

Chemical Profile of Lebanon's Potential Contaminated Coastal Water

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Abstract: Lebanese marine water is exposed to multi-point source contaminants. Risk assessment associated with deteriorative water quality profile is not only affected by the disposed quantities of specific contaminant, but also its chemical speciated forms. The objective of this study is to quantify the Lebanese chemical marine water profile. Sea water samples were collected based on GIS map. The chemical water quality was assessed by measuring the macro water parameters and potential existing metals. The microbiological profile of water was evaluated by fecal coliform. Results showed contamination by fecal coliform and high levels of toxic metals. However, the actual projected impact of the detected metals on human health were assessed using geochemical models "FREEQCE" and "Mineq+" that predict the metal species forms, mainly, the free aqua-metal ion, most toxic form. Thus, these results necessitate the proposal of integrated intervention plans for the protection of this marine source and consistent with international treaties.

Key words: Point source contaminants, coastal water, toxic metals, metal speciation, environmental interventions, Lebanon.

1. Introduction

Lebanon is a small Mediterranean country (surface area 10,452 km², and average width 45 km) located South-West Asia, between N latitude 34°42' and 33°3' and E longitudes 35°6' and 36°37'[1]. The country is bordered by the Syrian Arab Republic to the north and east, Israel to the South, and Mediterranean Sea to the west. Lebanon's physiography is unique, dominated by two mountain ranges which run parallel to the sea (NNE-SSW) and are separated by the Bekaa valley. Lebanon has a mild, dry summer and a cold, wet winter. Heaviest rainfall occurs between November and April, with relatively minimal precipitation, if ever, between July and August [2]. The Lebanese coastal line stretches 225 km covering 162,000 hectares of coastal plains and hills (over 16% of Lebanon's surface area), with approximately a total

of 2.6 million inhabitants (70% of the population) [3, 4]. Mostly, Lebanon's economic activity is concentrated along this coastal zone, which contributes to about 75% of the national income [1, 5]. Additionally, this coastal zone experiences busy transport-export-transit services, and is an attractive site for tourism. Lebanon has signed at least 13 international environmental conventions to protect and sustain the Mediterranean Sea ecosystem. The Barcelona Convention for the protection of the Mediterranean Sea against pollution [6], specifically, stipulated the development in Lebanon of a National Emergency Reconstruction Program (NERP) and the launching of a major program (the Coastal Pollution Control Program-CPCP) to combat the coastal pollution [1, 7].

Lebanese marine water is exposed to the major point sources of pollution, such as sewage outfalls, industrial wastewater effluents, coastal agricultural runoffs, seafront dumps leachates, and oil spills [1, 4, 5, 7, 8]. These sources, approximately, release

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daily 950,000 m³ of wastewater directly into the sea [3, 7]. Moreover, nearly 60% of Lebanon's sewage is poured in the sea (53 sewage outfalls have been identified along coast and dozens of short outfalls) [4, 7, 9, 10]. As for solid waste dump sites, eight major coastal dumpsites have been located [5, 10, 11], in addition to the dumpsite resulting from the Beirut slaughterhouse in the absence of composting plants to handle such types of solid wastes [4].

Major industries are, also, located outside the industrial zone (about 28 different coastal industries), and dispose cement, plastic, fertilizers, pharmaceutical,

tanneries, textile, paper, paints, and metal processing wastes directly without prior treatment along coastal line [1, 5, 10]. For example, it was estimated that tanneries discharge about 40 tones of chromium yearly into the Mediterranean Sea [7, 12]; and a fertilizer company discharge about 0.7 tons of cadmium, 2 tons of lead, and 2 tons of nickel into the sea yearly [7, 13]. These heavy metals are non-biodegradable and accumulate in aquatic organism ecosystem, impacting the seawater quality [8, 14] and subsequently human health as presented in Table 1 [15-17].

Data on quality of Lebanese coastal waters is highly

Table 1 Sources of metals and projected health risks.

Metal	⁽¹⁾ Source	⁽¹⁾ Projected health risk	⁽²⁾ TRV* (ug/L)
Al	Construction material, aluminum plants, ceramics, pharmaceutical and cosmetics products	Kidney and brain disfunctions, Anemia	87
As	Pestisides, wood preservatives, glass products	Liver and nervous system damage, cancer	190 ^a
Ba	Cement, ceramic glazes, glass and paper making, pharmaceutical and cosmetics products	Little is known about possible health effects. The degree of absorption depends on solubility of compound. High amounts > 2 mg/L cardiovascular diseases	4
Cd	Batteries, plastics, fertilizers, pesticides, paints, electroplating	Bone and cardiovascular diseases, cancer, liver and nerve cell damage	0.66
Co	Alloy, ceramics, paints	Respiratory irritation, heart damage and failure, thyroid problems	23
Cr	Stainless steel, alloy, cast iron, pigments and wood treatment, tanneries	Cr(III) has bioavailability and toxicity than Cr(VI). However high doses of both cause gastrointestinal irritation, stomach ulcer, kidney and liver damage, Cr (IV) is carcinogenic	117 ^a
Cu	Smelting and metal plating operations, fertilizers and animal feeds, electrical works, pesticides and fungicides	Gastrointestinal diseases, anemia, liver and kidney damage	6.54 ^b
Hg	Electrical industry, paints, pesticides and fungicides	Adrenal disfunction, brain and central nervous system damage, haring loss. research suggests that it may contribute to autism and multiple sclerosis	0.012
Mn	Steel and alloys; MnSO ₄ is used as fertilizer, ceramics, and fungicide, MnO ₂ dry-cell batteries, fireworks, KMnO ₄ as disinfectant	Little is provided for its toxicity or health and it is related to water hardness	120
Ni	Alloys, electroplating, ceramics, pigments, alkaline batteries, catalyst in plastic and rubber industry	Gastrointestinal distress and intestinal cancer, kidney and heart damage, disfunction	87.71 ^b
Pb	Smelting operation, automobile emission, urban runoffs, pesticides, plastics, paints, ceramic glaze	Centralnervous system and kidney damage. fecal development, delay growth and learning disabilities	1.32 ^b
V	By product of processing of phosphate rock which is used for production of fertilizers and phosphoric acid	Most studies of health effect is related to inhalation, less is known about effect of ingestion by food or water	20
Zn	Galvanization works, motor oil, tire wear, pigments, pesticides	Little is known about long term effects of ingesting Zn from food or water. It might cause anemia and pancreas damage	120 ^b

⁽¹⁾Perfect Life Institute, 2002 [15]; Selinus et al., 2005 [16];

⁽²⁾ERD, 1999 [17].

* TRVs is toxicological benchmarks for screening potential contaminants of concern for effects on aquatic biota;

^a Values are for arsenic iii and chromium III;

^b Hardness dependent.

limited. A study conducted by the American University of Beirut (AUB) Water Resources Center in the year 2000 showed levels of BOD ranged between 5 mg/L and 95 mg/L; and toxic metals ranged as follows: arsenic between 10 µg/L and 51 µg/L, lead between 2 µg/L and 17 µg/L, zincs between 9.6 µg/L and 32 µg/L, and chromium between 23 µg/L and 100 µg/L [18]. Additionally, it was also noted by the National Center for Marine Science of Lebanon [7] that water of nine coastal areas out of ten exceeded WHO fecal coliform standards for recreational water (Table 2). As such given the deficiency in the existing data base, the study aimed at identifying and evaluating the coastal water quality profile and accordingly proper viable interventions plans to sustain this vital resource.

2. Material and Methods

2.1 Sampling Sites and Sampling

The coastal line was monitored throughout the dry season. Seventeen sampling sites were selected (Fig. 1) based on GIS map of all discharged zones. Types of surrounding area (industries and sewage outfalls) are presented in Table 3. One liter polyethylene bottle was used for sea water (near shore) samples collection; and 300 mL water samples were collected in borosilicate glass bottles for bacteriological analysis.

2.2 Field Analysis

The following parameters were measured on site: temperature, electrical conductivity (EC_w), and total dissolved solid using HachModel 44600 Conductivity/TDS Meter and pH using Hach Pocket pH Model, and dissolved oxygen (DO) by membrane electrode.

2.3 Laboratory Analysis

The collected water samples were filtered through 0.45 µm filter and divided into two portions. To one portion (250 mL) of each collected sample nitric acid

Table 2 Quality of water for swimming* (WHO, 2006) [19].

Water quality	<i>E. Colli</i> (count/100 mL)
Very bad	> 2000
Middle pollution	1000-2000
Soft pollution	50-200
Very satisfying	< 50

was added to $pH < 2$ and stored at 4 °C for future metal analysis: Al, As, Ba, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, V, Zn by ICP-MS technique. Working standards were prepared by dilution of stock solution (1 mg/mL in 2% HNO_3) with MillQ water. The other water portion was used for an immediate analysis of other parameters: titration procedure was used for alkalinity (0.02 N H_2SO_4), chloride (0.0141 N mercuric nitrate), and spectro-photometric methods SO_4^{2-} (turbidimetry) and PO_4^{3-} (ascorbic acid) using Hach Model ("HACH" Odyssey, DR, 2500). The bacteriological analysis was determined by membrane filtration technique (Millipore).

2.4 Software Used in Analysis

The statistical analysis of the measured parameters was performed using statistical package SigmaStat. The metal speciated forms were predicted using AquaChem software interfaced to the PHREEQC Geochemical and MINEQ+ geochemical software.

3. Results and Discussion

3.1 Sea Water Quality Profile

Table 4 presents the overall mean seawater quality profile of dry season studied period, primarily in terms of metal content.

3.1.1 pH

The pH of seawater ranges between 7.5 and 8.5. However, due to burning of fossil fuels and the production of carbon dioxide gas, surface seawater pH will decrease [20, 21]. The mean overall reported pH value in current study is 7.85, ranging between 4 and 10. This low pH value cannot only be just attributed to "green house CO_2 effect", but impacted by sewage

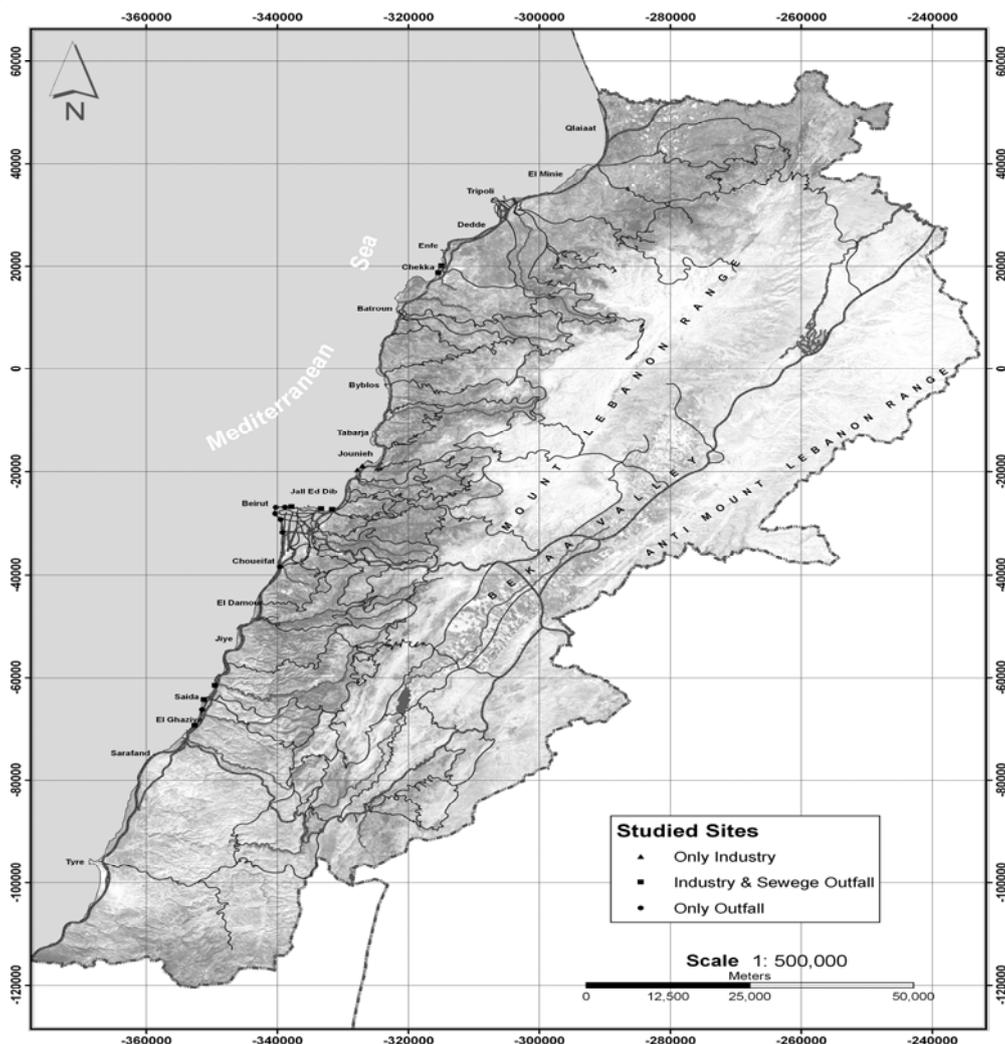


Fig. 1 Map of studied sites.

Table 3 Characteristics of sampling sites.

Site	Types of surrounding area
1	Cement factory, sewage outfall
2	Fertilizer factory, acid company, small sewage outfall
3	Paper processing, paints factory, ceramic works, plastic factory, electroplating , and pesticide factory
4	Pharmaceutical company, metal processing, paper processing, textile, paint factory
5	Metal processing, tanneries factories, sewage outfall
6	Metal processing, plastic factory, detergent, textile, paints factory, sewage outfall
7	Metal processing factory, tannery factory, slaughter house, waste site dump, sewage outfall
8	Sewage outfall, recreational activities
9	Sewage outfall, site of four hospitals
10	Recreational activities
11	Sewage outfall
12	Sewage outfall
13	Sewage outfall
14	Plastic factory, chemical industry, sewage outfall
15	Metal processing, galvanization work, textile, electroplating, waste dump site, sewage outfall
16	Sewage outfall
17	Metal processing, tannery factory, ceramic works, textile, paint factory, sewage outfall

Table 4 Mean concentration of studied seawater parameters.

Indicator	Min	Max	Mean	SD	⁽¹⁾ Sea Water	⁽²⁾ TRV
Temp. (°C)	22	28	25	1.92	-	-
pH	4	10	7.85	3.397	8.2	-
DO (mg/L)	1.20	8.80	7.60	3.37	5.13	-
Al (µg/L)	2.00	5780	693.82	1676	1.10	87
As(µg/L)	nd	50.00	18.74	15.09	1.80	190 ^a
Ba(µg/L)	5.00	1600	152.94	382	282	4
Cd(µg/L)	nd	10	1.13	2.38	0.125	0.66
Co(µg/L)	3.00	70.00	19.05	24.1	0.006	23
Cr(µg/L)	4.00	1800	215	450	0.260	117 ^a
Cu(µg/L)	3.50	475	84.88	130	0.380	6.54
Fe(µg/L)	30	100700	1359	2528	0.140	1000
Hg(µg/L)	nd	41.00	4.57	10.22	0.002	0.012
Mn(µg/L)	4.00	1015	129.27	241	0.165	120
Ni(µg/L)	2.00	150.00	34.65	52.23	0.700	87.71 ^b
Pb(µg/L)	0.50	182	18.88	44.14	0.036	1.32
V(µg/L)	5.00	444	37.56	105	0.0018	20
Zn(µg/L)	7.00	3880	404.71	915	0.590	120
NO ₃ (mg/L)	0.9	25.00	7.46	7.82	-	-
PO ₄ (mg/L)	0.07	5.23	1.68	1.65	0-0.3	-

⁽¹⁾Quinby-Hunt and Turekian, 1983 [25]; Holmes-Farley, 2011 [24];

⁽²⁾ ERD, 1999 [17].

nd: not detected.

and industrial wastes [20, 22, 23]. Statistical significant correlation occurred between pH and dissolved oxygen ($r = 0.71$, $p < 0.01$) levels. Still, the reduction of pH is direct outcome of the industrial wastewater effluents, and this is reflected by the very low pH (pH = 4) near sites of acidic companies.

3.1.2 Trace Metals

As for trace metals, the levels in seawater are minimal. Still, higher levels of these metals outcome industrial activities, atmospheric deposition and sewage discharges. Table 4 presents the mean concentration of detected metals along coastline in comparison to expected levels in seawater not exposed to contamination [24, 25]. It was observed that most of the studied sites had levels of metals far above the expected, exposing the high pollutants sources pouring in the sea.

3.1.2.1. Al, Fe, Mn, Zn

Although Aluminium is very abundant in the Earth's crust, it is a trace metal in the open ocean and/or sea [26]. The detected mean level of Al in

seawater is 694 µg/L, ranging between 2 µg/L and 5,780 µg/L. This mean level is approximately 650 times those expected (1.1 µg/L), and ten times more than the recommended TRV level of 87 µg/L. Moreover, Al levels (Fig. 2) were the highest at sites 4, 7, and 17 corresponding to Al waste discharges from the metal processing, ceramics and pharmaceutical products activities at these sites (Table 3). This is concurrent with previous studies that showed high levels of dissolved aluminium in the Mediterranean Sea [27], resulting from dust of aluminium activities.

The mean iron level is 1,359 µg/L, ranging between 30 µg/L and 10,000 µg/L. Similar to Al, the highest Fe levels were also reported at sites, 4, 7, 17. The mean level of iron is 1,000 times more than those expected for sea water (0.140 µg/L). The main source of iron in seawater is an outcome of the metal processing activities, the dust input and direct industrial waste effluents into the sea. A strong statistical positive correlation occurred between Al and Fe ($r = 0.920$, $p < 0.01$) which explains the

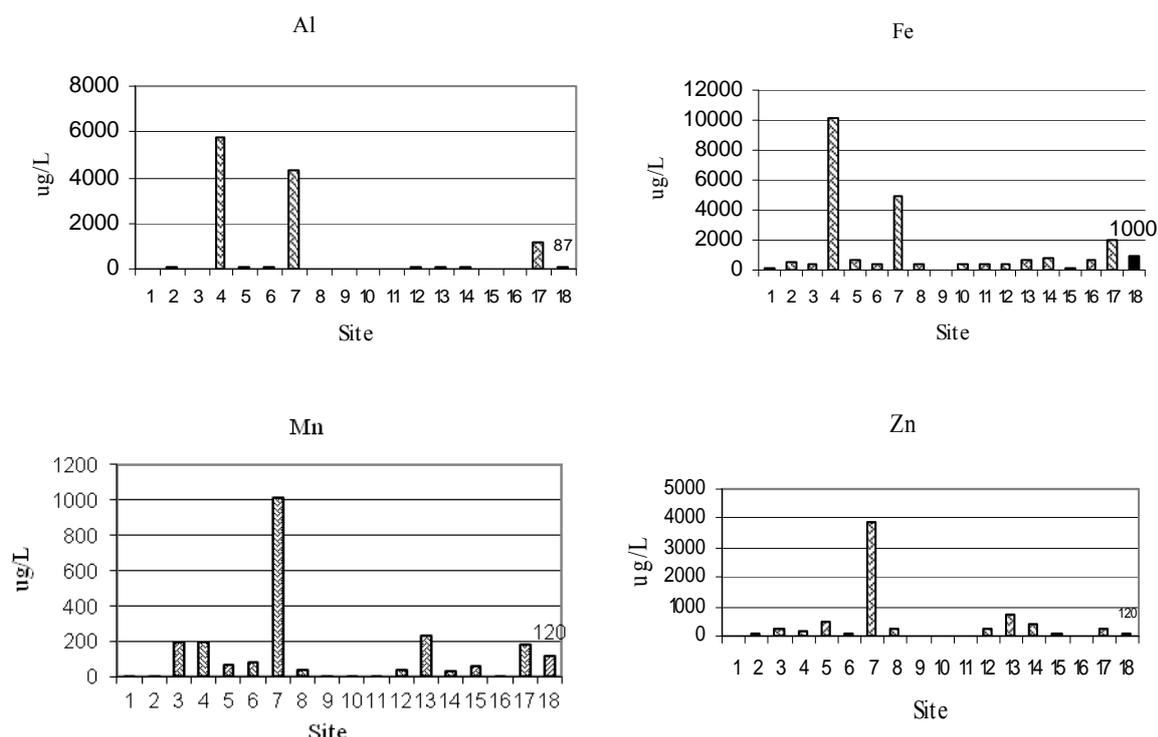


Fig. 2 Variation of Al, Fe, Mn, Zn along coastal line.

common sources contributing to the presence of these metals.

Additionally, Mn and Zn showed high strong positive statistical correlation ($r = 0.983$, $p < 0.01$), reflecting on similar sources of pollution. Both Mn and Zn mean levels (Mn: $129.27 \mu\text{g/L}$, Zn: $404.71 \mu\text{g/L}$) are 1,000 times more higher than those expected for sea water (Mn: $0.165 \mu\text{g/L}$, Zn: $0.590 \mu\text{g/L}$), but compared to TRV levels: Mn (TRV $120 \mu\text{g/L}$) was nearly at an acceptable level and Zn (TRV $120 \mu\text{g/L}$) was four times higher. Manganese levels ranged between $4 \mu\text{g/L}$ and $1,015 \mu\text{g/L}$, and those of Zn ranged between $7 \mu\text{g/L}$ and $3,880 \mu\text{g/L}$. The highest level for Mn was reported at sites 4, 7 and 13, and those for Zn at sites 7 and 13 (Fig. 2). Site 7 is a solid waste dumpsite site, and site 13 is in the vicinity of ceramic factory, where Mn and Zn are found in paints stabilizers [15, 16]. Additional is the metal processing factories are in the vicinity of sites 4 and 7, contributing to the presence of metals in seawater. This is more explicit by the statistical positive

correlation between Mn and Al and Fe; and correlation of Zn with Al and Fe. The Mn correlation were (Al: $r = 0.70$, $p < 0.05$; Fe: $r = 0.50$, $p < 0.05$), for Zn correlation (Al: $r = 0.42$, $p < 0.05$, Fe: $r = 0.653$, $p < 0.05$).

3.1.2.2 Cu, Co, Ni

The mean level of Cu in the studied area is $84.88 \mu\text{g/L}$, ranging between $3.5 \mu\text{g/L}$ and $475 \mu\text{g/L}$. This level is 200 times higher than expected value for sea water ($0.38 \mu\text{g/L}$), and 13 times higher than TRV value ($6.54 \mu\text{g/L}$). On the other hand, the detected mean level of Co is $19.05 \mu\text{g/L}$, ranging between $3 \mu\text{g/L}$ and $70 \mu\text{g/L}$. This level is much higher than the expected level of sea water ($0.006 \mu\text{g/L}$), but it is approximately equal to recommended TRV value ($23 \mu\text{g/L}$). The variation of Ni level is similar to that of Co. The mean level of Ni is $34.65 \mu\text{g/L}$, ranging between $2 \mu\text{g/L}$ and $150 \mu\text{g/L}$. The mean value of Ni is 50 times more than expected sea water level ($0.7 \mu\text{g/L}$), but it is lower than the set recommended TRV value ($87.71 \mu\text{g/L}$). The highest detected levels of Cu, Co

and Ni is at same sites 3, 4, 7 and 15 (Fig. 3). These sites are in the vicinity of paints factory, ceramic works, plastic factory and electroplating contributing Cu, Co and Ni levels in seawater. Further, a strong statistical positive correlation occurred among the three metals. The statistical correlation between Co and Ni ($r = 0.890$, $p < 0.01$) and Co and Cu ($r = 0.810$, $p < 0.01$), while correlation of Cu and Ni is ($r = 0.770$, $p < 0.01$).

3.1.2.3 Cr, Pb, Cd, Hg

The detected mean level of Cr is 215 $\mu\text{g/L}$, ranging between 4 $\mu\text{g/L}$ and 1800 $\mu\text{g/L}$, highest at site 7, in the

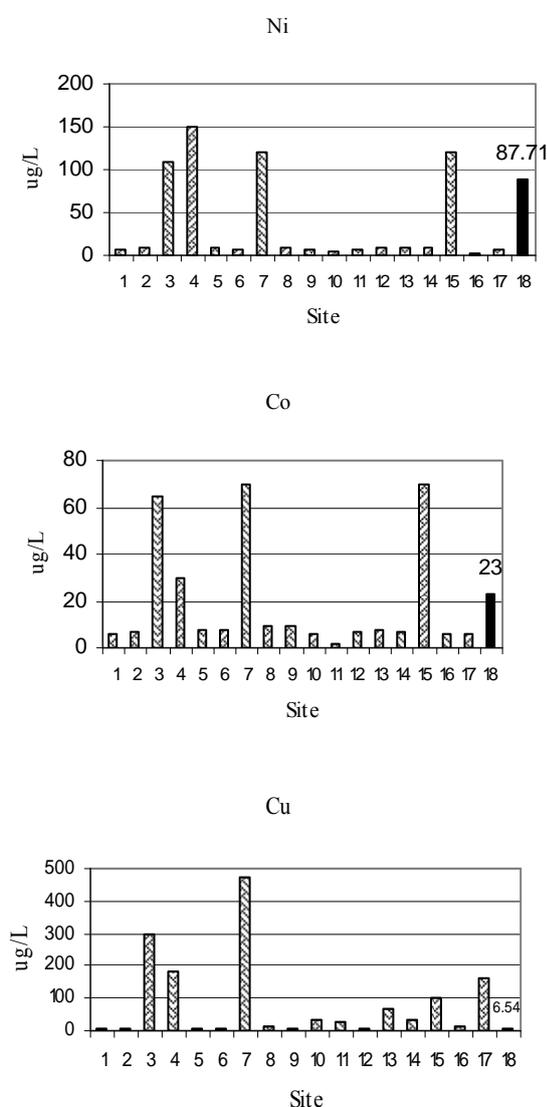


Fig. 3 Variation of Ni, Co, Cu, along coastal line.

vicinity of tanneries, slaughter house and metal processing. Also, sites 5 and 17 showed high in levels of Cr but of lower extent than site 7 (Fig. 4), resulting from the contribution of nearby tanneries (Table 3). A strong statistical positive correlation occurred between Cr and Pb ($r = 0.942$, $p < 0.01$), and this high correlation resulted from similar or wide range of industrial waste water effluents. The mean detected level of Pb is 18.88 $\mu\text{g/L}$, ranging between 0.50 $\mu\text{g/L}$ and 182 $\mu\text{g/L}$. This mean level is 500 times more than expected seawater levels, but compared to values reported in the Mediterranean Sea which is between 0.018 $\mu\text{g/L}$ and 0.14 $\mu\text{g/L}$ [28, 29], the levels of Pb in our study is about 100 times more (compared to the higher range). The high reported value of Pb were at site 7 (Fig. 4), resulting from the metal processing, in addition to the existence of a petroleum station that contribute to lead levels.

In regard to Hg, the mean level is 4.57 $\mu\text{g/L}$, ranging between not detected (nd) and 41 $\mu\text{g/L}$. The mean level is 2000 times higher than expected level sea water (0.002 $\mu\text{g/L}$), and about 400 times more than TRV levels (0.012 $\mu\text{g/L}$). The high concentration of Hg occurred at site 9 (near hospital waste water effluents), and to lesser extent at site 7 (slaughter house, solid waste dump).

Examining Cd, the mean detected level is 1.13 $\mu\text{g/L}$, ranging between not detected (nd) and 10 $\mu\text{g/L}$. The mean level of Cd is nearly equal to expected level of Cd in sea water (0.125 $\mu\text{g/L}$), but two times higher than TRV levels (0.66 $\mu\text{g/L}$). The highest Cd level was at site 2 and to a lesser extent at site 7 (Fig. 4), and both sites in the vicinity of fertilizer producing factories. This is emphasized by the strong statistical positive correlation between PO_4^{3-} and Cd ($r = 0.721$, $p < 0.01$), and between Cd and NO_3^- ($r = 0.625$, $p < 0.05$).

3.1.2.4 Ba, V

In regard to these twometals Ba and V, literature cites limited analysis of their concentration in sea water and little is known about their possible health effects

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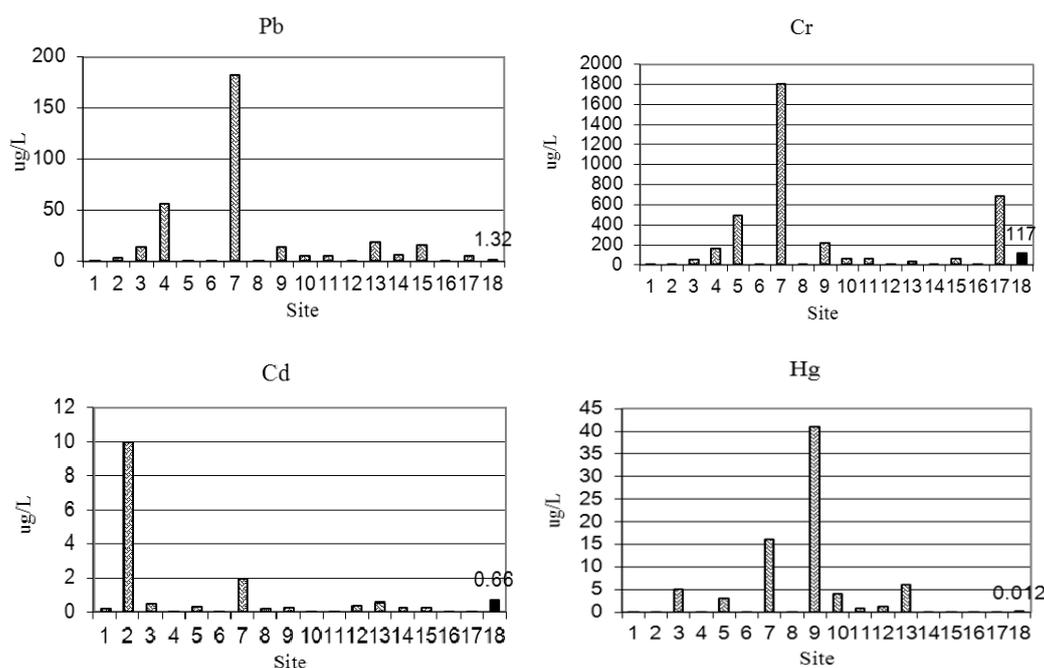


Fig. 4 Variation of Pb, Cr, Cd, Hg along coastal line.

[15]. The mean level of Ba is $152.94 \mu\text{g/L}$, ranging between $5.00 \mu\text{g/L}$ and $1600 \mu\text{g/L}$. The mean level of Ba is lower than expected levels in sea water ($282 \mu\text{g/L}$), but much higher than TRV level ($4 \mu\text{g/L}$). The highest level of Ba is at site 9 (Fig. 5). Site 9 is in the vicinity of hospitals (Table 3), as such it is most probably receiving hospital discharges.

Whereas, the mean detected level of V is $37.56 \mu\text{g/L}$, ranging between $5 \mu\text{g/L}$ and $444 \mu\text{g/L}$. The mean level is tremendously higher than those expected for sea water ($0.0018 \mu\text{g/L}$), and only 1.5 times more than TRV levels ($20 \mu\text{g/L}$). The highest level is at site 2 (phosphate processing for fertilizers and phosphoric

acid companies), where, V is released during process of phosphate rocks [16].

3.1.3 Microbiological Profile

Table 5 presents the microbiological profile of seawater samples. The profile is deduced from *E.coli* amounts. Comparing to WHO norms for swimming (Table 2), twenty percent of sites (site: 6, 13, 14, 15, 17) can be classified as very bad water ($> 2,000 E.coli/100 \text{ mL}$) for swimming. These sites had sewage canal directly discharging into the sea. Whereas, twenty three percent had the water quality of "middle pollution"; and only about eighteen percent of water sites can be classified as satisfying for swimming.

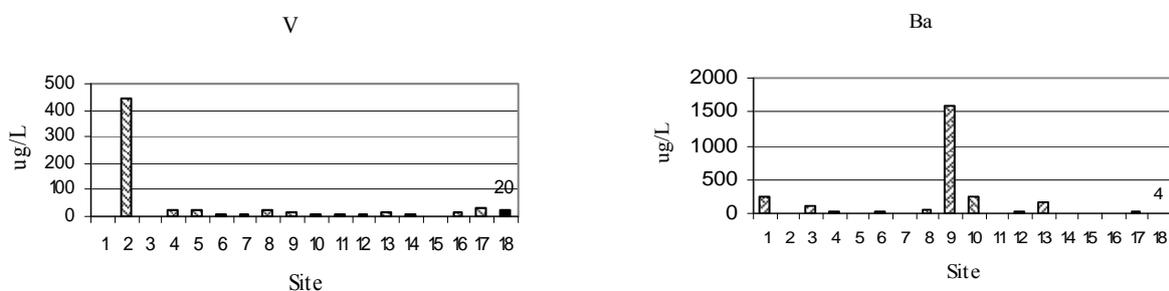


Fig. 5 Variation of V and Ba along coastal line.

Table 5 Microbiological profile.

Station	<i>Fecal coliform</i> /100 mL
1	1200
2	400
3	0
4	0
5	1200
6	TNC
7	90
8	1900
9	250
10	0
11	225
12	500
13	TNC
14	TNC
15	TNC0
16	1200
17	TNC

TNC: too numerous to count.

As such, the coastal line is heavily exposed to fecal contamination and even the sites that are microbiologically safe are not chemically safe.

3.2 Speciation of Metals in Sea Water

Monitoring investigations usually report the total content of the pollutants but not their chemical speciation, which determines the toxicity and bioavailability of the pollutants [30-33]. For this, chemical speciation is essential for discussing the chemical reactivity of trace constituents in the environment, such as biological availability and toxicity. The term "chemical species" is a specific form of an element, like isotopic composition, electronic or oxidation state, and complex or molecular structure. The fraction(s) of metal(s) forming strong complexes with ligands may not be thermodynamically or kinetically available to organisms. The bioavailable, or labile forms of metals include the free or uncomplexed metal ion (aqua metal ion), and the weak metal-ligand complexes [32-36].

Seawater is a chemically complicated system because many kinds of inorganic and organic chemical species are dissolved in solution of high salt

concentrations. The levels of trace metals in seawater were established as a result of the development of analytical techniques. The chemical speciation of trace inorganic and organic constituents in oceanic water samples has been studied for more than four decades [36]. Many analytical techniques have been developed for the chemical speciation of elements in environmental samples, such as sequential leaching methods, GC-ICP-MS, Voltammetry, X-ray spectroscopic techniques [35, 36]. These methods are labour consuming, expensive and applicable to a limited number of species. On the other hand, thermodynamic modelling is used as a tool for evaluation of inorganic chemical species in fresh water [32, 33, 37] and seawater [35].

The metal speciation of the sea water sample in current study was predicted using two geochemical modelling software, the PHREEQC interfaced to AquaChem software, and MINEQL+. The main interest is the percentage of the free aqua metal ion (toxic form) and conditions that enhance its formation in sea water. Table 6 presents the different chemical species of studied metals and their percentages occurrence from total metal content.

3.2.1 Al, V

The highest percentage of aluminium chemical specie form is $\text{Al}(\text{OH})_4^-$ and it exhibited strong statistical significant coloration with pH ($r = 0.822$, $p < 0.01$). However, the percentage of the free aqua metal ion Al^{3+} is low (Table 6), and it had an inverse significant correlation with pH ($r = -0.787$, $p < 0.01$) and HCO_3^- ($r = -0.622$, $p < 0.01$). These results are in accordance with cited works that specify metals that form strong complexes with hydroxide undergo significant changes in speciation as the pH of seawater decreases [35]. Similar to Al, vanadium speciated highly as hydroxide (VOH^+) and exhibited statistical significant correlation with pH ($r = 0.429$, $p < 0.05$), and with HCO_3^- ($r = 0.631$, $p < 0.01$). Still, the percentage of the free aqua metal ion V^{2+} is low (Table 6).

Table 6 Percentages of metal species in sea water samples.

Element	Speciated form	% range of total in samples	% samples
Al	Al ³⁺	1-46	9
	Al(OH) ₄ ⁻	0-99	90
As	HAsO ₄ ²⁻	1-98.5	77
	H ₂ AsO ₄ ⁻	0-98	9
Ba	Ba ²⁺	69-100	86
	BaSO ₄ ⁰	3-30	20
Cd	Cd ²⁺	1-63	14
	CdCl ⁺	0-44	59
	CdCO ₃ ⁰	10-85	9
Co	Co ²⁺	1-93	77
	CoCO ₃	0-99	41
	CoSO ₄ ⁰	0-34	63
Cr	CrO ₄ ²⁻	1-99	80
	HCrO ₄ ⁻	1-99	12
	Cu ²⁺	1-62	18
Cu	Cu(OH) ₂	1-95	14
	CuCO ₃ ⁰	0-85	63
Hg	HgCl ₄ ²⁻	0-73	78
	HgCO ₃ ⁰	0-52	9
Mn	Mn ²⁺	14-63	95
	MnCl ⁺	0-27	95
	MnSO ₄ ⁰	0-16	45
Ni	Ni ²⁺	1-88	41
	NiCO ₃	1-93	75
Pb	Pb ²⁺	1-21	27
	PbCO ₃ ⁰	1-68	73
V	V ²⁺	0-10	90
	VOH ⁺	0-100	82
Zn	Zn ²⁺	0-68	82
	ZnCl ⁺	0-14	86
	ZnCO ₃ ⁰	1-99	50

3.2.2 Ba, Co, Mn

Barium, Co and Mn showed similar speciation, the highest percentage of total metal is the free aqua metal (Table 6). Moreover, the free aqua ion of barium (Ba²⁺) exhibited no correlation with pH or any other water parameters. This in accordance with cited Literature as the free form of metals are not strongly influenced by a change in Ph [35]. On the other hand, for both, the free Mn²⁺ and Co²⁺ had a statistical negative correlation with pH ((Mn free metal and pH correlation ($r = 0.501, p < 0.05$); Co free metal and pH correlation ($r = -0.609, p < 0.01$)). Additionally, the three metals showed occurrence of species as metal sulphate ion pair, the percentages of metal sulphate ion pair were higher for Mn and Co and exhibited an inverse correlation with pH. This observation could explain the dependency of Co and Mn occurrence as free ion on pH, where the ion pair sulphate complex

has a higher tendency to be formed, but as pH decreases, the complex will be destroyed and metal as free ion prevailed.

3.2.3 Cd, Zn

Speciation of Cd and Zn existed as metal ion and metal chloride complex. High speciation of Cd as chloride complex was exhibited and the speciation as free ion was lower. A statistical negative correlation occurred between free Cd metal ion and pH ($r = -0.434, p < 0.05$). However, for Zn, speciation as free ion occurred at a higher percentage than as Zn chloride complex, and the free aqua zinc had an inverse correlation with pH ($r = 0.923, p < 0.01$). It was expected as others have indicated that the metals that form strong complexes with chloride or are mainly in the free form will not be strongly influenced by a change in pH. In this study, the dependence of free metal on pH could be due to speciation of both Zn and Cd (lower extent) as carbonate ion pair. Previous studies have shown for surface water with higher pH and HCO₃⁻ content, Zn and Cd high speciation occurred as carbonate ion [32, 33].

3.2.4 Cu, Pb, Ni

The main chemical specie for these metals is the carbonate ion pair (Table 6). The speciation of these metals as carbonate complex has been reported previously, whether for sea water or surface water [32-36]. A statistical positive correlation occurred with respect to these metals carbonate ion pair and pH and HCO₃⁻: for Cu, correlation with pH and HCO₃⁻ were respectively ($r = 0.702, p < 0.01$; $r = 0.460, p < 0.05$), for Pb ($r = 0.465, p < 0.05$; $r = 0.552, p < 0.05$), and for Ni ($r = 0.598, p < 0.05$, $r = 0.495, p < 0.05$). Whereas, speciation as free metal ion showed minimal occurrence (Table 6).

3.2.5 Cr, As, Hg

Chromium and As speciation occurred mostly as their anion complex form (CrO₄²⁻ and HAsO₄⁻). Speciation of these metals in sea water have not been reported extensively in literature. Both speciated forms were correlated to pH and dissolved oxygen (DO).

The correlation was respectively for pH and DO as such: for Cr ($r = 0.625$, $p < 0.01$, $r = 0.756$, $p < 0.01$) and for As ($r = 0.598$, $p < 0.05$, $r = 0.535$, $p < 0.05$). Whereas, Hg speciated mainly as chloride complex (HgCl_4^{2-}).

4. Environmental Intervention Plan for Marine Water Protection

Based on presented study, there is an utmost need to propose and implement an intervention plan for marine water protection. Such plan should also relate to the integrated management of waste water. This management tackles three aspects: sewage, industrial and storm water wastewater.

4.1 Domestic Waste Water (Sewage) Intervention Plan

This intervention plan should address three issues:

(1) Revised comprehensive national plan

A re-examination of the national plan is of utmost priority to identify responsibilities and provision of resources needed to set attainable targets with a defined time line in response to international agreements signed and committed by the government.

(2) Instating wastewater quality monitoring

This is needed to evaluate the effectiveness and efficiency of the developed units to monitor impacts on ecological wellbeing and public health. These activities should be coordinated by the three ministries: Ministry of Energy and Water (MOEW), Ministry of Health (MOH), and Ministry of Environment (MOE).

(3) Poling of resources

Resources should be pooled towards the implementation of revised comprehensive national plan.

4.2 Industrial Waste Water Intervention Plan

The industrial wastes management should be implemented by all small and all large scales industries:

(1) Small scale industries

In Lebanon, more than 2,500 industries are

scattered among residential areas impacting the quality of wastewater to be treated (requiring advanced treatment processes). Hence, there is a need for reallocating into designed industrial zones to centralize activities. In addition, shared treatment plants and shared tariff can be adopted.

(2) Large scale industries

Action should be considered to implement cleaner production through applying onsite pre-treatment of industrial water before disposal into sewage sewer system and consequently into the coastal water.

(3) Legislations enforcement

The enforcement of existing legislation of cleaner production should be imposed and monitored.

4.3 Storm Water

Storm water should be properly collected and managed through separate systems. This will lead to reducing the hydraulic load of waste water reaching treatment plant. Moreover, storm water can be used to recharge groundwater aquifers and subsequently protect these aquifers from quality deterioration by seawater intrusion. Additionally, storm water can be recycled for municipal use and irrigation.

5. Conclusion

In conclusion, results of this study reflect on continuous exposure of the coastal line to various types of contaminants resulting from, mostly, domestic and industrial activities. As such, the water quality profile and metal speciation is expected to impact the quality of seawater, aquatic organisms and consequently human health. Thus, it is critical to implement the recommended intervention plans to safe guard the "Mediterranean Sea" in accordance with international treaties and conventions.

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