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# Assessment of Chemical Pollution in Water and Suspended Matter in the Gulf of Skikda (Northeastern Algeria)

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#### **ABSTRACT**

The assessment of marine environmental quality along the Skikda coastline, by analyzing physicochemical parameters (temperature and pH) and concentration of trace metals (Cd, Cu, Pb, and Zn) in both the dissolved phase and suspended particulate matter at five stations, allowed us to establish a preliminary diagnosis of the chemical pollution status of this coastal. The results reveal that the distribution of trace metals between the two compartments is not identical across the five sampling stations. A strong affinity for suspended matter (particulate phase) was observed for all investigated elements during both campaigns, with a partition coefficient (Kd) of approximately 106. According to the LAWA classification, suspended matter at stations 5 (Tedj) and 4 (Oued Safsaf) was contaminated by Zn, Pb, Cu, and Cd, ranking their particles as polluted to highly polluted. The slightly alkaline pH of the waters favored the adsorption of very high concentrations of trace metals in suspended matter (Zn: 2785.16  $\mu g/g^{-1}$ ; Pb: 609.03  $\mu g/g^{-1}$ ; Cu: 79.18  $\mu g/g^{-1}$ ; Cd: 2.60  $\mu g/g^{-1}$ ), mainly at stations 4 and 5. However, these metals also showed significant concentrations in the dissolved phase (Zn: 1093.36 µg/l<sup>-1</sup>; Pb: 49.91  $\mu g/l^{-1}$ ; Cu: 20.80  $\mu g/l^{-1}$ ; Cd: 2.36  $\mu g/l^{-1}$ ), exceeding the recommended standards (WHO/US-EPA) at station 5 for all studied elements, and at station 4 for Pb. Linear regression test indicates that, except for zinc, temperature exhibits a negative (inverse) correlation with metal distribution, whereas pH shows a positive (proportional) relationship. In conclusion, the Skikda coastline is enriched in trace metals as a result of anthropogenic activities, whether industrial, petrochemical, or domestic. This phenomenon is further amplified by currents, climatic conditions, and especially river inputs. Such contamination represents a potential threat to aquatic life and the balance of the entire coastal ecosystem.

#### INTRODUCTION

Rapid industrialization and economic development in coastal areas have increasingly introduced heavy metals into estuaries, rivers, and streams, posing major environmental







challenges (Zhang et al., 2007; Zhang & Gao, 2015; Qu et al., 2018; Singh & Mishra, 2021). Heavy metals, also referred to as trace metal (TM), naturally occur in aquatic ecosystems at low concentrations, typically in the nanogram or microgram per liter range (Biney et al., 1994). However, their presence at concentrations above natural levels poses a serious threat to aquatic environments due to their persistence and toxicity (Diop et al., 2016; Belabed et al., 2017; Ouali et al., 2018a; Safiur et al., 2019; Son Chen et al., 2020; Fan et al., 2021; Roy & Bharadvaja, 2021; Zeghdoudi et al., 2024).

Unlike organic pollutants, trace metals are not biodegradable and tend to accumulate in food chains, negatively affecting humans, animals, and plants (Nazir et al., 2015; Kinuthia et al., 2020; Kumar et al., 2020a; Abdulla et al., 2021; Zamora-Ledezma et al., 2021; Ahmadijokani et al., 2022; Feng et al., 2022; Jiao et al., 2022). This bioaccumulation varies across trophic levels and is influenced by species distribution, feeding habits, and environmental conditions. Upper predators, such as larger fish and benthic animals, often exhibit the highest TM concentrations (Tao et al., 2012; Younis et al., 2015; Amankwaa et al., 2021; De Castro-Fernández et al., 2021). In humans, heavy metal exposure is linked to growth impairments, organ damage, nervous system disorders, and even cancer (Martin et al., 2015; Anant et al., 2018; Wei et al., 2019; Zhang et al., 2019; Chan et al., 2021; Safiur et al., 2021).

Contamination in aquatic ecosystems is not restricted to a single compartment (water, sediment, or biota) or the immediate vicinity of the pollutant source. Intercompartment exchanges allow contaminants to spread throughout the ecosystem. Biogeochemical and physico-chemical factors, such as pH, temperature, salinity, dissolved oxygen, and suspended matter concentration, influence the speciation, mobility, and bioavailability of heavy metals (USEPA, 2011; Diop et al., 2014b).

Metals in water exist in two main fractions: dissolved and particulate (or suspended matter: SM). Natural turbidity in rivers, streams, and coastal areas is often mistakenly considered pollution. True suspended matter pollution occurs when pollutants bind to suspended particles, which are transported via atmospheric deposition, runoff, leaching, and erosion. Furthermore, activities such as flooding and dredging can resuspend contaminated sediments, spreading pollutants downstream. The transport of pollutants with suspended matter constitutes a significant portion of organic and inorganic contamination in aquatic systems. (CIPR, 2005; CIPR, 2009; Michael, 2017). The SM compartment is taken into account in this study.

With its 1622km of coastline stretching, Algeria boasts a diverse and remarkable natural heritage and significant potential for socio-economic development. The sea and coastline are the focus of numerous anthropogenic processes, including industry, urbanization, tourism and fishing. The growing pressures of these human activities on natural marine and terrestrial coastal environments are disrupting the stability of ecosystems (Belabed *et al.*, 2013b; Mihoubi *et al.*, 2014; Benzaoui *et al.*, 2015;

Bachouche et al., 2016; Boucetta et al., 2016; Belabed et al., 2017; Belhadj et al., 2017; Ouali et al., 2018b, b; Gherib et al., 2020; Alik et al., 2021; Kaddour et al., 2022; Rouidi et al., 2022; Boudeffa et al., 2023; Tata et al., 2023; Belhouchet et al., 2024). The Gulf of Skikda is the second largest tourist and economic center on the Algerian coast. The city has experienced rapid population growth, urbanization and industrialization, all of which have had a significant impact on the influx of materials and pollutants into its bay.

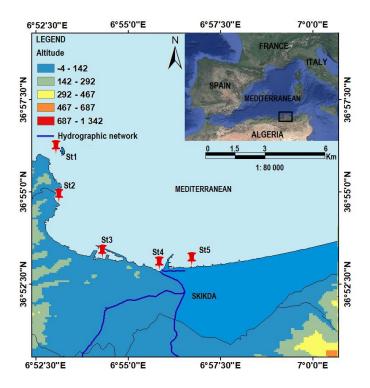
Its aquatic resources are threatened by pollution linked to burgeoning economic activity (Nafissa et al., 2005; Cheggour et al., 2014; Gueddah et al., 2014; Maatallah & Borhane, 2014; Benmecheta & Belkhir, 2016; Ouamane et al., 2016; Zeghdoudi et al., 2018; Atoui et al., 2019; Zeghdoudi et al., 2019, 2024; Tahar et al., 2021; Grini et al., 2022; Rouidi et al., 2022; Belahmadi et al., 2023; Bouhayene et al., 2024; Grini et al., 2024).

This study aims to evaluate the current status and potential sources of trace metal (TM) contamination along the coast of the Gulf of Skikda. Four trace metals (Zn, Pb, Cu and Cd) were determined in separated surface waters (dissolved phase) and suspended matters (SM) (particulate phase) in this area. These levels were then compared with accepted standards, and the toxicological quality of these compartments was deduced, with the aim of safeguarding public health.

#### MATERIALS AND METHODS

#### 1. Study area

The city of Skikda is located in northeastern Algeria, covering an area of 4118km². This study was carried out in the Skikda Gulf, which has a coastline that stretches over a distance of 160km. It is limited to the west by Cape Bougaroune, and Cape Fer to the east between 06°27′10′′E and 07°10′02′′E (Fig. 1). The area is characterized by strong anthropogenic pressure: petrochemical industrial complex (refinery: number one in Africa, Polymed: high-density polyethylene industry), three ports (fishing and marina port, oil port and mixed port), tourism and agriculture and a main river crosses the study area (**Grini** *et al.*, 2024). The climate of our study area is Mediterranean with two distinct seasons: hot and dry summer (from April to September), rainy and humid winter (from October to March). The average annual temperature is 17.9°C and the annual rainfall is approximately 671mm (worldclim.org).



**Fig. 1.** Map of the Gulf of Skikda displaying locations of the five sampli (northeastern Algeria)

In the present study, the sampling points were chosen on the basis of their representativeness and proximity to pollution sources, such as: urban agglomerations, industrial zones, among others. The sites subject to control are numbered at five stations (St1, St2, St3, St4 and St5) (Fig.1 & Table 1), are as follows:

**Table 1.** Sampling stations (water and suspended matters) and sources of contamination

Station	GPS	Pollution source					
	Coordinate						
St1	36°56'15"N	Is supposed to be far from any source of pollution, apart from					
(Serigina	6°53'02"E	accidental pollution caused by maritime traffic. It is subject to					
Island)		strong currents.					
St2	36°54'53"N	A relatively urban station. It receives domestic and					
(Lions'	6°53'05"E	stormwater effluent, as well as discharges from restaurants in					
Ravine)		the area. This beach is very popular in summer.					
St3	36°54'11"N	It ensures the transit of passengers, goods and hydrocarbons,					
(Mixte	6°54'03"E	it is separate from the new port, which is exclusively					
harbour)		dedicated to the transport of petroleum products, It receives					
		municipal waste. In addition, this station receives operational					
		discharges from boats (various oil leaks or other substances,					
		in addition to wash water) and accidental discharges					
		(explosion, collision, or grounding).					

		, ,					
St4	36°52'33"N	It flows into the Mediterranean at the site known as l'îlot over					
(Oued	6°56'49"E	a distance of approximately 60km, with a watershed area of					
Safsaf)		about 1165km² and an average annual discharge of 1500hm³.					
		In addition to the drainage of domestic wastewater through					
		the Zeramna Wadi (small river), which flows into the Safsaf					
		Wadi, the latter is subjected to several sources of pollution,					
		including the Refining Complex (RA1/K), the Thermal Power					
		Plant (CTE), ENAMARBRE, and the Gas Liquefaction					
		Complex (GL1/K).					
St5	36°52'13"N	Receives industrial waste (The CP1/K Petrochemical					
(Tedj)	6°57'35"E	Complex covers 54 hectares) and urban waste.					

## 2. Sampling of surface water and suspended matter (SM)

Sampling of surface waters associated with SM and measurement of physicochemical parameters (T°C and pH) were carried out during the 2023 summer season (June, July and August) and the 2023/2024 winter season (December, January and February). For each site, the concentration of 4 trace metals (Cd, Cu, Pb and Zn) was determined in the water and associated SM. Temperature and pH were measured *in situ* at all five study sites using a WTW multi-parameter type 2F30104211 (Multi 340 I/Set) at a depth of 30 - 40cm.

To minimize contamination and optimize results, high-purity reagents were used. Equipment cleaning was necessary to ensure optimum analysis results. Plastic and glass equipment was washed with a non-ionic detergent and copious amounts of deionized water, then treated with a 10% v/v nitric acid (HNO<sub>3</sub>) solution for 48 hours, and finally rinsed three times with double-distilled water.

Sampling was carried out seasonally according to standard procedures. Water samples associated with suspended matter were collected at five stations. For each water sample, 250 ml were taken at a depth of 50 cm or at mid-depth in shallow waters (**Rodier** *et al.*, 1996), at a distance of around 15 meters from the sampling station. Samples were collected in decontaminated polyethylene bottles. A total of 90 water samples were collected, with three replicas per station, month and compartment.

#### 3. Chemical analysis

The collected water samples were filtered using a 0.5% vacuum pump with a SARTORIUS membrane of 0.45% µm porosity. The filtrates (100ml dissolved phase) were acidified with HNO<sub>3</sub> (D=14g/cm3) to achieve a pH below 2 (**Rodier** *et al.*, 1996) (**IGCC/UNIDO/UNDP/UNEP/GEP/NOAA/NEPAD, 2009**), then stored at 4°C prior to metal analysis. Regarding suspended matter (SM), the filters (particulate phase) were recovered in crucibles and underwent HNO3 acid digestion in a muffle furnace at 160°C.

Ash redissolution was carried out by adding 5ml of concentrated HNO<sub>3</sub>, then filtering  $(0.45 \mu m)$  and adjusting the solution (50ml) with distilled water.

For each series of samples, a digestion blank and a reference sample (Quality control samples) were determined using a NASS-5, National Research Council of Canada reference material (Table 2) of known concentration and were analyzed to ensure quality control of the results. Results were expressed in  $\mu g/l$  for separated water and in  $\mu g/g^{-1}$  for suspended matter (SM).

The elements studied (Cd, Cu, Pb and Zn) were measured using a flame atomic absorption spectrophotometer (type Pye Unicam SP 939/959). Detection limits were 0.009, 0.007, 0.03 and 0.007 $\mu$ g/l<sup>-1</sup> for Zn, Pb, Cu and Cd, respectively.

**Table 2.** Certified and observed values of elemental concentrations in sea water reference materials (NASS-5/NRC, 2011) (values are expressed as mean ± Standard Deviation)

Metals	Sea water (NASS-5/NRC, 2011) (μg/l <sup>-1</sup> )					
	Certified	Observed				
Zn	$0.102 \pm 0.039$	$0.098 \pm 0.047$				
Cu	$0.297 \pm 0.046$	$0.305 \pm 0.055$				
Pb	$0.008\pm0.005$	$0.10\pm0.005$				
Cd	Nd	Nd				

Table (3) shows the permissible limit values for trace metals (surface water and suspended Matter) in accordance with international guidelines.

**Table 3.** Trace metal concentrations in surface water (WHO/USEPA) and suspended matters (SM) (LAWA classification, **Irmer**, **1997**)

	Surface water	Suspended matter (SM)						
	$(\mu g/l^{-1})$	$(\mu g/g^{-1})$						
		LAWA Classification (Irmer, 1997).						
Metal	OMS/USEPA	I	I-II	II	II-III	III	III-IV	IV
Pb	50	≤ 25	≤50	≤100	≤200	≤400	≤800	>800
Cd	10	≤0.3	≤0.6	≤1.2	<b>≤</b> 2.4	<b>≤</b> 4.8	≤9.6	>9.6
Cu	10	≤20	≤40	≤80	≤160	≤320	≤640	>640
Zn	3000	≤100	≤200	≤400	≤800	≤1600	≤3200	>3200

## 4. Statistical analysis and modelling

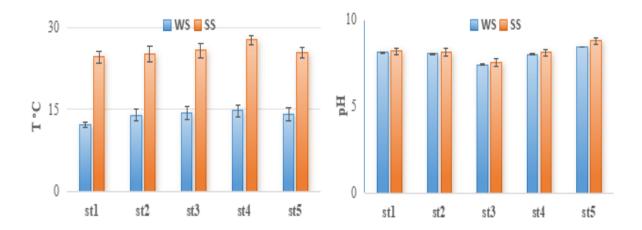
Statistical analysis was carried out using R software version 4.4.1 (R Core Team, 2016). Spatial data for physico-chemical water parameters and trace metal concentrations in separated water and suspended matter (SM) were expressed as mean  $\pm$  standard error of the mean (mean  $\pm$  SD) [minimum-maximum].

A one-factor analysis of variance (ANOVA) was used to test the variation of variables (physico-chemical parameters and TMs) between study sites as well as between seasons, and Student's t-test was applied to compare physicochemical parameters and TMs between the two seasons and the two compartments (separated water and SM). Pearson correlations were performed, and correlation matrices were plotted using the correlation coefficient r to correlate the relations between physicochemical water parameters, and metal concentrations in separeted water and SM. The influence of water parameters on metal contamination of the two compartments was studied using the linear regression test (Bivariate Analysis) adapted to the Gaussian family and the identity link. Variations in the concentration of each element (Cd, Cu, Pb and Zn) were summarized for each model, using the water parameters of the study stations as explanatory variables. The map was realized with ArcGIS software version 10.8.2.

#### **RESULTS**

#### 1. Physico-chemical parameters

The analysis of physico-chemical parameters was carried out in reference to the permissible limits set by the European Community directive (**CE**, **1975**). When looking at seasonal variations in water temperature, the changes appear fairly consistent. Average values shift depending on the station and the season, ranging between 24.6±1.06°C and 27.66±0.75°C in summer, and between 12.3±0.46°C and 14.47±0.98°C in winter (Fig. 2). In summer, the warmest waters were recorded at St4 (Oued Safsaf) with 27.66±0.75°C, while in winter, St5 (Serigina Island) showed the coldest waters, with an average of 12.3±0.46°C. Regarding pH, the average values display similar trends across all stations during both summer and winter (Fig. 2). Overall, the waters at the five stations tend to be slightly alkaline, with values generally ranging from 8±0.03 to 8.78±0.01 at St5, St4, St2, and St1. The St3 stands out as an exception, showing a value closer to neutrality in winter (7.42±0.01). All measured pH values remain within the acceptable limits of 6 to 9 set by the European Community directive (**CE**, **1975**), with the highest average, 8.78±0.20, recorded at St5 (Tedi).

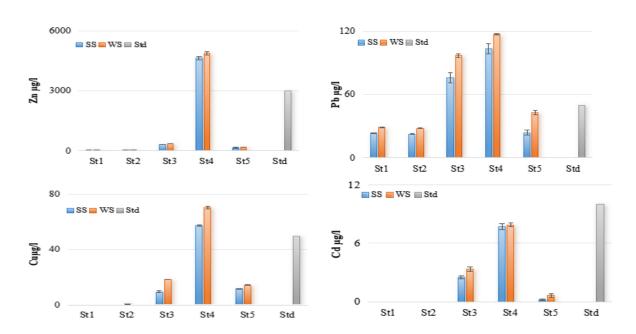


**Fig. 2.** Spatial and seasonal variations of physicochemical parameters of surface water of Skikda coast, (northeastern Algeria). Values are given as mean±standard deviation (mean±SD)

#### 2. Trace metals in separated water

Overall, the highest concentrations of trace metals in surface waters were observed during the winter season. This period seems to favor an increase in levels, with recorded values of Cd:  $2.36\pm0.11~\mu g/l^{-1}$ , Cu:  $20.80\pm0.31~\mu g/l^{-1}$ , Pb:  $49.31\pm0.6~\mu g/l^{-1}$ , and Zn:  $1093.36\pm19.71~\mu g/l^{-1}$ . From a spatial perspective, the St4 (Oued Safsaf) showed the highest concentrations for all the analyzed elements, with the exception of lead. While, the lowest values were measured at St1 (Serigina Island) (Fig. 3).

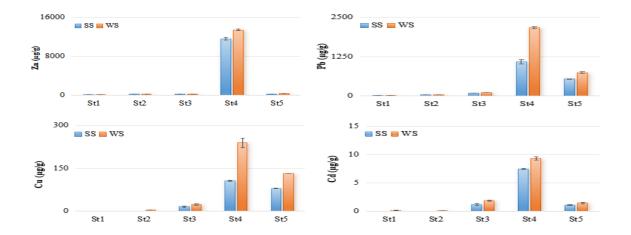
The average zinc concentrations in surface waters varied both by season and by station. The lowest concentration of  $5.8\pm0.79~\mu g/l^{-1}$  was measured in summer on St1 (Serigina Island), while the highest concentration of  $4892.66\pm74.47~\mu g/l^{-1}$  was recorded in winter at St4 (Oued Safsaf). Lead concentrations range from  $22.48\pm0.44~\mu g/l^{-1}$  at St2 (lion ravine) to  $117.16\pm0.76~\mu g/l^{-1}$  at St4 (Oued Safsaf). Copper concentrations displayed an irregular pattern across the five stations. The lowest concentrations were measured during summer at St2 (lion ravine) and St1 (Serigina Island), where levels even dropped below detection limits. In contrast, the highest concentrations were recorded in winter, reaching  $70.32\pm0.88~\mu g/l^{-1}$  at St4 (Oued Safsaf) and  $14.43\pm0.41\mu g/l^{-1}$  at St5 (Tedj) (Fig. 3). As shown in Fig. (3), only Station 4 exceeded the WHO/USEPA guideline value of  $3000~\mu g/l^{-1}$  for zinc and  $50~\mu g/l^{-1}$  for lead and copper, as well as for lead at Station 3 in both summer and winter. Throughout the study period, cadmium concentrations were below the guideline value required by WHO/USEPA ( $10~\mu g/l^{-1}$ ) with a maximum of  $7.86\pm0.11~\mu g/l^{-1}$  recorded at St4.



**Fig. 3.** Trace metals concentrations ( $\mu g/l^{-1}$ ) in separated water of study sites in the Skikda coast, (northeastern Algeria). Values are given as mean±standard deviation (mean±SD)

### 3. Trace metals in suspended matter (SM)

The trace metal concentrations studied in SM are considerably higher than those in the dissolved phase (Figs. 3, 4). The highest concentrations were recorded in winter (Cd:  $2.60\pm0.09~\mu g/g^{-1}$ ; Cu:  $79.18\pm4.13~\mu g/g^{-1}$ ; Pb:  $609.03\pm15.08~\mu g/g^{-1}$ ; Zn:  $2785.16\pm51.51~\mu g/g^{-1}$ ) in comparison with summer (Cd:  $1.96\pm0.05~\mu g/g^{-1}$ ; Cu:  $40.42\pm1.14~\mu g/g^{-1}$ ; Pb:  $345.94\pm176.87~\mu g/g^{-1}$ ; Zn:  $2383.35\pm92.77~\mu g/g^{-1}$ ) (Fig. 4). The average values reflect a high variability of these elements. Stations St4 and St5 generally have the highest concentrations in both summer and winter, while station St1 records the lowest levels. Zinc is the most abundant element, with particularly high concentrations at stations 4 and 5, ranging from  $10.97\pm0.11~\mu g/g^{-1}$  to  $13,427.66\pm164.11~\mu g/g^{-1}$ . Lead levels range from  $2.75\pm0.18~\mu g/g^{-1}$  to  $2177.91\pm36.61~\mu g/g^{-1}$ . As for copper and cadmium, their concentrations range from 0 to  $239\pm17.17~\mu g/g^{-1}$  and from 0 to  $9.36\pm0.28~\mu g/g^{-1}$ , respectively. These two elements were absent from the SM of the St1 (Serigina Island) during the summer campaign (Fig. 4).



**Fig. 4.** Trace metals concentrations  $(\mu g/g^{-1})$  in suspended matter of study sites in the Skikda coast, (northeastern Algeria). Values are given as mean±standard deviation (mean±SD)

According to the LAWA classification (Table 3), the seasonal and spatial mean values indicate that the suspended matter (SM) at St4 is highly polluted, particularly with lead and zinc (class IV). Cadmium is classified as category III (heavily polluted), while copper falls into class II–III (polluted). Stations 5 and 3 also show cadmium contamination (class II) and strong lead pollution (class III). In contrast, throughout the study period, stations 1 and 25 exhibited no signs of pollution from the analyzed elements.

The partition factor (Kd,  $\mu g/kg$ ), calculated using equation (1) for the trace metals studied (Cd, Cu, Pb, and Zn) at the various sampling stations, generally reaches values of approximately  $10^6$  (Table 4). The only exception is copper at station 5, where the Kd is zero.

$$Kd = \frac{[M] SM}{[M] Water} \mu g/kg ... ... (1)$$

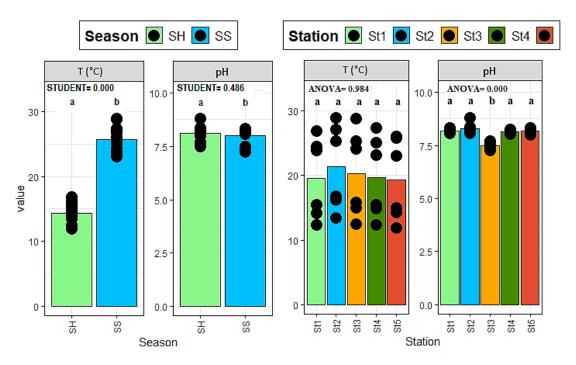
**Table 4.** Distribution of the partition factor (*Kd*) in the surface waters of the Skikda Gulf, Northeastern Algeria

	<i>Kd</i> (μg/kg <sup>-1</sup> )						
Study sites	Cd	Cu	Pb	Zn			
St1	$1.08 \times 10^6$	$2.70 \times 10^6$	$14.79 \times 10^6$	$2.61 \times 10^6$			
St2	$3.14 \times 10^6$	$8.11x1x^{6}$	$19.22 \times 10^6$	$1.83 \times 10^6$			
St3	$0.52 \times 10^6$	$1.38 \times 10^6$	$1.10 \times 10^6$	$0.20 \times 10^6$			
St4	$0.07 \times 10^6$	$2.96 \times 10^6$	$0.49 \times 10^6$	$2.04 \times 10^6$			
St5	$0.09 \times 10^6$	0	$0.10 \times 10^6$	$2.02 \times 10^6$			

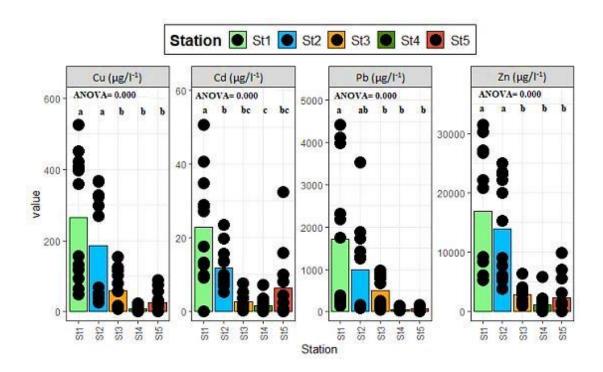
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## Results of the statistical study

Student's t tests showed highly significant seasonal variations (P < 0.001) only for temperature at the sampling stations (Fig. 5). Similarly, the one-factor ANOVA statistical test, highly significant spatial differences (P < 0.001) were revealed for: pH (between St3 and the other stations) (Fig. 5), Cu and Zn (between the two stations St4 and St5 on one side and the other stations on the other side), Pb (between station St4 on one side and the other stations on the other side, also between stations St5 and St2) and Zn (between station St4 on one side and stations St3, St2, St1 on the other side) (Fig. 6).

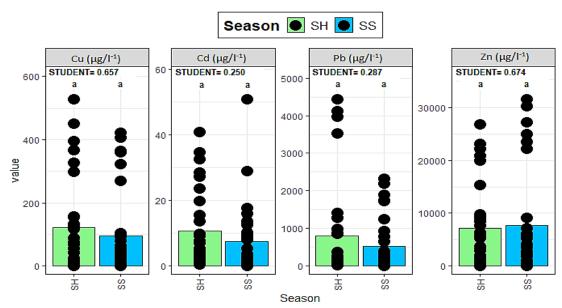


**Fig. 5.** Inter-site and inter-season comparison of changes in abiotic parameters of the five sampling sites (northeastern Algeria). (Statistical significance: ns P>0.05; P<0.05; P<0.05; P<0.01)

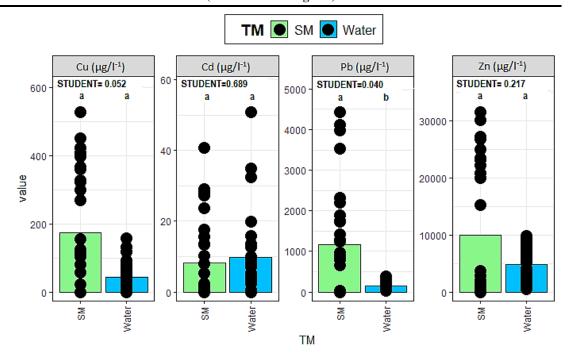


**Fig. 6**. Inter-site comparison of trace metals distribution of the five sampling sites (northeastern Algeria). (Statistical significance: ns P>0.05; P<0.05; P<0.01; P<0.001)

The concentrations of trace metals did not show any significant seasonal variations  $(P \ge 0.5)$  (Fig. 7) as well as between the two compartments (separated water and SM), with the exception of Pb, where a significant  $(P \le 0.05)$  variation was found in the distribution of the latter (Fig. 8).

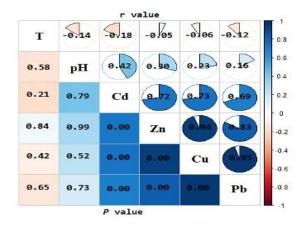


**Fig. 7.** Inter-season comparison of trace metals distribution of Skikda Coast (northeastern Algeria). (Statistical significance: ns P>0.05; P<0.05; P<0.01; P<0.001)



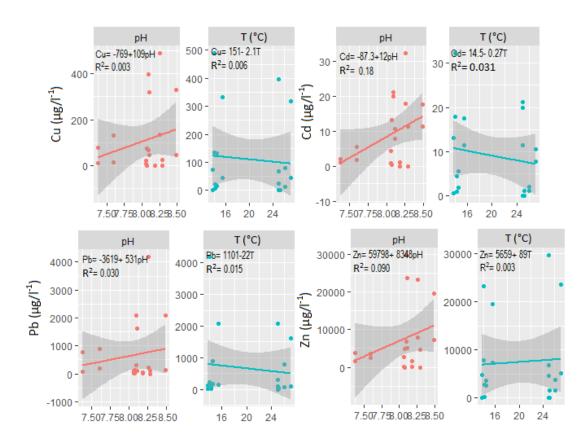
**Fig. 8.** Comparison of the distribution of trace metals in separated waters and SM (northeastern Algeria). (Statistical significance: ns P>0.05; P<0.05; P<0.01; P<0.001)

Fig. (9) presents the outcomes of Pearson's correlation analysis between abiotic parameters and trace metals in both dissolved and suspended forms. The analysis highlights very strong and highly significant positive correlations, particularly between Cd–Zn (r = 0.72, P < 0.001), Cd–Cu (r = 0.73, P < 0.001), Cd–Pb (r = 0.69, P < 0.001), Zn–Cu (r = 0.94, P < 0.001), Zn–Pb (r = 0.83, P < 0.001), and Cu–Pb (r = 0.95, P < 0.001). On the other hand, correlations between pH and Cd (r = 0.42, r = 0.79) or Zn (r = 0.30, r = 0.99) appeared weak and statistically non-significant.



**Fig. 9.** Correlation matrix between physico-chemical water parameters and TMs concentrations of the two compartments of Skikda Coast (northeastern Algeria)

The linear regression test showed a proportional relation between pH and the degree of accumulation of all trace metals Cu, Cd, Zn and Pb, and also between temperature and Zn. However, this test revealed oppositional relationships between temperature and Cu, Cd and Pb (Fig. 10).



**Fig. 10.** Relationships between physicochemical parameters and concentrations of trace metals (Zn, Pb, Cu, Cd,) of the five sampling sites (northeastern Algeria). Lines in solid color indicate linear regression with 95% confidence intervals in light gray.

## **DISCUSSION**

In this study, trace metals were examined by identifying their potential sources and analyzing their distribution between dissolved waters and suspended particles along the Gulf of Skikda.

The results relating to the concentration of TMs in the separated waters of the five stations indicate that, with the exception of St5, the levels vary from West to East according to a decreasing gradient, with Zn predominating, followed by Pb, Cu and Cd. Taking into account the standards in force, the highest values are found at station 4 and in the Mixte Harbor (St3) by lead. This situation is due to the fact that St4 is an outlet of the Safsaf Wadi, which daily drains downstream various types of waste, mainly industrial

and petrochemical waste from the Skikda region (RA1/K; CTE; ENAMARBRE; GL1/K and C.FEL.OIL) and domestic wastewater via the Zeramna Wadi which flows into the Safsaf Wadi (**Belahmadi** *et al.*, **2023**; **Zeghdoudi** *et al.*, **2024**).

As for lead, St3 (Mixte Harbor) stands out with a level of 75.95±4.80 in summer and 97.3±1.7 in winter which also exceed the guideline value required by WHO/USEPA. This situation could also be due to the harbor activity and use of antifouling paint in the coating of boat hulls (**Augier** *et al.*, **1998**; **Demaneche** *et al.*, **2023**), and the amount of domestic emissions in this location. In addition, this station receives operational discharges from boats (various oil leaks or other substances, in addition to wash water) and accidental discharges (explosion or collision) (**Gueddah** *et al.*, **2014**).

With the exception of station4 and Cd from stations 1 and 2, the permanent presence of metals at St1, St2, and especially St3 and St5 could probably be explained by the dispersion phenomenon caused by hydrodynamics, and the ability of some metals to follow the direction of the current, being the main factors behind this situation (Ennouri et al., 2013). Indeed, during flood periods, the plumes of the Safsaf Wadi extend over a large distance, carrying significant quantities of sediments, suspended matter, nutrients and various terrestrial contaminants (Zeghdoudi et al., 2024). Maritime traffic could constitute an additional source of Cd and Pb at coastal discharge points. Zn is a naturally abundant element, present as a common contaminant in agricultural and food wastes, in the manufacture of pesticides and in antifouling paints (Casas, 2005). It is an essential trace element for humans, and its deficiency leads to dwarfism (Chiffoleau, 2003). Indeed, zinc levels of between  $10\mu g/l^{-1}$  and  $40\mu g/l^{-1}$  have been shown to have adverse effects on the life of marine organisms. Pb contamination can be direct by atmospheric deposition or indirect following leaching of roads by rainwater (Obhodas & Valkovic, 2010). In fact, studies carried out across the western Mediterranean have shown that the input of heavy metals through precipitation is of the same order of magnitude, if not greater, than the input of lead, zinc, chromium and mercury in dissolved form from rivers and effluent (Culicov et al., 2002). The presence of cadmium is generally linked to industrial effluents, domestic effluents (detergents, biocides) and city sewage (fuels, batteries and other electrical appliances), as well as to maritime traffic. It is listed by the EPA as one of 129 priority pollutants and one of 25 hazardous substances. In addition, there is an international agreement that cadmium should not be discharged into the sea, as it is included in the black list (Kiss, 1983). Criteria for acute and chronic effects on marine organisms are set at 4.3 and 9.3µg/l<sup>-1</sup> respectively by **Epa Us.** (2001). Cu enters the aquatic environment through industrial effluents and domestic runoff, among others (INERIS, 2005b). The toxicity of this metal to aquatic organisms depends on its chemical form (and in particular its oxidation state).

The average TMs values observed in surface water during flood periods are higher than those observed during dry periods (Zn:  $2785.16\pm51.51~\mu g/l^{-1}$  and  $2383.35\pm92.77~\mu g/l^{-1}$  / Pb:  $609.03\pm15.8~\mu g/l^{-1}$  and  $345.94\pm16.87~\mu g/l^{-1}$  / Cu:  $79.18\pm4.13~\mu g/l^{-1}$  and

 $40.42\pm1.14 \, \mu g/l^{-1}$  Cd:  $2.60\pm0.09 \, \mu g/l^{-1}$  and  $1.96\pm0.05 \, \mu g/l^{-1}$ ). Water is the main weathering agent and the vector for transporting metals from the continent to the sea. For this reason, high metal concentrations have been observed during the rainy season. Our study area, during this period, receives enormous quantities of water via the mouth of the Oued Safsaf, whose flow is sufficient to supply waters loaded with suspended matters (average annual flow is 1500 hm<sup>3</sup>). The role of suspended matters in the transport of metals in rivers is generally much more important than that of the dissolved phase (Martin & Meybeck, 1979; Makepeace et al., 1995; Gromaire et al., 2001). Suspended solids are known to represent 90% of the sediment flux in rivers (Walling & Fang, 2003). All high concentrations of trace elements in suspended matters are noted at stations close to St4, such St5 (Tedj) and St 3 (Mixte Harbor). Atmospheric deposition during this flood period also reveals a very high load, leading to increased pollution of marine waters by minerals and non-biodegradable organic matter (Angelidis & Catsiki, 2002). Suspended matter affects the aquatic environment; its direct action on fish is manifested by phenomena such as thickening of gill epithelial cells, a detrimental effect on eggs with reduced productivity and changes in fish movements. Weather conditions play an important role in disrupting element concentrations. Contrasting behaviors have been observed between trace metals during wet and dry seasons. During the rainy season, meteoric waters favor much more the mobilization of metals in the SM and metal leaching processes (Ansart, 2022). The pH of the water in the study area is slightly alkaline, ranging from 7.42±0.015 to 8.78±0.017. According to the results, Zn is the most abundant element, mainly bound to the particulate fraction, a situation that could be due to Zn adsorption on SS (Bouabdli et al., 2005). Several studies have shown that pH conditions > 7.7 favor Zn complexation by the organic load in suspension (Serpaud et al., 1994; Bouabdli et al., 2005). For the same pH range and in an oxidizing environment, Pb precipitates as lead sulfate (anglesite) or lead carbonate (cerussite), which is probably responsible for the high trace metal values in suspended matter (Mouvetv & Bourg, 1983; Salvarredy-Aranguren et al., 2008).

Comparison of trace metal values in the SM with those of the LAWA classification (Irmer, 1997) (Table 3) shows that particles from stations 1, 2, and 3 are considered polluted to very heavily polluted by all the metals studied (classes II, III, IIIV, and IV). The partition coefficient (*Kd*) describes the relationship between metal values in the dissolved and particulate phases. It can be likened to a sorbent-sorbent relationship (Langmuir, 1997; Lu & Allen, 2001). This factor, *Kd* for the entire study area, is almost 10<sup>6</sup> (Table 3), confirming that suspended solids play a key role in the transfer and stabilization of metal pollution in the waters of these stations. The *Kd* values in this sector are close to those found in other studies carried out in waters influenced by various human activities in similar pH ranges (Benoit & Rozan, 1999; Shafer *et al.*, 1999; Gueguen & Dominik, 2003; Brunel, 2005; Smail *et al.*, 2012; Khadhar *et al.*, 2013). The partition coefficient (*Kd*) is pH dependent (Peng *et al.*, 2003) and adsorption of

metals on the solid phase is preferred at neutral to alkaline pH (Webster et al., 1998). In contrast, in streams affected by acid drainage, metals are preferentially found in solution (Johnson, 1986; Johnson et al., 2002), because the main sorbents are iron oxyhydroxides, whose adsorption capacity is reduced in acid drainage (Webster et al., 1998).

#### **CONCLUSION**

The preservation of coastal marine water quality requires not only a quantitative understanding of pollutant inputs into the marine environment but also an assessment of the levels of occurrence of the various identified chemical and organic contaminants. Our findings allowed us to evaluate the quality of surface waters along the Skikda coastline. In order to provide a quantitative assessment of water contamination by four metals (Cd, Cr, Pb, and Zn), water samples (dissolved fraction and suspended particulate matter) were collected from five stations (St1, St2, St3, St4, and St5), following a sampling strategy designed to ensure broad spatial coverage representative of the coastal area. These data on chemical contamination were complemented by measurements of physicochemical parameters (Temperature and pH).

The results concerning micropollutants indicate that each metal exhibits a distinct behavior and that concentrations vary significantly between stations. Station 4 is characterized by the highest concentrations, exceeding the standards established by WHO/USEPA for all the analyzed elements. At Station 3, an exceedance was also recorded for lead (Pb). Stations 3 and 5 showed relatively high levels of metals, although they remained below regulatory thresholds. This situation can be attributed to the influence of port activities and the load from Oued Safsaf, which is subject to the greatest degree of anthropogenic impact, particularly from industrial and petrochemical activities. While the lowest values were recorded at station 1 and station 2.

We found also that all the TMs studied show a higher concentration gradient in the particulate phase. This phase is of major interest in the contamination of the coast, given its major role in the transport of trace metals in these waters. The main vector of contamination is liquid flows (Safsaf wadi and land leaching), which have a major impact on downstream regions (the sea). We can deduce that, the order of enrichment of the stations by SM for all the elements studied is as follows: St4 > St5 > St3> St2> St1. In separated water, the order is as follows: St4 > St3 > St5> St2 > St1. Nevertheless, the average concentrations of trace metals studied in the two compartments followed a decreasing order as follows: Zn>>>Pb>>Cu>Cd.

The LAWA classification identifies the SM of stations 3, 4 and 5 as polluted, and the calculation of the partition factor (Kd) confirms its key role in the transfer of metal pollution into the waters of these stations. These concentrations could represent a significant ecotoxic risk for the benthic organisms that reside in this ecosystem and which

cause risks for people using these environments. The results obtained from statistical analysis (bi-variate analysis) of the physico-chemical parameters studied and TM in separated water and SM show that, with the exception of zinc, temperature shows a negative (oppositional) relationship with the distribution of metals, while pH shows a positive (proportional) relationship.

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