Seasonal assessment of metal trace element contamination by PCA in Seybouse wadi (Algeria)

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ABSTRACT

The seasonal assessment of trace metallic elements in Seybouse wadi waters and sediments is performed by principal component analysis (PCA). This wadi is the second of Algeria considering its length and vast basin, and opens into the coastline of Annaba in the Mediterranean Sea. Monitoring mineral micropollutants showed that waters are primarily contaminated by aluminum Al, selenium Se, zinc Zn, copper Cu, chromium Cr, lead Pb, cadmium Cd and arsenic As, whereas sediments are essentially soiled by arsenic As, chromium Cr and nickel Ni. PCA shows a clear relation between the season and the type of metallic contamination, and it also helps in understanding its origins.

Key words | Gulf of Annaba (Algeria), PCA, sediments, surface water, trace metallic elements

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INTRODUCTION

Trace metallic element contamination is an important issue but very few studies concern African countries and their specificities. Algeria (North Africa) faces nowadays important ecological concerns and experiences serious pollution issues. Water resources, whether they are from surface or ground waters, are polluted by domestic, industrial and agricultural effluents that contribute notably to the degradation of watercourses and dam waters.

In the absence of treatment stations, wastewaters are directly dumped into the wadis and mainly Seybouse wadi to end in the bay of Annaba (Mediterranean Sea). Seybouse wadi is considered as one of the most polluted wadis in Algeria (Mate 2002) as its lowlands comprise a wide range of anthropogenic activities.

This assessment is part of a vast study of mass transfer towards the Gulf of Annaba and its impact on the pelagic system (plankton, chemistry, food web, biology and fishing statistics). These terrigenous inputs high in nutrient salts and organic matters could have severe consequences on the receiving environment e.g. hyperfertilization and dystrophication of these waters. Previous studies, set up from 2002 to 2004 and focusing on physico-chemical quality of Seybouse waters, showed that Seybouse wadi is eutrophic and polluted (Khaled-Khodja *et al.* 2012; Khaled-Khodja 2016).

In the present study, we assess the contamination of Seybouse wadi waters and sediments by trace metallic elements (TME) in relation to seasons, by principal component analysis (PCA). TME are rarely studied in land and marine Mediterranean areas, and the literature dealing with this area reported essentially studies about polychlorinated biphenyls (PCBs), dichlorodiphenyltrichloroethane (DDT) and polycyclic aromatic hydrocarbons (PAHs). The approach by PCA of the contamination assessment would allow a fine discrimination between the various origins of the TME. These TME, by their massive use, their relatively high toxicity, their persistence and bio-accumulating capacity, are major environmental issues (Bandela *et al.* 2016; El Nemr *et al.* 2016), in addition to the fact that their fate and effect on aquatic ecosystems are still under scientific investigation.

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STUDY AREA (FIGURE 1)

Seybouse wadi (north-east of Algeria, Africa) is the biggest wadi of Algeria (6,471 km^2) with an average annual flow of 11.5 m^3·s^{-1}. It comes from the Tell mountains and ends in the Mediterranean Sea on the coastline of Annaba city. It is 240 km long and goes through seven cities (Kherraz 2008).

Its lowland is the seat of high industrial activity that generates a large amount of diverse waste types: steel industry, cement, wood, paper and cellulose industries, truck mechanics and rental, manufacturing of medical materials, plastics, rail equipment, milk, chemical fertilizers, agri-food industries, and paint and varnish industries. This fertile region has intensive farming activities: cattle farming, polyculture e.g. market gardening, tobacco, forage crop, grain and fruit cultivation (Derradji *et al.* 2004). All discharges from agriculture and industries end in Seybouse wadi, without prior treatment.

METHODS

A seasonal sampling was carried out in order to evaluate water and sediment quality at the mouth of Seybouse wadi, during the 2009–2010 year, through four campaigns: October 2009 (autumn period), February 2010 (winter period), May 2010 (spring period), August 2010 (summer period). The samples of waters and sediments were collected at the interface, at 100 m from the mouth of the wadi, where all the terrigenous releases are conflated, before reaching coastline waters. The samples were collected according to the French agencies Agence de l'eau Loire-Bretagne (2006) and Schiavone & Coquery (2011). Waters were collected in polyethylene vials, filtered through 0.45 μm glassfiber membranes (Whatman) that were previously washed with 1% nitric acid then thoroughly rinsed with distilled water. The filtrate was immediately acidified with concentrated nitric acid (pH < 2). The surface sediments (0–5 cm) were collected in a polyvinyl chloride (PVC) scoop and stored in polyethylene vials. The vials were transported, in darkness, at 4°C. Once at the laboratory LABOCEA (Bretagne Océane), the samples were frozen at −20°C until analysis.

All TME, except arsenic, were analyzed by inductively coupled plasma emission spectrometry (ICP-OES, Vista-Pro, Varian, USA). Arsenic was analyzed by atomic fluorescence (Excalibur 100 SS, PS Analytical Millenium System, UK).

The standards used for the assessment of raw water and sediment quality are: French system for quality assessment of water streams (SEQ-Eau) recommended by water agencies for raw waters (Agences françaises de l'eau 2003) and the circular of 7 May 2007 DCE/23 defining 'standards of provisional environmental quality (NQEp)' for surface French waters (Rodier *et al.* 2009). The TME were classified according to their level of toxicity (priority hazardous substances, priority substances and relevant substances) listed in Annex X of the water framework directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in

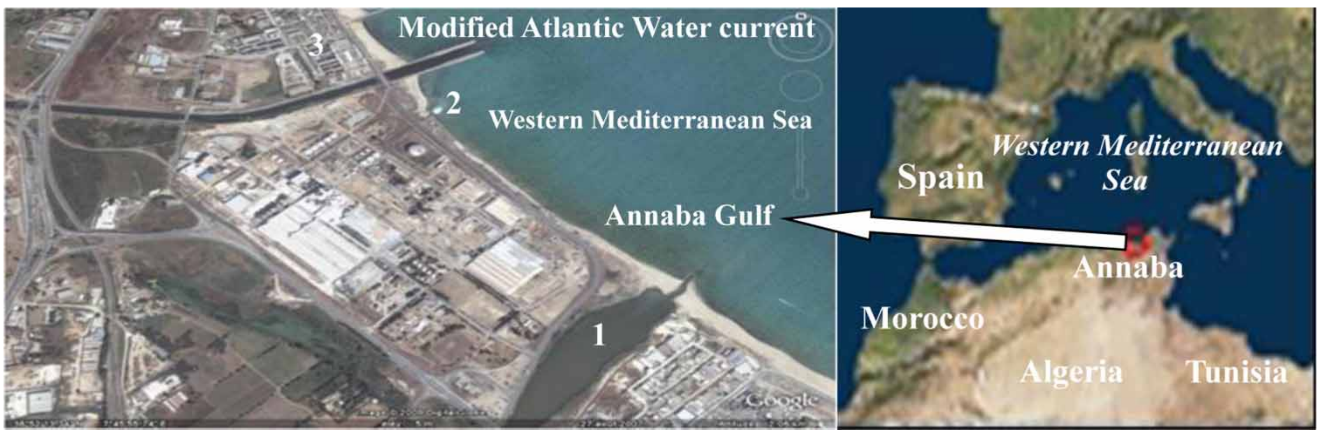

Figure 1 | Study area: Seybouse wadi mouth at the Gulf of Annaba (1. Seybouse effluents, 2. industrial effluents (Fertial), 3. Annaba port).

the field of water policy and list II of the Council Directive 76/464/EEC on pollution caused by certain dangerous substances discharged into the aquatic environment of the Community. For the statistical treatment, PCA, which is a multivariate statistical method based on correlation between variables, was used for the analysis of data. The software used for statistical analysis was FactoMine R.

RESULTS AND DISCUSSION

TME in water

Seybouse waters contain many mineral micro-pollutants in relatively high concentrations (Table 1). TME are found in all the samples, with concentrations varying from 0 to 3,328 $\mu g{\cdot}L^{-1}$.

In the autumn period, nine TME are detected with concentrations varying from 2.80 to 600 $\mu g{\cdot}L^{-1}$: Al, As, Ba, Fe, Mn, Ni, Pb, Se and Zn. All of them exceed the standard values recommended by SEQ-Eau and NQEp. Thus, Seybouse wadi waters have a passable suitability for biological life with respect to Zn and Al but a poor biological potential with respect to Pb, Se, Zn and Fe. Ten TME are detected during the winter period with concentrations varying from 0.94 to 1,054 $\mu g{\cdot}L^{-1}$: Al, As, Ba, Cr, Cu, Fe, Mn, Ni, Pb and Zn. Among them, seven exceed the standards: this water has a poor quality regarding biological life with respect to Zn, Al, Pb, Fe, Mn, Cu and As.

The spring period recorded the highest TME concentrations and eleven TME are detected, with concentrations varying from 0.16 to 3,328 $\mu g{\cdot}L^{-1}$. All the detected TME concentrations exceed the SEQ-Eau and NQEp standards limits: Al, As, Ba, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn. The water has a poor quality for biological life with respect to Al and a poor biological potential with respect to Pb, Fe and Zn.

Eleven TME are detected during the summer period, and their concentrations vary between 2.06 and 2,140 $\mu g{\cdot}L^{-1}$. All of them, except Ni, exceed the SEQ-Eau and NQEp limits: Al, As, Ba, Cr, Cu, Fe, Mn, Pb, Se and Zn. The poor quality regarding the suitability for biological life is due to Se and Al. In view of the most downgrading TME concentrations, Seybouse wadi water is very altered and has a very poor suitability for biological life. Additionally, the majority of TME found in Souybouse wadi are highly toxic: cadmium is classified as a priority hazardous substance; nickel and lead are classified as priority substances in Annex X of the water framework European Community Directive 2000/60/EC of 23 October 2000;

Table 1 | Trace metal elements concentrations in Seybouse waters and their limits in two quality systems SEQ-Eau and NQEp ($\mu g{\cdot}L^{-1}$)

Trace metal elements	October 2009	February 2010	May 2010	August 2010	SEQ-Eau	NQEp
Aluminum (Al)	**280**	**544.40**	**1,652**	**1,266**	200	200
Arsenic (As)	**8.80**	**4.80**	**12.40**	**5.92**	10	4.2
Barium (Ba)	**92**	57.40	**75.60**	**72.20**	700	58
Cadmium (Cd)	0	0	**0.16**	0	0.04	5
Chromium (Cr)	0	0.94	**8.20**	**2.92**	1,8	3.4
Copper (Cu)	0	**5**	**5.06**	**3.26**	1	1.4
Iron (Fe)	**600**	**1,054**	**3,328**	**2,140**	–	200
Manganese (Mn)	**116**	**52.40**	**155.60**	**154.80**	–	50
Nickel (Ni)	**2.80**	1.24	**5.58**	2.06	6.2	2.1
Lead (Pb)	**4.60**	**2.20**	**22.80**	**9.78**	5.2	0.4
Selenium (Se)	**6**	0	0	**13.42**	10	1
Tin (Sn)	0	0	0	0	10	1.5
Zinc (Zn)	**24**	**32**	**42.40**	**39.60**	4.3	7.8

In bold: exceeds the standard; –: no standard value; SEQ-Eau: French system for quality assessment of water streams of 2003 (Agences françaises de l'eau 2003); NQEp: standards of provisional environmental quality for surface waters (Rodier et al. 2009).

arsenic, barium, chromium, copper, selenium and zinc are classified as pertinent substances in list II of the Council directive 76/464/EC of 4 May 1976.

The TME in Seybouse wadi could have various origins but the main origin is surely due to anthropogenic activities that concentrate in the lowland of the wadi. These waters are degraded mainly by lead, selenium, zinc, copper, chromium, cadmium, arsenic, nickel and barium.

Lead (Pb) is so widespread and used by industries that the possibilities of pollution are extremely varied (Rodier *et al.* 2009). However, the wadi being near a gas station and under a bridge with intense road traffic, these high lead concentrations could come from the use of tetraethyl lead in fuels. It could also originate from the diverse industrial wastes of the local industries and mainly the discards of the chemical production complex of phosphate fertilizers and plant protection chemicals (Fertial) that is located a few metres from the wadi mouth.

Selenium is a component of numerous pesticides (Savary 2003; Rodier *et al.* 2009). The most likely origin of this element is the discharge of wastewaters by the Fertial Plant. The other origin could be the cropping activities, the use of pesticides and soil leaching that are intensive in the lowland of Seybouse wadi.

The pollution of the hydrosystems by zinc could originate from diverse industrial local sources (Savary 2003) and the nearby chemical complex Fertial probably has a high influence on this metal concentration. However, zinc can also originate from domestic and agricultural sources: pesticides containing this metal (e.g. Zineb) and phosphate fertilizers (Gaujous 1995). Given that the sampling site is not far from the port of Annaba, high zinc concentrations can also be attributed to the dissolution of sacrificial anodes used for the cathodic protection of ship hulls (Séguin *et al.* 2016).

Copper is widely used in the production of pesticides (insecticides, fungicides and algicides) so the first contributor to copper occurrence in the wadi water is probably the Fertial Plant. Another origin could be agriculture where copper salts are widely used for pest control (Gaujous 1995; Savary 2003; Rodier *et al.* 2009).

Chromium is rare in waters, and its presence is mostly related to electroplating factories. This metal is mainly used for chromium plating, producing alloys, oxidizing agents and corrosion inhibitors (Gaujous 1995; Rodier *et al.* 2009). These latter could be added to the industrial cooling waters as anti-corrosion media. Once again, it is the Fertial plant that could be the source of chromium in the wadi, by the release of their cooling waters into the wadi.

Cadmium is usually associated with zinc or lead. Generally, only a few micrograms per litre are found in waters. When higher concentrations are met in surface waters, cadmium origin should be related to agriculture or industrial effluents like electroplating. Cadmium is also used in the manufacture of phosphate fertilizers (Gaujous 1995; Le Goff & Bonnomet 2004), which is the main activity of the Fertial Plant.

High arsenic concentrations in surface waters can be attributed to agricultural and industrial effluents. Among others, arsenic is used in chemical industries for the manufacture of phosphate fertilizers and detergents (Savary 2003; Rodier *et al.* 2009). The possible origins of arsenic are the same as selenium: the Fertial Plant and leaching of cropland.

The presence of nickel is mainly linked to anthropogenic activities (Gaujous 1995; Savary 2003). It is widely used in the chemical industry as a catalyst (Rodier *et al.* 2009) and is a component of many fungicides (Savary 2003), which links its origin to the Fertial Plant.

Barium can only be in the form of barium carbonate in water (Savary 2003; Rodier *et al.* 2009). It probably comes from ceramic or varnish and paint industries.

Trace metal elements in the sediments

All the analyzed TME are found in Seybouse wadi sediments, during the four seasons, except barium, tin and selenium, which are never detected (Table 2). During the year, considering the four sampling seasons, the concentrations varied ($mg \cdot kg^{-1}$) as follows: aluminum (6,063.16 to 45,300.3), arsenic (10.42 to 19.07), cadmium (0.23 to 0.33), chromium (16.33 to 59.82), copper (4.08 to 20.96), iron (11,822.2 to 28,797.8), manganese (202.06 to 514.53), nickel (8.44 to 22.24), lead (9.94 to 23.19) and zinc (33.53 to 81.34). The higher concentrations are found in May, during spring.

Table 2 | The concentrations of TME in the sediments at the mouth of Seybouse wadi and their limits in SEQ-Eau quality system (mg·kg^{-1})

Trace metal elements	October 2009	February 2010	May 2010	August 2010	SEQ-Eau
Aluminum (Al)	6,063.16	9,050.30	45,300.3	9,321.5	–
Arsenic (As)	10.65	11.89	19.07	10.42	9.8
Barium (Ba)	<DL[a]	<DL[a]	<DL[a]	<DL[a]	–
Cadmium (Cd)	0.25	0.33	0.30	0.23	1
Chromium (Cr)	16.33	19.33	59.82	19.33	43
Copper (Cu)	4.08	5.29	20.96	4.36	31
Iron (Fe)	14,773	15,628	28,797.8	11,822.2	–
Manganese (Mn)	202.06	239.51	514.53	233.24	–
Nickel (Ni)	8.44	10.74	22.24	10.17	22
Lead (Pb)	12.26	11.83	23.19	9.94	35
Selenium (Se)	<DL[a]	<DL[a]	<DL[a]	<DL[a]	–
Tin (Sn)	<DL[a]	<DL[a]	<DL[a]	<DL[a]	–
Zinc (Zn)	33.53	40.97	81.34	34.94	120

[a]DL: detection limits.

Most of the TME concentrations do not exceed the limits as set out in SEQ-Eau, except arsenic, which exceeds the limits (9.8 mg·kg^{-1}) in all the seasons, and chromium and nickel (respectively 43 and 22 mg·kg^{-1}) in spring. There are also rather high iron, aluminum and manganese concentrations, elements that are not framed by the quality system SEQ-Eau. These sediments have a passable potential for biological life all through the year with respect to arsenic, and in spring with respect to chromium and nickel.

In view of the most downgrading TME concentrations, Seybouse wadi sediments are contaminated by metals, essentially arsenic, nickel and chromium. The origin of these elements could mainly be agricultural and industrial effluents as detailed above.

The TME found in these sediments are also listed in Annex X of the water framework directive 2000/60/EC of the European Parliament and the Council of 23 October 2000 establishing a framework for Community action in the field of water policy and list II of the Council Directive 76/464/EEC on pollution caused by certain dangerous substances discharged into the aquatic environment of the Community. Thus, the sediments of Seybouse wadi are as degraded as the waters at its mouth, and the three concentrated TME accountable for this state have a relatively high toxicity.

Principal component analysis

The data obtained by analysis of waters and sediments from Seybouse wadi mouth were studied by PCA in order to establish the typology of the wadi.

PCA of TME in Seybouse wadi waters

The application of PCA to the results of the TME analysis of waters at the mouth of Seybouse wadi reveals that the cumulative contribution of the three first axes explained totally the variance (100%). The eigenvalues are respectively 7.25, 3.12 and 1.61 for the three axes. Their respective contributions to the total variance are 60.48, 26.06 and 13.46. Since the first two axes explain 86.54 of the variance, they will be used for the factorial analysis.

By applying PCA (Table 3), it appears that chromium, lead, iron, cadmium and aluminum highly contribute positively to the first axis. Nickel, zinc and arsenic also contribute positively to the first axis, but to a lesser extent. Copper and manganese contribute positively to the second axis whereas barium highly contributes negatively to the second axis.

The correlation circle (Figure 2) shows a high correlation between chromium, lead, iron, cadmium, aluminum, nickel, zinc and arsenic. These elements are not correlated to copper, manganese and barium. This finding suggests that these two groups of metals do not have the same

Table 3 | Correlation of the variables (TME) to the first two main factorial axes

Variables	Axis 1	Axis 2
Chromium (Cr)	0.99	0.09
Lead (Pb)	0.99	−0.12
Iron (Fe)	0.96	0.14
Cadmium (Cd)	0.95	−0.02
Aluminum (Al)	0.92	0.16
Nickel (Ni)	0.89	−0.35
Zinc (Zn)	0.82	0.39
Arsenic (As)	0.78	−0.50
Copper (Cu)	0.52	0.85
Manganese (Mn)	−0.45	0.82
Barium (Ba)	0.02	−0.99

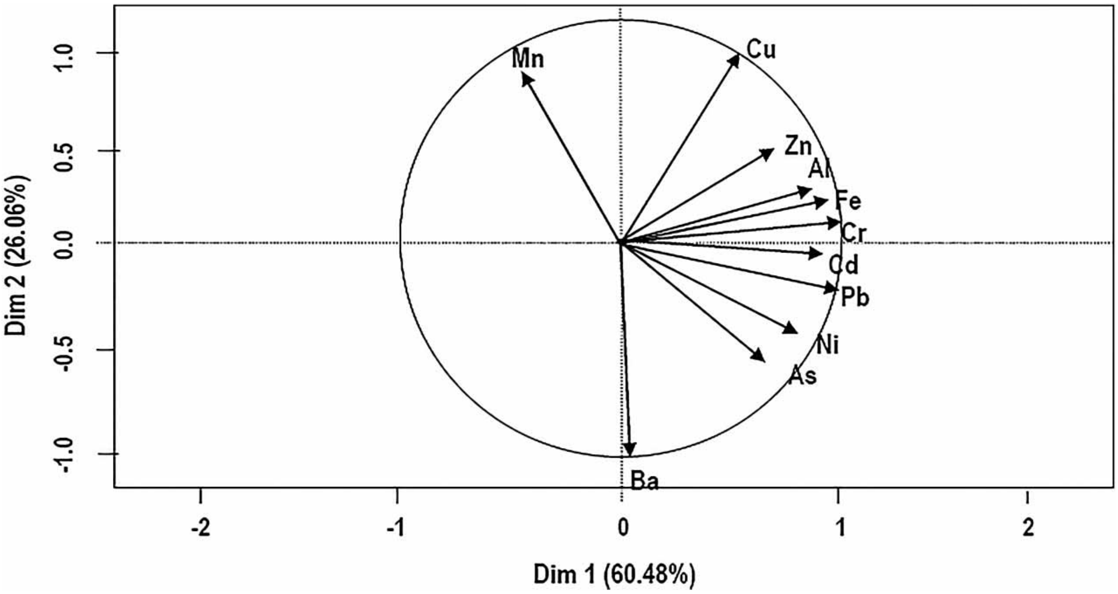

Figure 2 | PCA applied to TME in Seybouse wadi waters (first axis: dim 1 and second axis: dim 2).

origin. By observing the second axis, it can be stated that copper, manganese and barium probably have the same origin and that barium is negatively correlated to copper and manganese. Barium appears in an opposite manner in this environment with regard to copper and manganese. Copper and manganese have probably two origins.

The first axis could represent the TME derived from the nearby Fertial Plant. This plant is specialized in the manufacture of mineral fertilizers consisting of phosphate fertilizers, super simple phosphate, urea and ammonium nitrate. Due to this industry, this region is considered to be the most polluted of all the Algerian coastline (Zegaoula & Khellaf 2014). The metals exclusively contributing to this axis, and probably originating exclusively from this plant, are chromium, lead, iron, cadmium and aluminum. These metals are found in the mineral phosphate fertilizers where some of them like lead and cadmium are usually studied (Jiao *et al.* 2012). The TME that are mainly but not exclusively contributing to this axis are nickel, zinc and arsenic. Copper and manganese are mainly contributing to the second axis, but not exclusively. Whereas barium contributes exclusively to the second axis, the second axis could possibly represent the waters originating from more upstream of the wadi mouth. Copper and manganese should originate from the same source, which could be leachate from agricultural fields. In that case, manganese could originate from manganese sulfate as fertilizer and as Maneb, a broad-spectrum fungicide. Copper could originate from different copper salts used in agriculture (e.g. copper sulfate, 'Bordeaux mixture', cupric carbonate). Since barium could only exist as barium carbonate in water, it probably comes from ceramic industries. Additionally, manganese and copper, contributing to both axes, probably have both origins: industrial and mainly agricultural.

To this typology of variables (TME) corresponds a typology of records (sampling or seasons) that can clearly identify the prevailing trends. Factorial design of the seasons (Figure 3) is numbered from one (1) to four (4) by beginning at autumn and ending at summer. With respect to the second axis, the samples of the fall season (point 1) are opposed to the samples of the winter season (point 2).

The factorial map shows that the industrial effluents (represented by the first axis) are associated with the spring season (3). This could indicate an important anthropogenic activity with a discharge of large quantities of waste better carried by the waters at their high levels. The point representing the summer season (4) stands at the middle of the map, influenced neither by the industries nor by the origin of the waters. This result is expected since the wadi is dry during the summer season. Low water levels during autumn and high water levels during winter could explain the opposition between the seasons.

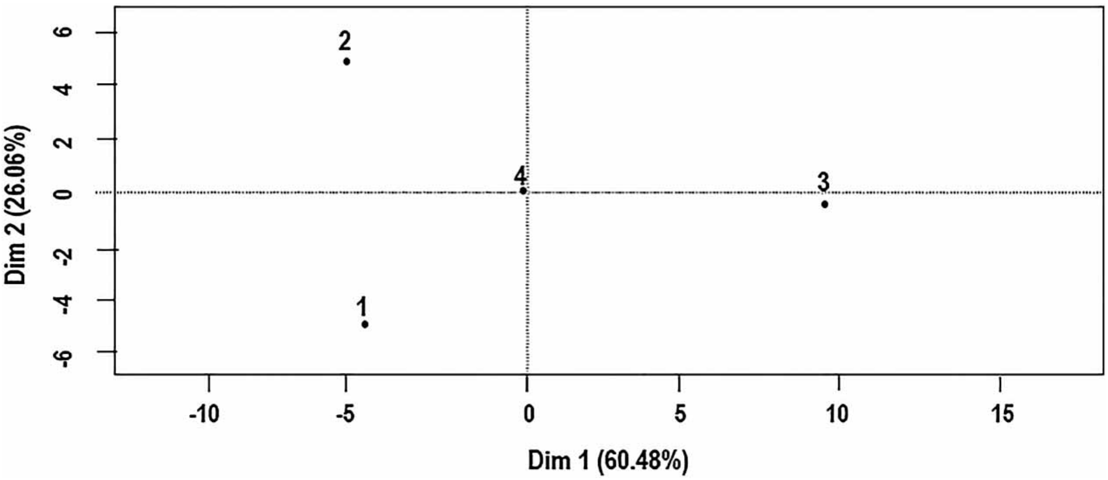

Figure 3 | PCA applied to individuals (seasons) for TME in waters (1: autumn; 2: winter; 3: spring; 4: summer).

The first winter rains (September and October 2009) after the drought of the summer season (June, July and August 2009) restore waters in the wadi. The wadi is, by definition, a dry and ephemeral riverbed that contains water only during times of heavy rain. This phenomenon enables the barium that was discarded upstream by industries to be detected near the mouth of the wadi, where it has been carried by the new rains. Copper and manganese are probably found in higher concentrations in late spring and summer because of the period of their applications on crops, in late spring.

Table 4 | Correlation of the variables (TME) to the first two main factorial axes

Variables	Axis 1	Axis 2
Arsenic (As)	0.99	0.03
Zinc (Zn)	0.99	0.001
Copper (Cu)	0.99	−0.07
Manganese (Mn)	0.99	−0.08
Chromium (Cr)	0.99	−0.11
Nickel (Ni)	0.99	−0.05
Aluminum (Al)	0.99	−0.11
Iron (Fe)	0.98	0.05
Lead (Pb)	0.98	−0.04
Cadmium (Cd)	0.45	0.89

PCA of TME in Seybouse wadi sediments

The study of TME in Seybouse wadi sediments by PCA shows that the first three eigenvalues are respectively 9.08, 8.41 and 7.28. The cumulative contribution of the first three axes explain totally the variance (100%). Their respective contributions to the total variance are 90.85, 8.42 and 0.73. Since the first two axes explain 99.27 of the variance, they will be used for the factorial analysis.

In this case, all the metal elements found in the sediments are highly correlated to the first axis with values from 0.98 to 0.99, and only cadmium contributes to the second axis with a value of 0.89 (Table 4).

All the TME, except cadmium, are correlated with each other and highly contribute positively to the first axis. This high correlation between these different TME could be explained by their relatively high concentrations in the sediments and their common seasonal variations. Cadmium contributes significantly to the second axis and slightly to the first. Cadmium differs from the other elements by its low concentration in the sediments and by rather constant concentration through the seasons. Cadmium has been described for its low tendency to be adsorbed, its stability in the form of chlorocomplex and its rapid desorption during its estuarine transit (Chiffoleau *et al.* 1999). Additionally, cadmium does not have a well-known metabolic role and does not seem to be essential biologically or beneficial to the metabolism of living organisms. Cadmium is one of the most toxic TME for living organisms.

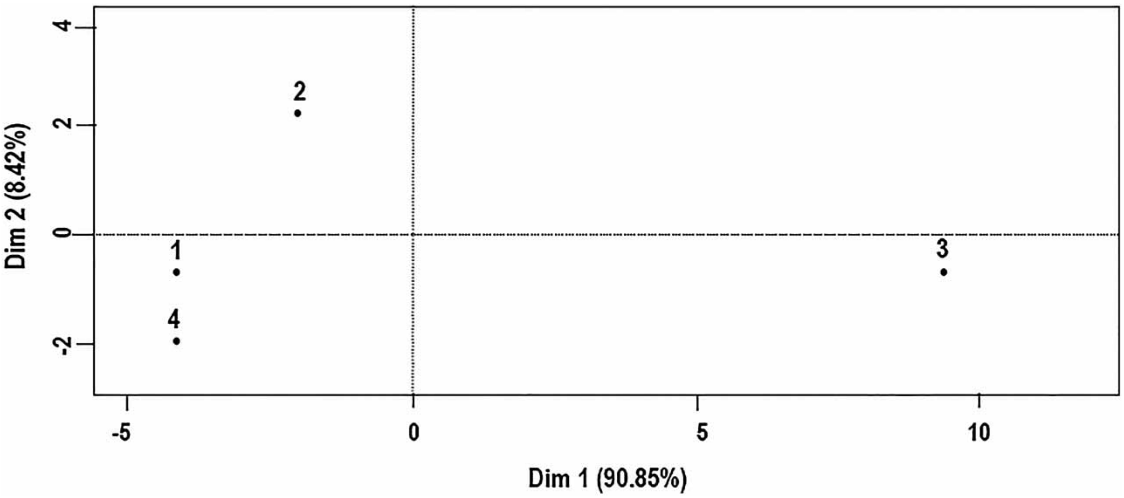

Figure 4 | PCA applied to individuals (seasons) for TME in sediments (1: autumn; 2: winter; 3: spring; 4: summer).

The first axis could be considered, by a first approach, as the occurrence during the spring season when all the TME are at their higher concentrations, and the second axis simply considered as the cadmium concentrations. The factorial analysis of individuals (Figure 4) representing seasons clearly shows that the first axis is well represented by the spring season (point 3) and that the other seasons are on the negative side of the first axis. The order of the seasons according to the second axis reflects the order of cadmium concentrations throughout the year, from the lesser concentrations in August (point 4) and October (point 1) to relatively higher concentrations in May (point 3) and February (point 2).

This design shows that summer and autumn are very close seasons according to TME concentrations in sediments probably due to the dryness of the wadi during these periods that brakes the movement of TME between sediments and water. The behaviour of the TME during spring on one side and winter on the other side seems to be completely different and different phenomena seem to be involved for each of these two seasons, as well as for the couple summer–autumn.

CONCLUSION

Seybouse wadi is the receptor without pre-treatment of diverse effluents. Relatively high concentrations of trace metal elements (TME) – Al, As, Ba, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn – are found at the mouth of the wadi in waters where they exceed the SEQ-Eau and NQEp standards. Sediments are mostly contaminated with arsenic, nickel and chromium, all through the year and especially in spring. The application of PCA on the resulting chemical data made it possible to suspect and explain the origins of each of the TME in the wadi waters and sediments. Chromium, lead, iron, cadmium and aluminum in waters are suspected to originate from the nearby chemical production complex of phosphate fertilizers and plant protection chemicals. Copper and manganese come probably from agricultural leachate, and barium from ceramic industries. The industrial effluent pollution of waters is related to the spring season while summer and autumn are very close as for TME in sediments. This can be explained by the fact that the wadi is a dry and ephemeral riverbed.

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