, the Tabarja area contains, in addition to the fishing port, a marina; activities related to the port (e.g. antifouling paints) can contribute to the discharge of ETM in the environment, including zinc as discussed above. This region is also experiencing relatively strong agricultural and tourist activities. Thus, the Tabarja site is under the wastewater pressure from a multitude of beach resorts that attract thousands of swimmers in summer. Note that the intense agricultural activity resulting in hundreds of greenhouses bordering the sea.

Anthropogenic contributions resulting from these tourism and agricultural activities are likely to cause trace elements pollution (including cadmium) in marine waters and fish at Tabarja. Indeed the domestic untreated effluents are discharged directly into surface waters of the coast, which promotes the contamination of *Siganus rivulatus*. Furthermore, the use of phosphate fertilizers in agriculture is a source of cadmium in the marine environment (CHIFFOLEAU 2001; INERIS, 2004). Copper is, in turn, contained in approximately 2000 pesticides including fungicides and in some fertilizers (GILBIN, 2001; INERIS, 2004). The variety of products used in the treatment of cultures, eventually reach the surrounding marine waters through agricultural runoff (MoE, 2012) which do not undergo any treatment. They probably end up contaminating the waters by trace elements and can be the source of the contamination of the sampled fish. Thus, according to CHIFFOLEAU (2001), high zinc concentrations in the marine environment, were mainly due to municipal and industrial effluents; these levels in fish increase with the concentration of zinc in the medium (GÜNDOĞDU et ERDEM, 2008).

Conclusion:

It is well obvious that the Lebanese coast suffers from an urban, industrial and touristic pressure. However, the fish collected from three sites, considered as polluted coastal areas, seems to be not affected by this pollution. In fact, the measured concentrations of the six traces elements studied are being equal or lower to the limits set by international bodies.

Our results showed throughout, that both sites Ouzaï and Dora are particularly affected by the metal pollution.

The intense planning, the presence of the wastewater treatment plant "El-Ghadir" (operating at its primary stage), the daily discharge of 250 tons of leachate (from the Naemeh dump) in the sea, the nearby of the fishing port from the Rafic Hariri International Airport in Beirut are all factors that may affect the metal contamination of fish that are found in marine waters of Ouzaï.

Regarding the site of Dora, it is likely that the presence of the dump and tanneries, the activity of oil companies and the effects of the river waters of Nahr Antelias and Nahr Beirut flowing to the north and west of Dora are behind the concentrations of various trace elements observed in fish collected from this site.

References

ABI-GHANEM, C., 2008. *Spéciation des trois éléments trace mercure, plomb et cadmium dans les sédiments marins des zones côtières libanaises.* Thèse de doctorat. Paris. p: 310.

ABU-JAWDEH, G., S. LARIA and A. BOURAHLA, 2000. *LIBAN : enjeux et politiques d'environnement et de développement durable.* Beyrouth : Éditions du Programme des Nations‑Unies pour l'Environnement/Plan Bleu/ Centre d'Activités Régionales, pp: 54.

ADJIZIAN-GERARD, J., P.C. GERARD, N. SALIBA, N. EL MASRI and N. MAATOUK, 2012. *Le bassin-versant du Nahr Beyrouth (Liban) : Un observatoire des relations nature-société en milieu méditerranéen ?* [on line]. 2005,. Available on : http://geolittomer.univ-nantes.fr/StockageUMR/COLLOQUE/pdf/C1_0405_ADJIZIAN -GERARD.pdf

ALI, 2011. Association of Lebanese Industrialists. . *Members.* [on line]. Available on: www.ali.org.lb

ATSDR., 2007. Agency for Toxic Substances and Disease Registry. *Toxicological profile for lead*. Department of Health and Human Services, Public Health Service. U.S., Atlanta, GA [on line]. [ref. of July 2011]. Available on: www.atsdr.cdc.gov

BENAMAR, N., M. BOUDERBALA and Z. BOUTIBA, 2010. Evaluation de la concentration en cadmium d'un poisson pélagique commun, Sardinella aurita, dans la baie d'Oran. *Journal des Sciences Halieutiques et Aquatiques,* 1: 16-20.

CAS., 2008. Central Administration of Statistics. Republic of Lebanon. *Statistical Bulletin.* [on line]. [ref. of July 2011]. Available on: www.cas.gov.lb

CDR., 2009. Council for Development and Reconstruction. . *Waste Water. Overview of the sector.* Republic of Lebanon. [on line]. [ref. of July 2011]. Available on: www.cdr.gov.lb

CDR., 2005. Council for Development and Reconstruction. . *Déchets Solides* . Republic of Lebanon. [on line]. [ref. of july 2011]. Available on: www.cdr.gov.lb

CHIFFOLEAU, J.F., 2001. (coord). *La contamination métallique*. Programme scientifique Seine- Aval. Région Haute Normandie. Editions IFREMER. 8 : 41.

COSSA, D., F. ELBAZ-POULICHET, M. GNASSIA-BARELLI and M. ROMEO, 1993. *Le plomb en milieu marin. Biogéochimie et écotoxicologie.* IFREMER. [on line]. [ref. of July 2011]. Available on: http://archimer.ifremer.fr/doc/00000/1449/

COSSA, D. and P. LASSUS, 1989. *Le cadmium en milieu marin, biogéochimie et écotoxicologie*. IFREMER, 16: 111.

EC. European Commission, 2006. *Support to DG Environment for development of the Mediterranean De-pollution Initiative "HORIZON 2020"*. Prepared by LDK-ECO S.A. Environmental Consultants. [on line].[ref. of August 2011]. Available on:
http://ec.europa.eu/environment/enlarg/med/pdf/review_report08_en.pdf

EL-FADEL M., R. KHOURY, A. ABOU IBRAHIM, M. ZEINATI, H. SBAYTI and E. BOU ZEID, 2000. *Preliminary characterization of Lebanese coastal waters.* Lebanon, Republic of LB. United States Agency for International Development (USAID).

FAOUR, G., A. SHABAN, J.-M. JAQUET, 2004. *Apport de la Bande Infrarouge Thermique du capteur ETM+ de LANDSAT-7 dans la Détection de la Pollution de l'Eau de Mer sur le Littoral Libanais*. 4(2): 197-209

GEARA, D., R. MOILLERON, A. EL SAMARANI, C. LORGEOUX and G. CHEBBO, 2010. State ot Art about Water Uses and Wastewater Management in Lebanon. Lebanese Science Journal, 11(2) : 139-152

GILBIN, R., 2001. *Caractérisation de l'exposition des écosystèmes aquatiques à des produits phytosanitaires : spéciation, biodisponibilité et toxicité. Exemple du cuivre dans les eaux de ruissellement de parcelles viticoles (Roujan, Hérault, France).* Thèse de doctorat. Genève. p: 192.

GUERRA-GARCIA, J.M. and J.C. GARCIA-GOMEZ, 2005. Assessing pollution levels in sediments of a harbor with two opposing entrances. Environmental implications. Journal of Environmental Management,77: 1-11

GÜNDOĞDU, A. and M. ERDEM, 2008. The Accumulation of the Heavy Metals (Copper and Zinc) in the Tissues Of Rainbow Trout (*Onchorhyncus Mykiss*, Walbaum, 1792). Journal of Fisheries Sciences, 2(1): 41-50.

HEALTH CANADA. 2008. Cadmium [Technical Document – Chemical/Physical Parameters]. [Electronic Resource]. [ref. of August 2012]. Available on: http://www.hc-sc.gc.ca/ewh-semt/pubs/water-eau/cadmium/index-fra.php#ref_7

IFREMER., 2011. *Contaminants chimiques* [Electronic Resource]. [Basse Normandie] : Institut Français de Recherche pour l'Exploitation de la Mer, 2011. [ref. of 15 July 2011]. France. Available on: http://envlit.ifremer.fr/

IFREMER., 2003. Institut National de l'Environnement Industriel et des Risques. *Dosage de certains métaux traces (Ag, Cd, Cu, Cr, Ni Pb, V, Zn) dans les organismes marins par absorption atomique.* Editions Quae, p: 36.

INERIS., 2006a. Institut National de l'Environnement Industriel et des Risques. *Eléments traces métalliques. Guide méthodologique. Recommandations pour la modélisation des transferts des éléments traces métalliques dans les sols et les eaux souterraines. Rapport d'étude.* [on line]. [ref. of October 2011]. Available on: http://www.ineris.fr

INERIS., 2006b. Institut National de l'Environnement Industriel et des Risques. *Fiche de données toxicologiques et environnementales des substances chimiques : NICKEL ET SES DÉRIVÉS.* [on line]. [ref. of May 2012]. Available on: http://www.ineris.fr

INERIS., 2005a. Institut National de l'Environnement Industriel et des Risques. *Fiche de données toxicologiques et environnementales des substances chimiques : CHROME ET SES DÉRIVÉS.* [on line]. [ref. of May 2012]. Available on: http://www.ineris.fr

INERIS., 2005b. Institut National de l'Environnement Industriel et des Risques. *Fiche de données toxicologiques et environnementales des substances chimiques : CUIVRE ET SES DÉRIVÉS.* [on line]. [ref. of May 2012]. Available on: http://www.ineris.fr

INERIS., 2005c. Institut National de l'Environnement Industriel et des Risques. *Fiche de données toxicologiques et environnementales des substances chimiques : ZINC ET SES DÉRIVÉS.* [on line]. [ref. of May 2012]. Available on: http://www.ineris.fr

INERIS., 2004. Institut National de l'Environnement Industriel et des Risques. *Devenir et comportement des métaux dans l'eau: biodisponibilité et modèles BLM. Rapport technique.* Ministère de l'Ecologie et du Développement Durable-Direction de l'Eau, Paris. [on line]. [ref. of octobre 2011]. Available on: http://www.ineris.fr

INERIS., 2003. Institut National de l'Environnement Industriel et des Risques. *Fiche de données toxicologiques et environnementales des substances chimiques : PLOMB ET SES DÉRIVÉS.* [on line]. [ref. of May 2012]. Available on: http://www.ineris.fr

IZA., 2010. International Zinc Association. *Le zinc…un matériau durable.* [on line]. [ref. of July 2011]. Available on: www.zinc.org

JENSEN, D.L., A. LEDIN and T.H. CHRISTENSEN, 1999. Speciation of heavy metals in landfill-leachate polluted groundwater, Water Research, 33(11): 2642-2650.

KHALAF, G., M. FAKHRI, C. ABI-GHANEM, M. ABBOUD ABI-SAAB and MINA Roula, 2009. Impact des activités anthropiques sur la détérioration de l'écosystème côtier de la ville de Beyrouth. Proceeding: Impact of large coastal Mediterranean cities on marine ecosystems – Alexandria, Egypt, pp: 97-102. Available on: http://www.ifremer.fr/medicis/documents/pdf/Proceedings_Alexandrie_final.pdf

KHALAF, G., K. SLIM and M.M. KRAIEM, 2001. Etude zoocénotique et qualité des eaux du Nahr-Beyrouth. *IEEE*. 00EX 493: 133-139.

KJELDSEN, P., M.A. BARLAZ, A.P. ROOKER, A. BAUN, A. LEDIN and T.H. CHRISTENSEN, 2002. Present and long-term composition of MSW landfill leachate: a review. Critical Reviews in Environmental Science and Technology, 32(4): 297-336.

LAUWERYS, R., 2007. *Toxicologie industrielle et intoxications professionnelles.* 5ème édition rev./HAHFROID Vincent, HOET Perrine, LISON Dominique. Paris : Elsevier-Masson, pp: XV-1252.

MeHSIP-PPIF., 2010. Mediterranean Hot Spot Investment Programme. Project Preparation and Implementation Facility. *Phase II. First Interim Progress Report. Final. TA 2008/S 140-186933. (RG/2008/01/FSF).* [on line]. [ref. of August 2012]. Available on: http://ec.europa.eu/environment/enlarg/med/pdf/mehsip_ppif_progress_report.pdf

MIQUEL, M., 2001. *Rapport sur les effets des métaux lourds sur l'environnement et la santé. Office Parlementaire d'évaluation des choix scientifiques et technologiques. N° 2979 Assemblée Nationale, N°261 Sénat.* [on line], [ref. of October 2011]. Available on: http://www.senat.fr/rap/l00-261/l00-2611.pdf

Middle East j. Appl. Sci., 4(2): 326-335, 2014

MoA/FAO., 2009. République Libanaise. Ministère de l'Agriculture. Direction des Etudes et de la Coordination. *L'agriculture au Liban-2008/2009 (In arabic). FAO. Projet "Assistance au Recensement Agricole".* [on line]. [ref. of Novembre 2013]. Available on: http:// www.agriculture.gov.lb

MoA/FAO., 2007. République Libanaise. Ministère de l'Agriculture. Direction des Etudes et de la Coordination. *L'agriculture au Liban-2006/2007(In arabic). FAO. Projet "Assistance au Recensement Agricole".* [on line]. [ref. of Novembre 2013]. Available on: http:// www.agriculture.gov.lb

MoA/FAO., 2004. République Libanaise. Ministère de l'Agriculture. Direction des Etudes et de la Coordination. *L'agriculture au Liban-2003 (In arabic). FAO. Projet "Assistance au Recensement Agricole".* [on line]. [ref. of Novembre 2013]. Available on: http:// www.agriculture.gov.lb

MoE., 2012. Ministry of Environment-Lebanon. *State and Trends of the Lebanese Environment 2010.* [on line], [ref. of August 2012]. Available on: http://www.moe.gov.lb/The-Ministry/Reports/State-Of-the-Environment-Report-2010.aspx

MoE., 1996. Ministry of Environment-Lebanon, Official Newspaper, Issue 45, September 12.

MOLL, M., N. et MOLL, 2000. *Précis des risques alimentaires.*2ème édition. Paris : Editions TEC & DOC, pp: XXII-383.,

NAKHLE, K., 2003. *Le mercure, le cadmium et le plomb dans les eaux littorales libanaises: apports et suivi au moyen de bioindicateurs quantitatifs (éponges, bivalves et gastéropodes).* Thèse de doctorat. Paris. pp: 255.

NASSIF, N., 2004. *Pollutions chimiques en milieu marin: essai de modélisation et approche réglementaire.* Thèse de doctorat. Paris. pp: 529.

RIZK, H. and J. ADJIZIAN-GERARD, 2001. Identification des sources de pollution de l'eau dans le bassin-versant du Nahr Beyrouth. Géosphères, Annales de Géographie, 21-22: 149-159.

SAAD, Z., K. SLIM, G. KHALAF and O. AL-SAMAD, 2004. Impacts des rejets des eaux résiduaires sur la qualité physico-chimique et algologique du Nahr Antélias. *Bulletin de la Société Neuchâteloise des Sciences Naturelles.*, 127 : 69-82.

SWEEPNET., 2010. *The Regional Solid Waste Exchange of Information and Expertise Network in Mashreq and Maghreb Countries. Rapport Pays sur la Gestion des Déchets Solides au Liban.* [on line]. [ref. of July 2011]. Available on: http://www.sweep-net.org

TRABELSI, S., 2012. *Études de traitement des lixiviats des déchets urbains par les Procédés d'Oxydation Avancée photochimiques et électrochimiques. Application aux lixiviats de la décharge tunisienne "Jebel Chakir".* Thèse de doctorat. Paris. p: 210.

US-FDA., 2011. Food and Drugs Administration. *Fish and Fisheries Products Hazards and Controls Guidance.* Third Edition. [réf. d'octobre 2012]. Available on:
http://www.fda.gov/Food/GuidanceComplianceRegulatoryInformation/GuidanceDocuments/Seafood/FishandFisheriesProductsHazardsandControlsGuide/ucm091998.htm

WHO., 2011. World Health Organization. *Guidelines for drinking water quality (fourth edition)*. [on line]. [ref. of July 2011]. Available on: www.who.int