Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2022.27974

245 (2022) 167–177
January

First assessment of domestic and industrial effluents impact on intertidal zone of Safi coastline (west of Morocco): physicochemical characteristics and metallic trace contamination

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Received 25 May 2021; Accepted 4 November 2021

ABSTRACT

This study aimed to evaluate the effects of urban and industrial effluents on the intertidal seawater and sediments quality of Safi coastline (western Morocco). This is a pioneer work carried out in the transition zone between seawater and wastewater. In addition, it sheds light on the destructive consequences of the aforementioned effluents on the biocenosis specific to this biotope. For this purpose, four sampling campaigns covering five critical stations were selected. We considered the seaside area as a reference station. All the indicators of the environmental health and metallic contamination used for this monitoring were measured at low tide: the mixing waters' physicochemical parameters (temperature, pH, conductivity, salinity, and turbidity), the levels of four metallic trace elements (copper, zinc, lead, and cadmium) in both water and superficial marine sediments, the pollution indices that reflect the level of biotope healthiness, as well as the pollution load parameters (BOD_5 and COD). The results indicated a great variability of physicochemical parameters measured at the seawater-wastewater mixing zone, with no significant difference observed between the reference station S0 and the investigated stations S1, S2, S3 and S4. However, these last three stations revealed a much lower environmental quality. Furthermore, the effluents were found to be loaded with lead, cadmium and, to a lesser extent, copper. In fact, the pollution indices had confirmed that the analyzed seawater as well as the surficial sediments were heavily polluted with trace elements. The statistical analysis of wastewater revealed four distinct groups; (i) domestic; (ii) food industry; (iii) domestic-industry; and (iv) phosphate industry. These effluents are generally biodegradable except for station S5. This study provides a solid baseline for a future sustainable monitoring program to rehabilitate Safi coastline and safeguard its biocenosis.

Keywords: Impact of effluents; Seawater-wastewater mixing zone; Trace metals; Physicochemical parameters; Effluents biodegradability; Safi coastline

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1944-3994/1944-3986

1. Introduction

Environment is highly subject to an increasing pressure due to the demographic explosion. This anthropic pressure is expressed through a massive and anarchic production of solid and liquid wastes (domestic and industrial), usually discharged to natural ecosystems such as rivers and marine areas, without any prior treatment. The pollution generated disturbs all natural ecosystem components including water, soil, sediments, fauna, and flora [1–6].

Recently, the economic importance of coastal environment, including estuaries, bays, shores, and lagoons, has emerged alarming concerns regarding solid and liquid wastes discharged through rivers or directly to these valuable ecosystems without any pre-treatment [7,8], putting its biocenosis in a serious danger.

For instance, the intertidal zone or tidal swing zone, reached by spring tides and undergo extreme variations in its physicochemical conditions, corresponds to medio-littoral and supralittoral levels. This biome which is rich in algae (red algae, green algae, and brown algae), hosts a particular fauna that is well adapted to these extreme variations of the intertidal zone. To withstand dehydration, some animals such as univalves, worms and crabs, retain seawater in their enclosures. Other animals like sea urchins, starfish, and anemones survive by inhabiting the pools and pits of the surf platform where water stagnates, whereas other forms live completely buried in the sediments [9,10].

The Atlantic coastline of Morocco has experienced an accelerated development of industrial units based primarily on economic benefit. At the same time, this industrial expansion has raised awareness on the risk of incorporating trace metals into coastal ecosystems and seafood, traditionally consumed by the indigenous populations [11–17]. Located on the Atlantic coast, the city of Safi is an urban agglomeration in full industrial expansion. In fact, this coastal area is an industrial hub of multifunctional activities with chemical and para-chemical industries, agro-industry, and mechanical and metallurgical industries. The entire urban sanitation network in the city is currently a combined sewer system. The wastewater is drained to eight coastal outlets following the natural gravity to meet the ocean water in the intertidal zone [18]. However, the industrial wastewater (fish cannery, olive and caper cannery, and phosphate processing plants) is not connected to the city's sanitation network but is discharged directly onto the coast without prior treatment.

Several studies assessing pollution on the Safi coast have been carried out [19–26]. However, these investigations have been far from reflecting the destructive aspects of urban and industrial wastewater on the coastal ecosystems. In fact, these investigations were always sporadic and occasional, without any specific monitoring over time. Moreover, the characterization of different types of effluents (domestic and industrial) has not been sufficiently carried out. Thus, to the best of our knowledge, none of these works have highlighted the physico-chemical and ecotoxicological characteristics of the seawater-wastewater mixing zone at low tide, nor the consequences on the biocenosis in this particularly sensitive area.

Therefore, the aim of the present work is, firstly, to shed additional light on a particular biotope that constitutes a sort of interface between the marine environment itself and an effluent of exogenous origin. Our approach is to evaluate the physico-chemical quality of seawater-wastewater and the degree of metallic contamination by copper, lead, zinc, and cadmium in seawater-wastewater and surficial sediments in the intertidal zone. These four trace metals have often been recognized as major pollutants in coastal ecosystems. Secondly, to assess the ecological risks incurred by the specific biocenosis dependent on such an intertidal biotope, through the calculation of several pollution indices. This work intends to provide a baseline for more regular monitoring in the future, in a coastal area increasingly disturbed by anthropogenic impacts.

2. Materials and methods

2.1. Description of the study zone

The coast of Safi belongs to the Atlantic shore of Morocco, representing an important morphology, topography, and landscape diversity [27]. The study area is located between longitudes [–9°1′50.01W; –9°27′41.77W] and latitudes [32°44′40.11N; 31°55′8.37N]. All the urban and industrial wastewater is discharged at the coastal cliffs, which end with a rocky plateau without any sediment cover. The general aspect of the slope at the seabed on which the wastewater discharged and mixed with the seawater does not exceed 3% [28].

Five stations (S1–S5) in addition to a reference station (S0) distributed along the coastline of Safi, were selected (Fig. 1):

- *Station 1*: Sea Castle (S1) close to the port. It is located in front of the bay of Safi. It receives domestic effluents and affected by the port activities (32.300528N, –9.243951W).
- *Station 2*: Mrissa I (S2) receives industrial effluents of fish-processing firm. This is the UNIMER sector for the processing and production of canned sardines and mackerel (32.269526N, –9.254053W).
- *Station 3*: Mrissa II (S3) receives industrial effluents of the CAPREL plant for the transformation and production of canned olive and caper (32.253717N, –9.260673W).
- *Station 4*: Mrissa III (S4) located to the south of the city. It is the main wastewater collector (32.244276N, –9.262508W).
- *Station 5*: (S5) located at 5 km south of Safi and nearby the effluents of three major industrial complex (Morocco Chemistry, Morocco Phosphore I, and Morocco Phosphor II). The complex is considering as one of the major platforms of phosphoric acid manufacturing worldwide (32.205285N, –9.252552W).
- *Station 0*: Cap Beddouza (S0) reference station, located at 34 km north of Safi. It is a balneary zone fare from any potential sources of industrial pollution (32.553614N, –9.271288W) [24].

2.2. Sampling

Four sampling surveys were carried out covering four seasons: February (winter) and October (autumn) 2017,

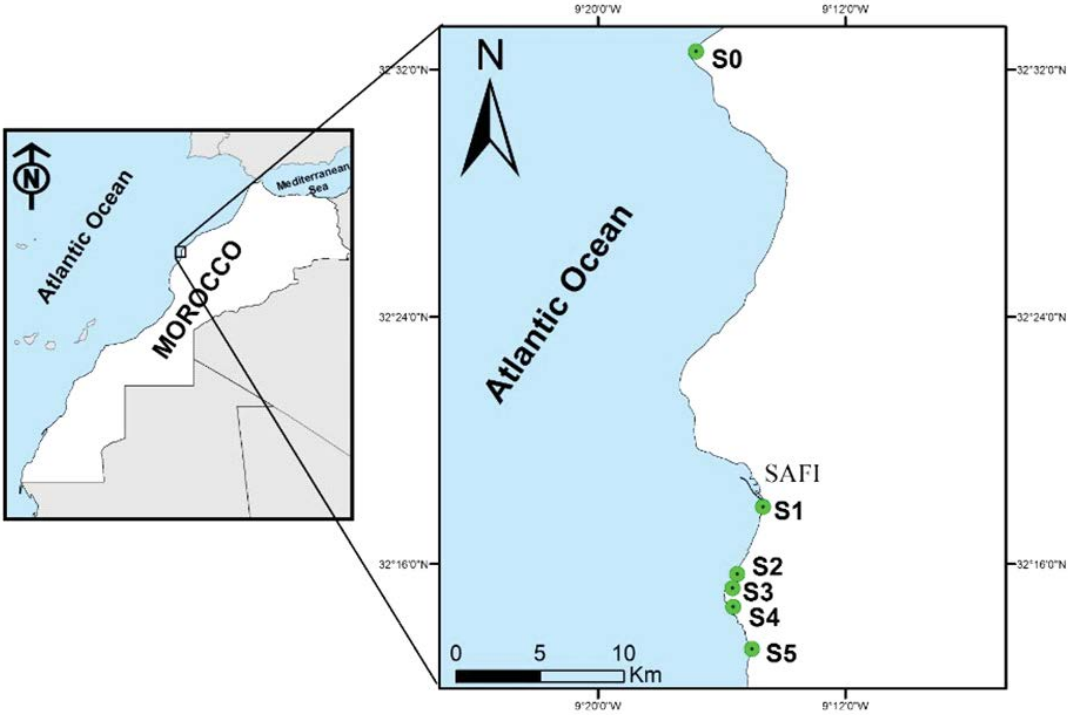

Fig. 1. Geographical location of the discharge, seawater and sediment sampling sites (GIS mapping technique; ArcGIS software (version 10.3) developed by ESRI (Environmental System Research Institute).

April (spring) and June (summer) 2018. In Safi, the tide is semi diurnal, and each tide lasts about 6 h. Thus, we referred to the local tide calendars to know the exact time of the lowest tide to allow sampling of sediments and wastewater, whereas the water from the mixing zone was sampled after one tidal hour (duration of high tide – duration of low tide/6). The samples were taken during sunny days with good weather (no rain or wind). We did not take into account the operation or shifting hours of the industries or the high flow of domestic sanitation for urban wastewater.

2.3. Physico-chemical parameters

For each samples, temperature of waters (*T* °C), electric conductivity (EC), salinity (Salt), potential of hydrogen (pH), and turbidity (Turb.) were measured in-situ using multi-parameters analyzer type VWR MU. The quality of physico-chemical parameters was controlled using certified standards CONSOR. Furthermore, samples were conserved at 4°C along the way to the lab, where they were analyzed within the following 24 h according to Rodier [29].

2.4. Pollution load parameters

Two parameters were used to evaluate organic pollution load: biochemical oxygen demand (BOD_5) and chemical oxygen demand (COD), using respectively BOD-meter Lovibond Water Testing (standard NF T 90 – 103) and AFNOR [30] COD standard (NF T 90 – 101). For best approximation of wastewater origin, the ratio COD/BOD_5, and the estimation of oxidizable matter turns out to be of great interest.

$$OM = \frac{\left(2BOD_5 + COD\right)}{3}\left[31\right] \quad (1)$$

2.5. Sediments

The sediments were sampled with plastic shovel at water–sediments interface with 5 to 10 cm depth (under water column sampling). We transported our samples to the lab in sterile plastic bags and conditioned at 4°C [29].

2.6. Metallic trace elements

Samples were collected in bottles rinsed with conservative stabilizing agent (0.5 mL HNO_3 50% V/V at pH = 2). Mineralization of seawater, effluents (after filtration using a 0.45 μm cellulosic filter) [29], and sediments was performed according to the protocol validated by Tahiri et al. [17]. Then the dilution process was done according to the procedures published by Chiffoleau and Truquet [32], El Abidi et al. [33], and El Morhit et al. [12]. The dosage of metallic trace elements (MTEs) was carried out using atomic absorption spectrometer (Aurora TRACE AI1200 flame air-acetylene (SAAF)). The validity of analytical methods was verified with internal control using standardized samples. The MTEs analyzed (Cd, Cu, Pb and Zn) were chosen as they have already been identified as major pollutants in Safi's coastal ecosystems [21,25,34].

2.7. Pollution indexes

We adopted two indices assessing marine sediments quality:

- Contamination factor (CF) expresses the contamination level in surficial sediments for each metal relative to its background level, independently to all other pollutants involved, through the following equation [35]:

$$CF = \frac{C_{Metal}}{C_{Background}} \quad (2)$$

where C_{Metal} is the measured metal concentration in the surficial sediments and $C_{Background}$ is the reference concentration of the metal in the marine sediments (the background concentration of the metal) [36]. Four levels in terms of CF were adopted to classify the level of surficial sediments' contamination by trace metals: Low contamination level (CF < 1), moderate level (1 ≤ CF < 3), considerable level (3 ≤ CF < 6), and very high level (CF ≥ 6) [35].

- Pollution load index (PLI) evaluates the sediments contamination degree considering all the studied metals. PLI provides a more global indication of the anthropogenic impact on the marine environment. It is defined as the *n*th root of the product of *n* CF according to the following equation [37]:

$$PLI = \left(CF_1 \times CF_2 \times CF_3 \times \ ... \ \times CF_n\right)^{1/n} \quad (3)$$

To assess seawater quality/pollution indices, Pollution Index (PI) was adopted. It considers every studied pollutant independently of other involved pollutants [38].

$$PI = \frac{M_i}{S_i} \quad (4)$$

where M_i: the measured concentration of the pollutant (i) in seawater (mg L^{-1}); S_i is the concentration of the stipulated standard of pollutant i in seawater (mg L^{-1}). When PI > 1, the discharge of pollutant i exceeds the required standards. In contrast, when PI ≤ 1, the pollutant discharge is in agreement with the required norms.

Compressive pollution index (CPI) is a method widely used to assess the contamination and pollution level in coastal waters. The CPI encompasses simultaneously the level of incidence of all studied pollutants (Table 1).

2.8. Statistical analysis

In the perspective to establish a typology of effluent and marine waters of different stations according to the nine studied parameters, we carried out a descriptive analysis (Mean ± Standard Deviation) followed by an Ascending Hierarchical Classification (ACH). The analysis was performed on the average values of different parameters according to Belkhiri and Narany's recommendations [39]. This analysis was performed using the XLSTAT software.

3. Results and discussions

3.1. Physico-chemical parameters

Before assessing the impact of metallic contamination of industrial and urban effluents on the intertidal zone, it is wise to present the physicochemical characteristics (Table 2) of such biotope, given their influences on pollutants dynamics.

3.1.1. Temperature

The average temperatures of the wastewater from the various studied effluents varied between 19.25°C and 23.5°C. These values remained below the discharge limit values, which is <30°C according to CNS [40], and stayed similar to those found in Settat, Berrechid, Benhmed, Elgara [41], and Mohammedia [42] for domestic effluents and those found by Benyakhlef et al. [14] at Agadir fish-processing firm. However, the station S5 receiving the phosphate treatment discharges remained the hottest (23.5 ± 9.19), and exhibited a fairly large standard deviation due to cooling water discharged as well. Whereas, the average seawater temperatures varied between 15.5°C and 25.65°C, reflecting a local seasonal variation (semi-arid climate), and even remained higher than the average seawater temperature at high tide [21]. Station S1 showed also a standard deviation of around 2.54°C, which was due probably to the topographical nature at this level (port).

The increase in seawater temperature can promote a release of metals from the surficial sediments, a decrease in dissolved oxygen, and can influence also the survival of biocenosis [43] and their biodiversity by promoting the progression and propagation of thermophilic species.

3.1.2. pH

The wastewater effluents had different pH values according to their nature/origin (domestic, industrial, mixed), the type of industrial process (fermentation, acidification), and the used raw material (fish, olive, caper, phosphate). Generally, all the stations presented acid effluents ranging from 3.85 to 6.65, and showed an industrial to domestic-industrial characters. The domestic effluents

Table 1
Levels of seawater quality according to Liu et al. [38]

CPI value	Water quality assessment	Description
CPI ≤ 0.8	Qualified	Some pollutants are detected but their concentrations accord with the standard.
0.8 < CPI ≤ 1	Basically qualified	Concentrations of some pollutants exceed the standard.
1 < CPI ≤ 2	Polluted	Concentrations of quite a part of pollutants exceed the standard.
CPI > 2	Seriously polluted	Concentrations of quite a part of pollutants exceed the standard many times.

Table 2
Physico-chemical parameters of wastewater and seawater (Means ± Standard Deviation)

	Parameters	S1	S2	S3	S4	S5	S0
Wastewater	*T* (°C)	22.10 ± 0.85	20.50 ± 0.71	21.85 ± 1.20	19.25 ± 0.35	23.50 ± 9.19	–
	pH	6.35 ± 0.21	6.65 ± 0.21	4.90 ± 0.14	6.00 ± 0.70	3.85 ± 0.35	–
	Salinity (g L^{-1})	1.30 ± 0.14	2.15 ± 0.21	2.05 ± 0.07	2.25 ± 0.35	33.00 ± 1.41	–
	EC (mS cm^{-1})	2.40 ± 0.42	4.35 ± 0.21	2.45 ± 0.49	2.85 ± 0.21	47.05 ± 5.73	–
	Turb. (NTU)	2.70 ± 0.14	2.95 ± 0.07	3.05 ± 0.07	1.80 ± 0.28	50.60 ± 0.85	–
Seawater	*T* (°C)	17.00 ± 2.54	25.65 ± 0.21	15.50 ± 0.70	20.05 ± 0.07	21.25 ± 7.42	21
	pH	7.75 ± 0.07	7.35 ± 0.21	6.25 ± 0.21	7.30 ± 0.14	6.05 ± 0.07	8.3
	Salinity (g L^{-1})	22.00 ± 0.25	24.00 ± 0.75	25.00 ± 1.02	25.50 ± 1.56	33.00 ± 1.82	35.5
	EC (mS cm^{-1})	24.00 ± 4.20	33.00 ± 2.72	27.00 ± 1.41	33.50 ± 2.12	47.60 ± 5.09	25
	Turb. (NTU)	2.25 ± 0.21	2.90 ± 0.14	2.90 ± 0.14	1.50 ± 0.42	50.25 ± 1.76	10

–: Absence of effluent

generally fluctuated between 7.5 and 8.5. These values greatly exceeded the Moroccan standards of 6.5–8.5 [44]. The average pH values observed for seawater in all the stations varied between 6.05 and 7.75. These values remained much lower compared to those recorded at Cap Beddouza control station (S0), where the pH was 8.3. However, all these pH values were generally lower than pH values characterizing coastal seawater, which exhibits a more alkaline pH values varying between 7.9 and 8.3 [43].

In the intertidal zone, at low tide, seawater failed to buffer the pH at the mixing zone with the wastewater for all the stations. Acidic pH would lead to the risk of metals being present in a more toxic ionic form, in addition to the risk of dissolving the shells of mussels and other intertidal species. A similar result was observed for discharges from the industrial zone of El Jadida-Safi [45].

3.1.3. Salinity

The salinity is a marker of the freshwater-saltwater mixture. It reflects the freshwater inputs from wastewater and the tidal cycle. The ocean is considered to contain an average of 35 g of salt per kg of seawater. The salinity of the studied wastewater varied between 1.3 and 2.25 g L^{-1} for stations S1–S4, whereas station S5 recorded the highest value (33 g L^{-1}) probably as a consequence of the release of phosphor-gypsum. However, the salinity of the sampled seawater fluctuated between 22 to 33 g L^{-1}. These values are low if compared to the control station (35.5 g L^{-1}) in Cap Beddouza. This can be explained mainly by the in-situ dilution caused by the effluents accentuated by the effect of saline intrusion, since the salinities recorded at high tide are always higher than those observed at low tide [45]. In the intertidal zone, there is a drop in salinity at low tide, aggravated and diluted by wastewater, thus putting the ecosystem in much stressed conditions.

3.1.4. Electrical conductivity

The measurement of conductivity informs about the degree of water mineralization where each dissolved ion acts through its specific conductivity. This conductivity changed between 2.4 and 4.35 mS cm^{-1} in the wastewater from the studied effluents. In fact, the studied industrial and urban wastewater, rich in organic matter, seem to be a poor conductor, with an exception observed at station S5 loaded with orthophosphate from phosphogypsum, which recorded 47.05 mS cm^{-1}.

The average conductivity of seawater varies between 24 and 47.6 mS cm^{-1}. A previous study undertaken in Agadir Bay has shown higher values up to 55.4 mS cm^{-1} [11]. The conductivity seemed to be affected by the dilution resulting from the effluents as well as by the nature of the salts released by the industries.

3.1.5. Turbidity

The turbidity of the studied wastewater recorded values between 1.8 and 3.05 NTU for all studied stations, except for station S5 (50.6 NTU). Whereas the turbidity of seawater varied between 1.5 and 2.9 NTU, except for station S5 (50.25 NTU). Samples were taken at low tide, with minimum water agitation, which explains the small variations between the turbidity of the wastewater and seawater. Station S5 showed high values due to the release of phosphogypsum on a regular basis.

3.2. Metallic trace elements

3.2.1. Sediments

The outcome of trace metal elements (TMEs) analysis of the surface sediments (Table 3) were compared to reference station Cap Beddouza (S0) and to GEODE standards [46]. The average TMEs contents of dry sediments was very fluctuating: Cd [1.22–7.67 µg g^{-1}], Pb [21.2–157.8 µg g^{-1}], Zn [148–307 µg g^{-1}] and Cu [15–101.1 µg g^{-1}]. The existence of these TMEs in the sediments of different stations reveals the long term and disparate anthropic impact on the intertidal zone, consisting mainly of effluents from agro-food processing industry and phosphate treatment industry, as well as domestic sewage. The average metallic (Pb and Zn) contents in sediments in the studied sites did not exceed the standards, except for Cd in stations S2, S3, S4 and S5, and Cu in stations S1 and S2. This is consistent with the study

Table 3
Mean concentration µg g^{-1} of metallic trace elements in the sediment (Mean ± Standard Deviation)

Stations	Cd	Pb	Zn	Cu
S1	1.22 ± 0.56	55.5 ± 1.2	231 ± 4	101.1 ± 7.0
S2	3.90 ± 0.05	157.8 ± 0.1	207 ± 0	94.7 ± 9.5
S3	3.77 ± 0.32	49.5 ± 0.4	173 ± 3	29.1 ± 0.4
S4	7.67 ± 0.04	91.0 ± 0.3	307 ± 0	71.4 ± 2.6
S5	3.97 ± 1.64	21.2 ± 0.4	148 ± 2	15.0 ± 1.2
S0	n.d	n.d	n.d	8.1 ± 0.2
GEODE [46]	2.04	200	552	90

n.d: not detected

of Berrahou [45] through the contamination of mussels by Cd and Cu along the coastal line of Safi.

3.2.2. Wastewater

The wastewater collected in stations S2, S3 and S5 (industrial discharges) had the highest levels of TMEs, in particular Cd and Pb which exceeded the allowed values according to the standards [44]. However, the Zn and Cu contents were lower than the VLGR standards for all the stations (Table 4). These results show most likely that the industrial effluents are probably the main sources of contamination by metals, particularly by Pb and Cd.

3.2.3. Seawater

The seawater average concentrations of Cd, Pb and Cu, with the exception of Zn, exceeded the standards of FAO [47] in all the stations (Table 5). The upwelling of deep water due to the upwelling phenomenon is also a source of contamination by ETMs [48]. In fact, Agadir-Dakhla coastline has high levels of Cd despite the long distance from industries. The violent hydrodynamics of the intertidal zone is responsible for the instability of the physicochemical parameters conditioning the behavior of metals in this zone. The acidic pH of wastewater and seawater at low tide in the mixing zone may also be implicated in the release of these metals from sediments to surface waters.

3.3. Analysis of load pollution parameters

For assessing effluents' nature and biodegradability, we have used BOD_5 and COD indices as well as the ratio COD/BOD_5 and content of oxidizable matters (Table 6).

Table 4
Mean concentration (mg L^{-1}) of trace metal elements in wastewater (Mean ± Standard Deviation)

Stations	Cd	Pb	Zn	Cu
S1	0.05 ± 0.03	0.8 ± 0.5	2 ± 0	0
S2	1.12 ± 0.39	2.5 ± 0.8	2 ± 0	0.2 ± 0.1
S3	0.91 ± 0.15	2.1 ± 0.7	3 ± 0	0.3 ± 0.1
S4	0.05 ± 0.04	0.5 ± 0.6	1 ± 0	0.1 ± 0.0
S5	1.15 ± 0.88	1.5 ± 0.5	2 ± 1	0.6 ± 0.2
VLGR [44]	0.02	1	5	3

Table 5
Average concentration (mg L^{-1}) of metallic trace elements at seawater level (Average ± Standard Deviation)

Stations	Cd	Pb	Zn	Cu
S1	0.18 ± 0.07	1.6 ± 0.1	1 ± 0	0.5 ± 0.2
S2	1.94 ± 0.02	1.9 ± 0.0	1 ± 0	0.6 ± 0.3
S3	1.07 ± 0.01	2.2 ± 0.6	1 ± 0	0.5 ± 0.0
S4	0.70 ± 0.42	2.2 ± 0.2	1 ± 0	0.4 ± 0.2
S5	0.54 ± 0.61	1.3 ± 1.3	1 ± 0	6.0 ± 0.1
S0	0.16 ± 0.06	n.d	n.d	0.1 ± 0.0
FAO standard [47]	0.02	0.05	5	0.05

n.d: not detected

The average BOD_5 values recorded in stations S1–S3 were between 223 and 448.33 mg O_2 L^{-1}, but the average value for station S4 was about 507 mg O_2 L^{-1}. These values remained close to the national average concentration which is 360 mg O_2 L^{-1} [41], and were in agreement with the values found in the Chaouiya Ourdigha region [41], but remained much lower than those found by Benyakhlef et al. [14]. However, they were above the up-limit value (120 mg O_2 L^{-1}) for direct liquid waste discharges (Order n° 1607-06 of 29 Joumada II 1427 "25 July 2006").

It is wise to know that operation of fish-processing factories depends on the arrivals of fish, and the discharges are function to the cleaning operations, which fluctuate widely. Thus, their wastewater can be segregated into guano water, brine water, washing water, and sanitary water. The same conclusion can be drawn for the olive and caper processing factories, which operates on a seasonal basis.

It should be noted that the presence of very active toxic elements could mask the presence of biodegradable

Table 6
Average contents of BOD_5, COD, COD/BOD_5 ration, and oxidizable matter (OM)

Stations	BOD_5 (mg O_2 L^{-1})	COD (mg O_2 L^{-1})	COD/BOD_5	OM (mg L^{-1})
S1	429.00	635.02	1.48	497.67
S2	223.00	576.00	2.58	340.67
S3	448.33	460.80	1.03	452.49
S4	507.00	751.00	1.48	588.00
S5	9.33	691.20	74.06	236.62

materials, and then seriously misrepresent the measurement of potential BOD_5. In the case of station S5, for instance, the concentration of BOD_5 was 9.33 mg O_2 L^{-1}. Note that, during the measurement of BOD_5, pH was adjusted to 7 with an alkaline solution.

The average COD values at different stations varied between 460.80 and 751 mg O_2 L^{-1}. These average values were above the up-limit value (250 mg O_2 L^{-1}) for direct discharges (Order n° 1607-06 of 29 Joumada II 1427 "25 July 2006").

The values of BOD_5 and COD remained higher for all stations if compared to the direct discharge limit values. Thus, the discharges seem far from being purely domestic discharges. On other hand, the biodegradability of an effluent is calculated by the ratio COD/BOD_5 and depends on the nature and origin of the wastewater (domestic or industrial), which requires different treatment routes [49]. The COD/BOD_5 ratio for purely domestic wastewater is generally between 1.25 and 2.5. When the COD/BOD_5 ratio is between 3 and 7, the wastewater may be difficult to biodegrade. But when it is less than 1.25, the wastewater is originated from agro-food activities.

The studied wastewater showed a COD/BOD_5 ratio varying from 1.03 to 2.58 (between 1 and 3). Therefore, it can be concluded that they are easily biodegradable, except for the station S5, in which this ratio was too high (74.06) given the nature of the mineral-based wastewater. According to IBGE data [43], the presence of toxic substances may justify such value.

The obtained ratios were similar to those reported by Abou Elouafa et al. [50] for Oujda wastewater, where the ratio was less than 2.5 (1.6). On the other hand, they remained lower than values found in Mohammedia (16.4) due to the effluent of textiles connected to the city sewage network [42]. The effluents of station S5 remains interesting to study further.

3.4. Pollution degree

3.4.1. Sediments

For contamination factor (CF), the obtained values showed a very strong to significant contamination by Cd and moderate contamination by Zn in surficial sediments of all the stations. On the other hand, those from stations S3 and S5 were weakly affected by Cu (FC < 1) but moderately affected by Pb (FC > 1) (Table 7).

For pollution load index (PLI), the trend was stronger since the sediments of stations S1, S2 and S4 turned out to be very polluted by all the studied metals (PLI > 1). Whereas, those from stations S3 and S5 had PLI less than one (Table 7), and thus can be seen as unpolluted given the low contamination by Cu and Pb.

3.4.2. Wastewater

The Cd and Pb IPs values were much higher in stations S2, S3, and S5 compared to stations S1 and S4 (Table 8). Similar trend was observed for PCI calculations in stations S2, S3, and S5, whereas it remained lower than 1 in stations S1 and S4 (Table 8). This trend confirms the output of our physicochemical analyzes with the agro-food and the phosphate processing industries being the source of Pb and Cd contamination in Safi's coastline environment.

Table 7
Contamination factor (CF) and pollution load index (PLI) of surface sediments collected from the sampling stations on the Safi coastline

Stations	CF				PLI	Qualitative status
	Cd	Pb	Zn	Cu		
S1	4.07	2.78	2.44	2.25	1.22	Polluted
S2	13.00	7.89	2.18	2.11	1.21	Polluted
S3	12.57	2.48	1.83	0.65	0.10	Unpolluted
S4	25.57	4.55	3.24	1.59	1.12	Polluted
S5	13.23	1.06	1.56	0.33	0.76	Unpolluted

Table 8
Pollution index (PI) and compressive pollution index (CPI) in wastewater collected from sampling stations on Safi coastline

Sampling stations	PI				CPI	Qualitative status
	Cd	Pb	Zn	Cu		
S1	0.25	0.87	0.44	0.01	0.39	Unpolluted
S2	5.60	2.56	0.44	0.07	2.17	Polluted
S3	4.55	2.13	0.60	0.11	1.85	Polluted
S4	0.25	0.53	0.24	0.04	0.27	Unpolluted
S5	5.75	1.53	0.54	0.20	2.00	Polluted

3.4.3. Seawater

PI_{cd} (except S1), PI_{Pb}, and PI_{Cu} (except S4) values were higher in all stations, whereas PI_{Zn} values remained <1 for all stations. The compressive pollution index (CPI) showed a very high level of seawater contamination in all stations with a value greater than 4 for station S5 (Table 9).

3.5. Typology of wastewater and marine water

The Ascending Hierarchical Classification (AHC) distinguished four classes for wastewater (Fig. 2). The first class of wastewater contained station S1 (domestic discharge), the second class included stations S2 and S3 (agro-food discharge), the third class comprised station S4 (mixed discharge), whereas the fourth class was represented by industrial discharge from phosphate treatment (station S5). The AHC inter-class variance for wastewater is 99.56%, the classes 1 and 2 were very similar and showed low variance compared to class 3 effluents (Table 10). The high inter-class variance was mainly due to the characteristics of phosphate treatment effluents, which were highly loaded.

However, only three classes resulted from AHC analysis of seawater physicochemical parameters (Fig. 3). The first class contained stations (seawater: SW), SW-S1, SW-S2, SW-S3, and SW-S4; the second class included the control station (EM-S0), whereas the industrial phosphate treatment

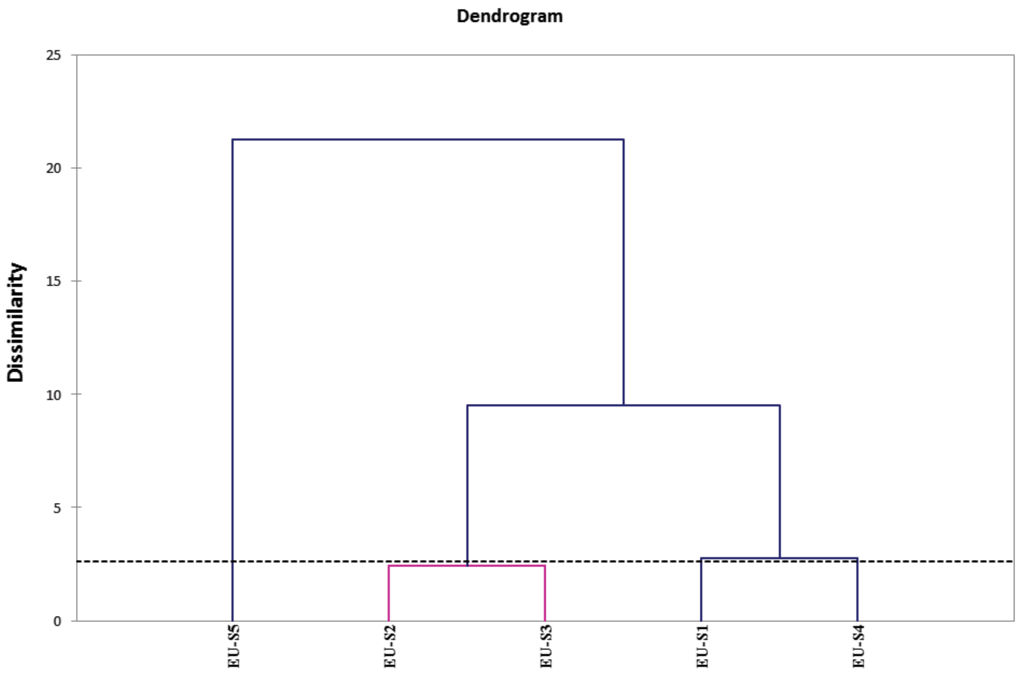

Fig. 2. Grouping of wastewaters studied using hierarchical clustering analysis.

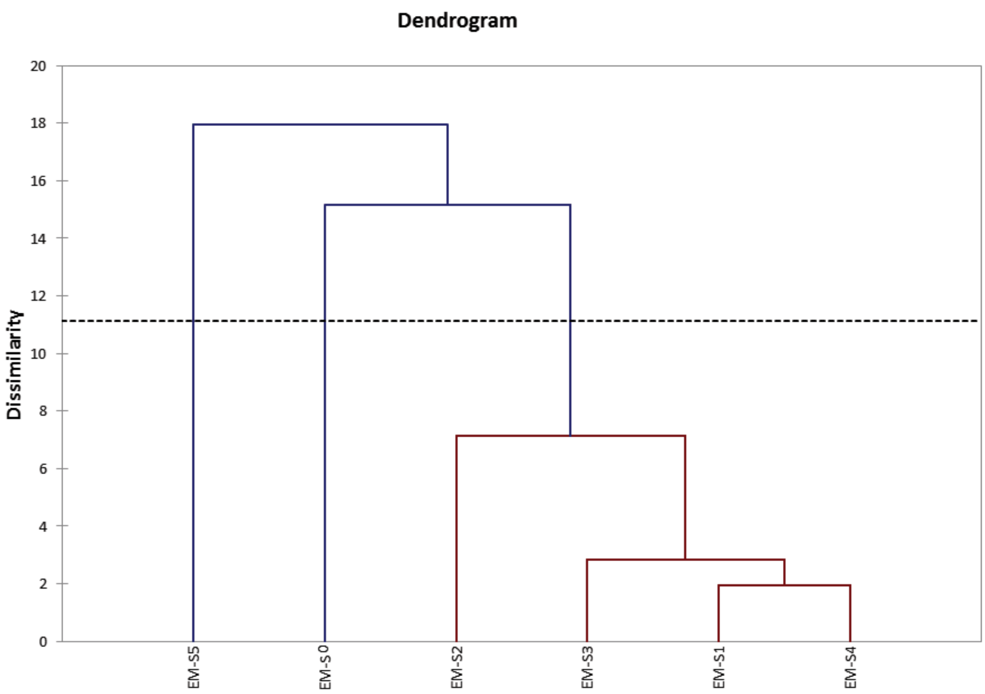

Fig. 3. Grouping of seawater studied using hierarchical clustering analysis.

effluent (SW-S5) constituted the third class. These results translate a strong impact of domestic and industrial effluents on the physicochemical characteristics of seawater as a natural environment. The fact that the stations SW-S1, SW-S2, SW-S3, and SW-S4 belonged to the same class implies that the impact of the pollutants carried by the effluents at these stations was statistically non-significant, but remained far from the quality of the reference station (SW-S0). However, at SW-S5, the impact was significant.

The interclass variance of seawater was 90.86%, and according to Table 11, classes 1 (S1, S2, S3, S4) and 2 (S0) showed some similarities in terms of physicochemical

Table 9
Pollution index (PI) and compressive pollution index (CPI) in marine water collected from sampling stations on Safi coastline

Stations	PI				CPI	Qualitative Status
	Cd	Pb	Zn	Cu		
S1	0.90	3.38	0.32	1.16	1.44	Polluted
S2	9.70	3.90	0.37	1.20	3.79	Seriously polluted
S3	5.35	4.50	0.36	1.12	2.83	Seriously polluted
S4	3.50	4.54	0.25	0.90	2.30	Seriously polluted
S5	2.70	2.72	0.39	12.10	4.48	Seriously polluted

Table 10
Average values of physicochemical parameters for different classes of the studied wastewater (Turb.: Turbidity; Sal.: Salinity)

Class	Turb.	T (°C)	pH	EC	Sal.	Cd	Pb	Zn	Cu
1	2.70	22.10	6.35	2.40	1.30	0.05	0.8	2	0
2	2.97	21.17	5.77	3.40	2.10	1.01	2.3	2	0.2
3	1.80	19.25	6.00	2.85	2.25	0.05	0.5	1	0.1
4	50.60	23.50	3.85	47.05	33.00	1.15	1.5	2	0.6

Table 11
Average values of the physicochemical parameters for the different seawater classes

Class	Turb.	T (°C)	pH	CE	Sal.	Cd	Pb	Zn	Cu
1	2.38	19.55	7.16	29.37	24.12	0.97	2.0	1	0.5
2	10.00	21.00	8.30	25.00	35.50	0.16	0	0	0.1
3	50.60	21.25	6.05	47.60	33.00	0.54	1.3	1	6.0

characteristics. This implies that class 1 waters were moderately polluted compared to the reference station.

All of these effluents induced a serious impact on the quality of seawater at the intertidal zone compared to the control station (Cap Beddouza), thus threatening the biocenosis of this intertidal ecosystem.

4. Conclusion

The results of this study showed significant influence of urban and industrial effluents on the physicochemical quality of intertidal ecosystem along the coastline of the city of Safi. Compared to the reference station (S0), this influence seemed to deteriorate the physicochemical quality of such an ecosystem. Moreover, this impact appeared to be similar on S1, S2, S3, and S4. In fact, at low tide, we recorded an unusual increase in seawater temperature compared to high tide. Station S5 having being the warmest due to the influence of boiler cooling waters produced by the phosphate industries. In all stations, the pH in seawater tended to be acid compared to the value measured at the reference station. The long-term change in seawater temperature, pH, and salinity at the intertidal mixing zone is more likely to disturb the intertidal ecosystem by favouring more thermophilic invasive species and dissolving the shells of mussels for instance. Moreover, acidity may promote MTEs mobility and increase their bioavailability from marine surficial sediments.

The high concentrations of MTEs recorded in the intertidal mixed waters were originated from the untreated effluents of agro-food (olive, caper and fish processing) and phosphate processing industries. In addition, due to the acidification of the environment, these trace elements may also be released from the intertidal loaded sediments previously contaminated.

The anthropogenic impact seemed to be diverse in the intertidal environment. The "Ascending Hierarchical Classification" translated different kinds of pollution, all exceeding the limit values recommended for disposal at sea. The AHC discriminated domestic wastewater (S1), agro-food wastewater (S2 and S3), mixed domestic-industrial wastewater (S4), and purely phosphate-industrial wastewater (S5). Nevertheless, all effluents were biodegradable and could be easily decomposed over time, except for those present in the phosphate treatment plant (S5).

Pollution indices showed severe contamination of seawater and surficial sediments from discharges. Station S5 remained a critical station that requires further studied to monitor its discharges and mitigate its effects.

The coastline, particularly the intertidal seawater-wastewater mixing zone, is under severe pressure in terms of hydrodynamic constraints exacerbated by the direct domestic and industrial discharge. This key habitat deserves specific measures to overcome its ecological and economic challenges, including threats to its biodiversity and ecosystem functioning. Faced with such a situation, it becomes necessary to set up, urgently, a pre-treatment station to strengthen the resilience of the intertidal biotope to withstand the effluents impact.

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