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Assessment of anthropogenic and natural factors on Cheliff river waters (North-West of Algeria) at two contrasted climatic seasons

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Abstract

Cheliff river is the most important permanent river of North-West Algeria which plays an essential role for irrigation and drinking water supply, but suffers from high anthropogenic pressure. Multi-dimensional and multi-factorial aspects of water pollution in Cheliff river and its tributary Mina river were evidenced during two contrasted climatic seasons. Urban discharges were identified as a major source of water organic pollution. The inputs of untreated sewages were characterized by maximum concentrations of tryptophan-like (5.7 $\mu mol.l^{-1}$) and tyrosine-like (9.8 $\mu mol.l^{-1}$) compounds during dry period, confirming these amino acids as fingerprints of untreated urban discharges. The synchronous monitoring and assessment of physicochemical parameters, fluorescent organic compounds and metallic elements of Cheliff river waters highlighted its global contamination, mainly in its downstream part.

Cheliff river was mainly affected by organic pollution with maximum COD (1536 mg $O_2.l^{-1}$) and BOD_5 (12 mg $O_2.l^{-1}$) during wet period, and by metallic contamination with maximum Fe (287±4.4 $\mu g.l^{-1}$) and Al (422.4±9.4 $\mu g.l^{-1}$) during dry period, exceeding the guideline limits. This chronic contamination was related to untreated domestic sewages, agricultural effluents and technical landfill center discharges in this area. Diffuse pollutions were also evidenced, which made the identification of different contamination sources complicated.

Mina river was mostly affected by non-treated domestic sewages with maximum COD (3161 mg $O_2.l^{-1}$) during wet period and maximum BOD_5 (12 mg $O_2.l^{-1}$) during dry period, exceeding the guideline limits. The correlation Li/Sr showed the contribution of natural influence from saline soils of Mina valley, particularly during dry period.

Keywords: Cheliff river, physicochemical parameters, organic compounds, metallic elements, water quality.

1. Introduction

Freshwater ecosystems (lakes, ponds and rivers) are considered one of the most important natural resources for preserving the living organisms of the biosphere. These ecosystems cover only 0.2% of Earth surface, representing a very small portion compared to the marine and terrestrial habitats (Singh et al. 2010). Besides, natural freshwater is also a fundamental element of many economic sectors including agriculture, industry, livestock production, hydropower generation, etc…(Effendi 2016). Continuous growing of global population increases obviously the demand of freshwater, while this resource tends to diminish due to global climate change. As a result, many people around the World, mainly in Africa, face an increasing risk of water shortages that are expected to cause thousands deaths every year and drives increased climate migration. Recent studies of United Nations, have predicted that about 1.8 billion people will face absolute water scarcity by 2025 (Naimi Ait-Aoudia and Berezowska-Azzag 2016).

Indeed, water resource is strongly affected by anthropogenic activities (industry, agriculture) as well as by the rapid urbanization. Many freshwaters have been shown to be contaminated by different pollutants including organic, inorganic and biological elements (Yan et al. 2016). It is worth noting that water pollutions are the origin of many serious problems to both environment and human worldwide. The increase of deaths and diseases due to water pollution has prompted many scientists to focus their studies on water quality (Cruz et al. 2019; Koukal et al. 2004; Perrin et al. 2014; Salam et al. 2019; Strady et al. 2017).

An important parameter to be considered for water quality evaluation is organic matter, which is ubiquitous in all aquatic systems. This organic matter can be of autochthonous origin due to microbial activity or algal productivity, or allochthonous origin, as a consequence of soil leaching (Winter et al. 2007). However, human activities can affect the organic matter fraction that is present in natural waters, which usually lead to a modification of their concentration and composition (Carstea et al. 2009). The organic matter in water under urban influence is generally analyzed and characterized by fluorescence spectrometry (Baker et al. 2003). Generally, the principal fluorescent components observed in rivers and wastewaters are ascribed to humic substances, including humic and fulvic acids (Baker and Spencer 2004; Hammou 2012). They are also related to fluorescent amino acids that correspond to tryptophan-like, tyrosine-like and phenylalanine-like compounds (Yu et al. 2015). In the case of waters contaminated by urban sewages, the aromatic peptides and their decomposition products can emit a high fluorescence (Carstea et al. 2009). Particularly, tryptophan-like and

tyrosine-like sewages tracers are used to follow the impact of domestic discharges into river courses (Baker 2001; Osburn et al. 2012).

Algeria is classified by the United Nations Organization as a semi-arid country affected by a water crisis, which facing a serious water shortage with a natural water supply below 500 cubic meters per capita per year (Naimi Ait-Aoudia and Berezowska-Azzag 2016). Moreover, the quality of water in Algeria is considerably altered in the recent years by a demographic growth from 11 million in 1960 to nearly 40 million inhabitants in 2015 (World databank 2017) and also by the industrial expansion.

The present work is focused on the greatest permanent river of Algeria, Cheliff river. This river is an essential water resource for drinking water and irrigation but it suffers from high anthropogenic pressure due to the increasing population density. In this area, the population rose from 5 221 800 inhabitants in 2008 to 8 596 527 inhabitants in 2012, producing a volume of domestic wastewater of 637 109 $m^3.d^{-1}$. The region hosts 228 industrial activity units and is also an important agricultural area (Watershed Agency Cheliff-Zahrez 2017). Wastewaters resulting from all these activities are unfortunately released into the natural aquatic environment without any treatment, leading to environmental damages (Belhadj et al. 2006).

Up to now, very few studies have been carried on the pollution of Cheliff river, focusing on physicochemical analysis of water compartment (Benson-Evans et al. 2006) and assessment of heavy metals in the superficial sediment (Belhadj et al. 2006). The present work was carried out within the framework of the project Hubert Curien Tassili Partnership Program (France- Algeria) entitled "Contribution to the improvement of environmental quality of the Cheliff river (Algeria)". The aim of this study was thus to assess the impact of urban, agricultural and industrial wastewaters on Cheliff river and its main tributary Mina river. Monitoring and assessment of waters quality were realized by analyzing organic components including fluorescent substances and mineral components including metals in river waters and also directly in identified untreated urban discharges. Two snapshot campaigns were performed along the river and its main tributary during two contrasted climatic periods (wet and dry seasons). Moreover a statistical study was carried out to highlight the potential relations between different pollution indicators.

2. Materials and methods

2.1. Study area

Cheliff river is a 750 km-long river located in the North-West of Algeria, which drains a watershed of 43.750 km^2 (Belhadj et al. 2006). This river has its source in the

Saharan Atlas, near Aflou in the mountains of Jebel Amour. As it is illustrated in Figure 1, the river mouth on the Mediterranean sea is located about 15 km from the city of Mostaganem.

In this area, the Mina river is the main tributary (135 km-long) of the Cheliff river. The Cheliff and Mina rivers are considered as important water resources for irrigation and drinking waters (Benson-Evans et al. 2006).

The climate of the region is semi-arid with two contrasted climatic periods: wet period characterized by an annual rainfall ranging from 250 to 300 mm between October and March and a dry period with high temperatures up to 40°C in august (Tutiempo Network 2018).

According to previous pedological studies (Boulaine and Bellon 1955; Douaoui et al. 2001), the soils of this region are limey with clay texture. These soils exhibit also distinct levels of sodicity (Na, Mg) in local saline depressions named Sebkha, which can be overflowed during the wet season (Douaoui et al. 2006). The lower Cheliff and Mina plain are among the most important Algerian agricultural regions (Watershed Agency Cheliff-Zahrez 2017) with quite annual diversified crops (citrus orchards, olive trees, melon, watermelon, artichokes and cereals) which are however affected by high soil salinity (Douaoui et al. 2006).

2.2. Monitoring and sampling site

The sampling points of water were chosen on the Mina and Cheliff rivers (Fig. 1):

(i) Mina river crosses the town of Relizane, a large agglomeration with a population of 17,832 inhabitants generating a volume of wastewater of 3,351 m^3 per day (National Sanitation Office of Relizane (Algeria) 2014).

Sampling stations are located inside the raw urban discharge (M2 station), upstream of the urban discharge (M1station) and downstream of urban discharge (M3 station).

(ii) The impact evaluation of Mina inputs inside the Cheliff river requires the sampling upstream of the confluence (C1 station) and downstream of the confluence (C2 station).

(iii) Cheliff river crosses an agglomeration called Sour, with an estimated 4,475 population (2013) rejecting approximately 430 m^3 of urban wastewater per day (Hydraulic Steering of Mostaganem (Algeria) 2013). The sampling was realized inside (C4 station), upstream (C3 station) and downstream (C5 station) of urban discharges. These stations are located near a technical landfill center.

To estimate the quality of Cheliff water inputs into the Mediterranean sea, a last sampling site (station C6) was chosen 300 m upstream from the river mouth close to a desalination plant.

To study the impact of urban discharges to both rivers, water samples were collected during the two characteristic climatic periods: in February–March 2015 (wet period) and August 2015 (dry period). The influence of Mina inputs for the Cheliff river was evaluated in a

second time with water sampling at the stations C1, C2 during the wet period on February 2016. During the dry period, the Cheliff river was dried in C1 and C2 stations, which made the sampling impossible. The flow data were not available for the studied period (2015-2016).

2.3. Samples preparation

Water samples were taken in 1.5 liter polyethylene bottles cleaned with 2% nitric acid. At each station, three bottles were sampled in order to obtain a composite sample after mixing. In the laboratory, the composite samples were divided into three aliquots: the first one for physicochemical analyses was filtered through cellulose filter (alpha-cellulose Grade 589/3). The second part, intended to metal analyses, was filtered through cellulose nitrate filters (porosity 0.45 μm) and acidified with 2% of concentrated nitric acid 65% of trace metal grade. The last part was intended for fluorescence analyses after filtration with cellulose nitrate filters (porosity 0.45 μm) and addition of 1% of sodium azide (1M) to prevent microbial activity. All samples were stored in the dark at 4°C before analysis.

2.4. Analysis

2.4.1. Physicochemical analyses

At each sampling station: pH, temperature and conductivity were measured *in situ* using adequate electrodes (Consort C562). The instrument was calibrated with standard solution before use. The total suspended materials (TSM) were used to measure the total particulate matter in waters. TSM were determined according to the normalized method NF T90-105 (AFNOR 1999). The organic pollution was evaluated through the determination of Chemical Oxygen Demand (COD), according to the normalized method NF T90-101 (AFNOR 1999) and Biochemical Oxygen Demand (BOD$_5$), according to the normalized method NF T90-103 (AFNOR 1999) using OxiTop^{TM} bottles. Mineral components determinations were carried out using an Optizen 3220 Spectrophotometer for sulphates (SO$_4^{2-}$), nitrites (NO$_2^-$), nitrates (NO$_3^-$) according to respective normalized methods NF T90-040, NF T90-013 and NF T90-012 (AFNOR 1999) based on calibration curves. Chloride (Cl$^-$) was measured according to the normalized method NF T90-014 (AFNOR 1999). For each analyze, a blank (purified water) was carried out in the same analytical conditions as samples. All samples were analyzed in triplicate in order to obtain reliable results.

2.4.2. Metals analyses

Metallic elements (Cu, Zn, Al, Fe, Mn, Cd, Pb, As, Ni, Cr, Sr, Li) were analyzed by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS Agilent 7700X). The instrument realized 300 measurement replicates for each sample. The detection limits of instrument for each metal are indicated in Table 1.

The certified reference material 1640a from the NIST (National Institute of Standards and Technology: https://www.nist.gov) was used in order to check the quality of the analysis. The recovery percentages relative to the reference material 1640a are given in Table 1. They varied from 81 to 105% depending on the element.

2.4.3. Fluorescent organic matter analyses

The fluorescent dissolved organic matter (DOM) was measured by three-dimensional Fluorescence Excitation-Emission Matrix (FEEM) technology using Safas-flx spectrofluorimeter. All samples were first analyzed in UV-Visible absorption spectroscopy to verify that the absorbance of each sample at $\lambda= 254$ nm is below 0.3 (Ohno 2002). If necessary, dilutions were carried out to correct samples for inner-filtering before fluorescence measurements. Excitation and emission slit widths were set to 10 nm bandpass and photomultiplier voltage to 800 V. Excitation wavelengths (Ex) varied from 200 to 500 nm every 10 nm intervals and emission wavelengths (Em) varied from 210 to 800 nm at 1 nm intervals. The fluorescence intensity was measured in arbitrary units (a.u.). The blank (purified water) was analyzed in the same conditions as the samples. FEEM of blank (purified water) acquired was subtracted from FEEMs of samples before to be modeled with PARAFAC (Parallel Factor Analysis) using the DOMFluor toolbox for Matlab to separate the fluorescent components (Stedmon and Bro 2008). The correction of Raman and Rayleigh diffusions was applied for all fluorescence spectra.

The number of components was tested between 3 and 10 components. The best model was determined from the shape of the component's spectra and the value of Core Consistency Diagnostic (CORCONDIA), which must be greater than 60% to validate the model (Bro and Kiers 2003).

2.5. Statistical analysis

Principal component analysis (PCA) was performed to study the potential correlations between physicochemical, fluorescent organic, mineral and metallic parameters. PCA was applied to the whole spatio-temporal data (9 stations, 2 periods) using following parameters: COD, BOD_5, Cl^-, SO_4^{2-}, NO_2^-, NO_3^-, TSM, tryptophan, tyrosine, Cu, Zn, Fe, Al, Mn, Cr, Ni, As, Cd, Pb, Li and Sr. The analysis was conducted using Addinsoft XLSTAT software.

3. Results and discussion

This study presents for the first time an integrative dataset concerning the urban discharges and the water quality characteristics of Cheliff and Mina rivers.

The results of the physicochemical and metallic composition of urban discharges will be first discussed before to present the spatial variations of those parameters in both rivers. The

fluorescence results will be exposed in the same way later to characterize the dissolved organic matter (DOM).

3.1. Characterization of untreated urban discharges (M2 and C4)

3.1.1. Physicochemical parameters

M2 and C4 represent two identified urban discharges rejected without any treatment into Mina and Cheliff rivers, respectively. Figure 2 shows the main physicochemical parameters measured for these samples collected during dry and wet periods.

The M2 station was characterized by high chloride content (887.5 ± 5.0 mg.l^{-1}) and elevated COD value (979 mg O$_2$.l^{-1}) during wet period, while high concentration of TSM (960.0 ± 1.5 mg.l^{-1}) was observed during dry period. Nitrites (0.50 ± 0.09 mg.l^{-1}) and sulphates (35.8 ± 2.8 mg.l^{-1}) had similar concentrations during both periods. The C4 station was characterized by high values of conductivity (8.6 ± 0.2 mS.cm^{-1}) during wet period and high concentrations of COD (1032 mg O$_2$.l^{-1}) and nitrites (0.90 ± 0.09 mg.l^{-1}) during dry period.

These results were compared with the Algerian guidelines for treated wastewater used for irrigation (Algerian guidelines 2012). The available parameters in these guidelines were conductivity, chloride and COD with permitted values 30 mS.cm^{-1}, 10 mg.l^{-1} and 90 mg O$_2$.l^{-1}, respectively. Despite the values of conductivity were far below the allowed limit, it was shown that chloride and COD largely exceeded the permitted limits, demonstrating that untreated urban discharges contribute to the global contamination of the rivers.

3.1.2. Metallic composition

The concentrations of metals (Cu, Zn, Fe, Al, Mn, Cr, Ni, As, Cd and Pb) are presented in Figure 3. The samples M2 and C4 (urban sewages) were compared to the Algerian guidelines for wastewater treated for irrigation (Algerian guidelines 2012). These guidelines fixed the following limits for metallic elements: Cu (5 mg.l^{-1}), Fe (20 mg.l^{-1}), Cr (1 mg.l^{-1}), Ni (2 mg.l^{-1}), As (2 mg.l^{-1}), Cd (0.05 mg.l^{-1}), Pb (10 mg.l^{-1}). It was shown that M2 and C4 samples were characterized by weak concentrations of metals in both seasons, in the µg.l^{-1} order, much lower than the permitted limits (in the mg.l^{-1} level).

M2 station was characterized by quite values of Cu, Zn, Ni, As, Cd and Pb. Except for Cd, the concentrations of these metals increased during the dry season up to maximal values of 6.1 ± 0.2 µg.l^{-1} for Cu, 5.33 ± 0.04 µg.l^{-1} for As and 7.5 ± 0.2 µg.l^{-1} for Ni.

C4 station showed predominant concentrations of Cu, Fe, Ni, As and Pb during dry season with a maximum for Fe (375.4 ± 7.9 µg.l^{-1}). Only Cr and Cd concentrations increased during wet period up to 119.8 ± 0.3 µg.l^{-1} (maximum) for Cr and 0.150 ± 0.007 µg.l^{-1} for Cd. In this region, the network collects sewages from urban and peripheral area which are mixed in a

single pipe system, so that the presence of metals in urban wastewaters may have different possible origins including domestic, industrial, farming and craft activities (National Sanitation Office of Relizane (Algeria) 2014). M2 sampling station is probably affected by agricultural activities around the area with the extensive and punctual use of agrochemicals (pesticides and fertilizers) along the seasons depending on the type of crop that can explain the presence of metals (Cu, Ni, As, Cd and Pb) at notable levels. On the other hand, C4 is located close to an urban area (Sour city) where household tanneries reject high Cr concentrations (Koukal et al. 2004) mixed with urban discharge metallic concentrations. However, farming activities are also intense around this area and may be responsible for important Fe and Cd release from fertilizers (Bu et al. 2017).

3.2. Spatio-temporal variations in watercourses (M1, M3, C1, C2, C3, C5, C6)

3.2.1. Physicochemical parameters

Seasonal and spatial variations of physicochemical parameters measured in Mina and Cheliff rivers are shown in Figure 2. Water quality characteristics were evaluated by comparison to Algerian guidelines concerning surface waters intended for human consumption, when available (Algerian guidelines 2011). During dry season, values at C1 and C2 were not available as the river was completely dried.

During wet period the pH of waters varied between 6.4 at M1 to 8.6 at C1, while at dry period the values recorded varied from 7.5 at C3 to 8.3 at C6. These pH values were in agreement with those permitted in the guidelines (6.5-8.5).

Water temperature ranged from 12.3°C at C6 to 26.1°C at C3 in wet period and from 27.2°C at M1 to 29.3°C at C6 during dry period.

The conductivity is strongly related to the presence of major species (Ca^{2+}, Mg^{2+}, K^+, Na^+, HCO_3^-, SO_4^{2-}, Cl^-,....) in water (Çadraku et al. 2016). Conductivity exceeded the permissible limit (2.8 mS.cm^{-1}) during wet period for C3 (9.2 ± 0.2 mS.cm^{-1}), C5 (8.9 ± 0.1 mS.cm^{-1}), and especially C6 (80.0 ± 1.3 mS.cm^{-1}). These stations are located downstream of the confluence. The high conductivities at C3 and C5 might be related to the 12 mm rainfall that was measured 2 days before sampling (Tutiempo Network 2018), which led to saline soil leaching and re-solubilisation of magnesium and calcium in river water (Daoud et al.1993). Inputs from technical landfill center could also reach the river after overflowing from retention basins and contribute to high conductivities. At C6, the maximum of conductivity reflected the marine influence.

The presence of high concentrations of chloride in the different samples collected could be attributed to the saline nature of soils within the study area (Douaoui et al. 2006). On Mina river, chloride concentrations were slightly higher than Algerian guideline limits (600 mg.l^{-1}) with averages concentrations of 666 ± 35 mg.l^{-1} during wet period and 797 ± 16 mg.l^{-1} during dry period. Along the Cheliff river, the C3, C5 and C6 stations displayed the highest chloride concentrations during dry period (1273.0 ± 50.2, 1287.0 ± 50.2 and 887.0 ± 30.7 mg.l^{-1}, respectively). The high temperatures (around 30°C) observed during this period may be responsible for increased evaporation, thus leading to an increase of chloride concentrations. During wet period, C1 and C2 stations presented the lowest recorded values (respectively 420.0 ± 7.5 and 166.0 ± 2.0 mg.l^{-1}) which can be explained by the dilution effect due to rainfalls.

The COD values during wet period ranged from 29 mg O_2.l^{-1} at C2 station to 3161 mg O_2.l^{-1} at M1 station. The values recorded at stations M1 (3161 mg O_2.l^{-1}), M3 (1056 mg O_2.l^{-1}), C5 (600 mg O_2.l^{-1}) and C6 (1536 mg O_2.l^{-1}) largely exceed the permitted value of 30 mg O_2.l^{-1}. During the dry period, lower values of COD were measured, with maximum at C3 and C5 (72 mg O_2.l^{-1}). On the other hand, BOD$_5$ was shown to be very weak during wet period with average value of 1.8 mg O_2.l^{-1}, except at C1 (12 mg O_2.l^{-1}) where BOD$_5$ exceeded the recommended value of 7 mg O_2.l^{-1}. During dry period, BOD$_5$ exceeded this limit in Mina river to reach 9.3 mg O_2.l^{-1} at M1, and 12 mg O_2.l^{-1} at M3, however BOD$_5$ was below the limit in Cheliff river with similar values measured in C3, C5, and C6 (average of 3.6 mg O_2.l^{-1}). Consequently, the mean value of BOD$_5$/COD ratio (0.07) for all samples during both periods was less than 0.3. Such ratio indicated that the biodegradability of pollutants was very low (Yu et al. 2015)in the Cheliff and Mina rivers.

The concentrations of nitrites, nitrates and sulphates were below the guidelines limits (0.5 mg.l^{-1}, 50 mg.l^{-1} and 400 mg.l^{-1} respectively) in all stations. Nitrites concentrations ranged from 0.10 ± 0.01 mg.l^{-1} at C2 to 0.30 ± 0.01 mg.l^{-1} at C1 and C6 during wet period and from 0.30 ± 0.01 mg.l^{-1} at M1 to 0.50 ± 0.02 mg.l^{-1} at C5 during dry period. The nitrates concentrations varied from 0.50 ± 0.01 mg.l^{-1} at C2 to 3.8 ± 0.3 mg.l^{-1} at C3 during wet period and from 0.80 ± 0.08 mg.l^{-1} at C6 to 2.0 ± 0.2 mg.l^{-1} at C3 during dry period. The sulphates concentrations ranged from 32.2 ± 1.5 mg.l^{-1} at M1 to 78.6 ± 3.0 mg.l^{-1} at C1 during wet period and from 33.1 ± 1.0 mg.l^{-1} at C6 to 81.3 ± 1.4 mg.l^{-1} at M1 during dry period.

There is no guideline for total suspended matter (TSM) to evaluate water quality. These values varied from 30 ± 13 mg.l^{-1} at C1 to 440 ± 1 mg.l^{-1} at C5 during wet period and from 57 ± 1 mg.l^{-1} at C6 to 645 ± 1 mg.l^{-1} at C5 during dry period. TSM often transported the different

contaminants adsorbed on particles in the water column. TSM can be originated from the anthropogenic activities (agricultural and urban sewages) (Houhou et al. 2010) and/or natural soil leaching. During dry period, evaporation of water and development of algal boom can induce an increase of TSM concentrations when the water flow was weak.

Some of the physicochemical parameters measured in the present study were compared with those obtained in previous studies concerning Cheliff river (Benson-Evans et al. 2006) and other rivers located in Morocco (Koukal et al. 2004) and Egypt (Elewa 2010) (Table 2). The previous study on Cheliff and Mina rivers showed approximately the same level of chlorides but lower values of BOD_5. In Morocco, the study of Sebou river indicated lower values of chloride and BOD_5 but higher values of sulphates compared to the present results. Another study carried out on Nile river in Egypt reported levels of chlorides, BOD_5 and sulphates much lower than those measured in this study. These comparisons showed that there was an increase of organic inputs (BOD_5) in the Cheliff river between previous and present studies. At this moment the Cheliff river was characterized by higher concentrations of chlorides, BOD_5, sulphates compared to Nil river and of chlorides, BOD_5 compared to Sebou river. However the concentrations of sulphates were lower than those found in Sebou river.

3.2.2. Metallic composition

The spatio-temporal variations of metals (Cu, Zn, Fe, Al, Mn, Cr, Ni, As, Cd and Pb) in river waters are presented in Figure 3. The results were compared to the Algerian guidelines of surface waters intended for human consumption (Algerian guidelines 2011). French guidelines were used only when the Algerian guidelines were not available (French guidelines 2013).

During dry period, the metallic contamination in Cheliff river results in high concentrations of Fe at C3 (287.0 ± 4.4 µg.l^{-1}) and C5 (255.6 ± 1.2 µg.l^{-1}), and also of Al at C5 (422.4 ± 9.4 µg.l^{-1}), exceeding the recommended values. At C3 the concentration of Al was also significant (183.3 ± 2.1 µg.l^{-1}), but below the limit. Regarding the other metals, the concentrations were always below the guidelines. However, two stations (C3 and C5) were characterized by notable concentrations of Zn, Mn, As, Cd, Pb and only station (C5) for Cu. During these samplings, the river flow was very weak, which may explain the obtained high metallic concentrations. C3 and C5 stations were also affected by crop treatments carried out over the seasons (crop rotation) and technical landfill center effluents, which can explain enhanced concentrations of Zn, Al, As, Cd, Pb. Moreover, the increase of Zn concentrations in the river might be related to the farming activities, as well as domestic effluents (Mendiguchía et al. 2007; Bu et al. 2017). High concentrations of Fe and Mn may be explained by colloid

destabilization and reduction of sedimentary iron/manganese oxyhydroxides in hypoxic conditions (Bu et al. 2017) especially during dry period. During wet period, only C2 presented significant concentrations of Zn, Ni, Cd and Pb. In this case, their potential sources were uncertain, one hypothesis may be the leaching from uncontrolled discharges which could not be identified in this work.

Mina river (M1 and M3) did not reveal specific metallic contamination. The concentrations measured in both seasons were weak and far below the guidelines limits. Despite this, Mina river was characterized by predominant concentrations of Cu, Zn, Ni, As, Cd and Pb, mostly during wet period. The presence of these elements may be related to farming activities and extensive application of fertilizers and pesticides as zinc arsenate ($Zn_3 (AsO_4)_2$) and lead arsenate ($Pb_3 (AsO_4)_2$) (Zhaoyong et al. 2015). The presence of metals as dissolved elements was probably due to leaching of soils after rainfalls.

Mina river was affected by identified urban discharge (M2) enriched in Cu, Zn, Ni, As, Cd and Pb which appeared more diluted at M3 station located 0.2 km downstream (Fig. 1). On the opposite, Cheliff river was moderately affected by identified urban discharges (C4) with the higher metallic concentrations in C5 station (2.5 km downstream) except for Fe and Ni. Besides, Cheliff inputs influenced the water quality of coastal zone as observed in the C6 station (mouth of Cheliff river). High concentrations of metals (Zn, Fe, Al, As, Cd, Pb) were mostly measured during dry period, mainly due to enhanced evaporation of waters at temperatures around 30°C.

Compared to other rivers like Moulouya in Morocco (Bouabdli et al. 2005), Guadalquivir in Spain (Mendiguchía et al. 2007), Nile in Egypt (Elewa 2010) and Rhône in France (Ollivier et al. 2011), Cheliff river presented higher concentrations (up to 14-fold) of Cu, Zn, Mn, Ni, Cd and Pb (Table 3). Higher levels of Cd and Pb were found only in Nile river, with concentrations 7-fold and 3-fold higher for Cd and Pb, respectively. When compared to others rivers the Cheliff river was globally characterized by a highe pollution by metallic elements (Cu, Zn, Mn, Ni, Cd and Pb).

3.3. Saline soils fingerprints through Li/Sr abundances

According to the soil map of study area ((Boulaine and Bellon 1955), this region was affected by the presence of saline soils in the watershed. The combination of the two elements Li/Sr was strongly used to identify the areas most affected by the problem of salinity (Laiche 2017). In order to study the natural influence of these saline soils on the waters of Cheliff and Mina rivers, we have drawn the Li/Sr concentrations during wet and dry periods.

Figure 4 shows the relationships between Li and Sr taking into account all sampling stations. The correlations Li/Sr were established on Mina river stations (R^2= 0.919) and Cheliff river stations (R^2=0.924) separately (Fig. 4). Sr was present in abundance in the soils rich on Ca^{2+} (Laiche 2017), which could be related to the limey composition of the lower Cheliff and Mina watershed soils (Boulaine and Bellon 1955; Douaoui et al. 2001). Particularly, Mina river (M1 and M3) exhibited higher Li concentrations than those measured on the Cheliff river, confirmed by higher slope of the linear regression obtained for Mina river (0.035) compared to Cheliff river (0.017). Higher Li concentrations in Mina river were related to the specific occurrence of Solonchak-type saline soils, which are deemed to contain this element in great abundance (Kabata-Pendias and Szteke 2015).

Seasonal trends were also observed, with highest concentrations of Sr and Li found during dry period both in Cheliff (C3 and C5 stations) and Mina rivers (M1 and M3 stations). Evaporation of waters during dry period led to increased concentrations of dissolved elements, it was the key process responsible for high concentrations of Sr and Li. During the wet period, Sr and Li concentrations were significantly diluted (M1, M3, C3, C5, C1, C2, C6). Their concentration therefore appeared to be controlled mainly by natural processes. However, two stations (C4 and M2) corresponding to urban discharges did not follow this trend and showed very low Sr and Li concentrations whatever the considered season. Those effluents were not influenced by the natural processes mentioned above, so that their specific signature with low Li and Sr concentrations could be used as a tracer of urban anthropogenic outflow.

3.4. Characteristics of fluorescent dissolved organic matter (DOM)

Figure 5 presents FEEM examples typical of DOM in the Cheliff river during two contrasted periods. These FEEMs might characterize the organic matter composition by the excitation/emission wavelengths and fluorescence intensities. Two peaks could be distinguished in the matrices obtained from Cheliff river DOM (Fig. 5). These peaks showed different fluorescence intensities (FI) depending on the station and season. Peak 1 was clearly noticeable at C3 and C4 during wet period with FI similar to those of peak 2. For the other FEEMs, peak 2 intensities were higher than those of peak 1, so that the latter appeared as a shoulder. However, FI of peak 1 were similar for both seasons at C3, C4 and C5. The highest FI was observed at C4 station (urban discharge) especially during dry period, with values of 200 a.u. for peak 2 and 90 u.a. for peak 1. A decreased of FI was logically observed downstream of urban discharge, at C5 station, with FI=15 a.u. and 50 a.u. for peak 2 and FI=6 u.a. to 15 u.a. for peak 1 during wet and dry periods respectively. Both peaks 1 and 2 showed

higher FI during the low water period. The presence of peak 1 in C3 station (upstream of urban discharge) can be explained by the non-point source pollution of Cheliff river.

The FEEMs obtained for all samples were modeled with PARAFAC application ((Stedmon and Bro 2008), revealing the presence of 6 components with a CORCONDIA of more than 95%. Fingerprints of 4 components allowed rapidly identifying them as humic substances (Osburn et al. 2012; Yu et al. 2015), while the two other corresponded to tryptophan-like and tyrosine-like amino acids, as confirmed by analysis of pure amino acids. These two amino acids present a special interest as urban pollution markers (Carstea et al. 2009) of Cheliff and Mina rivers.

3.5. Tryptophan-like and tyrosine-like variations

The fluorescence intensities of tryptophan-like and tyrosine-like amino acids were converted into concentrations using the calibration curves prepared with pure products. This allowed quantifying the tryptophan-like and tyrosine-like in each water sample during the two characteristic periods (Fig. 6).

3.5.1. Urban discharges (M2, C4)

Tryptophan-like and tyrosine-like compounds were detected in M2 and C4 stations during the two contrasted periods (Fig. 6). The highest concentrations of tryptophan-like peptides were detected at M2 station (5.4 µmol.l^{-1}) and C4 station (5.7 µmol.l^{-1}) during dry period, and only at C4 station (4.8 µmol.l^{-1}) during wet period. These concentrations were in the same order of magnitude as those measured in influents from the wastewater treatment plant (WWTP) of a French city of 120 000 inhabitants (Perpignan, France: 3.5 ± 0.4µmol.l^{-1}) (Hammou 2012).

The highest concentrations of tyrosine-like peptides were detected at C4 station, with values ranging from 4.8 µmol.l^{-1} (wet period) to 9.8 µmol.l^{-1} (dry period). At M2 station these concentrations were 1.9 µmol.l^{-1} during wet period and reached 5.4 µmol.l^{-1} during dry period.

According to previous studies (Carstea et al. 2009; Vouvé et al. 2009; Hammou 2012), tryptophan-like and tyrosine-like peptides are characteristic of urban wastewaters, especially when found at high concentrations such in M2 and C4 stations. Tyrosine-like compounds have been also described as markers of milk protein in urban wastewaters (Duée et al. 1973). Seasonal variations of tryptophan-like and tyrosine-like concentrations can also be related to microbial activities (Osburn et al. 2012; Stedmon et al. 2008) that are much more intense at dry period. It must be stressed during this period, and also the reduction of discharge flow

also led to increasing concentrations of dissolved compounds and solid materials (TSM) (Fig. 2).

3.5.2. Watercourses (C1, C2, M1, M3, C3, C5, C6)

Figure 6 shows the spatio-temporal variations of tryptophan-like and tyrosine-like compounds along the Cheliff river and its tributary Mina river. The concentrations of tryptophan-like varied from 0.1 µmol.l⁻¹ at M1 station to 0.7 µmol.l⁻¹ at C3 station during wet period and between 0.2 µmol.l⁻¹ at M3 station to 1.2 µmol.l⁻¹ at C5 station during dry period. The lowest concentrations were measured at C1 station (0.07 µmol.l⁻¹) and C2 station (0.06 µmol.l⁻¹) during wet period. At dry season, the concentrations of tryptophan-like compounds in Mina river (0.27 µmol.l⁻¹ at M1 to 0.20 µmol.l⁻¹ at M3) were similar to those found in Têt river (France) downstream of the Perpignan WWTP (France) (Table 2) (Hammou 2012). However, the concentrations in Cheliff river (1.20 µmol.l⁻¹ at C5 to 0.98 µmol.l⁻¹ at C6) were found to be respectively 5 to 33 times higher than in the Têt river (Table 2) (Hammou 2012). Tryptophan-like fluorescence has been described in many studies as a good indicator of the presence of sewage waters in rivers (Baker et al. 2003; Hudson et al. 2008; Vouvé et al. 2009; Hammou 2012). The presence of this fluorophore in all stations revealed the contamination of Cheliff river and its tributary Mina river by the identified untreated urban discharges (M2 and C4), but also by additional uncontrolled urban discharges (C1, C2, C3, C6 and M1). A dilution effect was logically observed in M3 station which is located 0.2 km downstream from M2 (4% of residual fluorescence), and in C5 station which is located 2.5 km downstream from C4 (21% of residual fluorescence).

On the other hand, low concentrations of tyrosine-like compounds were found in watercourses, ranging from 0.05 µmol.l⁻¹ at C2 station and 0.7 µmol.l⁻¹ at C3 station during wet period and from 0.05 µmol.l⁻¹ at M1 station to 0.3 µmol.l⁻¹ at C3 station during dry period. According to the study of (Hudson et al. 2008), tyrosine–like compounds in water systems originate from bacterial activity.

3.6. Statistical analysis

A Principal Component Analysis (PCA) was performed to study the potential relation between the studied parameters and sampling stations. The results of the PCA (Fig.7) indicated that two principal axes explained 55.72 % of the total variance with the contributions of F1 (33.02%) and F2 (22.70%).

In the corresponding chart (F1-F2) (Fig. 7a), along axis F1, variables Al, Mn, Zn, Cd, Pb, were positively correlated (Table 3), while variables NO_3^- and COD were negatively correlated (Table 4). Along axis F2, positive correlation concerned: tryptophan (tryptophan-

like), tyrosine (tyrosine-like), Cr, BOD_5 and negative correlation affected Li, Sr and SO_4^{2-} (Table 4).

According to positive F1 axis in the distribution of the observations (F1-F2) (Fig. 7b), the highest contamination by anthropogenic metals (Al, Mn, Zn, Cd, Pb, Fe and As) corresponds to C3 and C5 stations during the dry period (Fig. 3), which were affected by untreated domestic sewages, agricultural effluents and technical landfill center discharges as previously observed. In contrast (negative F1), the prevalence of high NO_3^- and COD levels in M1, M3, C3, C5,and C6 stations during wet period confirmed the influence of fertilizers source of organic compounds and nutriment through soil leaching (Nehme et al. 2013).

As already highlighted in the previous section, (Fig. 4) Sr was positively correlated with Li and also with Cl^- (Table 4), confirming the common origin of these components from saline soils of the watershed (Nishio et al. 2010). The additional presence of SO_4^{2-} arising from local evaporated rocks (Le Pape et al. 2013), was also positively correlated with Sr and Li, confirming the natural origin of this compound. According to negative F2 axis, the highest concentrations of Li, Sr, Cl^- and SO_4^{2-} were recorded at M1 and M3 stations during dry period (Fig. 2, 4), as a consequence of high evaporation. These results confirmed that the water composition of Mina river was mainly influenced by natural geological sources, namely saline Solonchack soils, more markedly during the dry period. In contrast (positive F2), Cr was highly positively correlated with BOD_5 (Table 4) and their high values corresponded to urban discharges at C4 station during wet period (Fig. 2, 3). The presence of Cr arising from artisanal tannery activities together with high contents of organic matter from untreated domestic wastes, confirmed that this element was mainly rejected through domestic wastes (Koukal et al. 2004). Tryptophan was highly positively correlated with tyrosine and NO_2^- (Table 4), showing the presence of high bacterial activities (Osburn et al. 2012; Stedmon et al. 2008) in M2 and C4 stations (urban sewages), particularly during the dry period. There microbial activities may be related to several types of bacteria, of which fecal coliforms such as *Escherichia coli* and fecal enterococci like *Enterococcus faecalis* are the most abundant (Ammor 2007; French guidelines 2016). The correlation between TSM and the presence of tryptophan and tyrosine (fingerprints of sewage waters) (Table 4) confirmed that these wastewaters were not treated before their rejection into the rivers. On the other hand, these urban sewages (M2 and C4 stations) contained more specifically particulate materials (TSM) positively correlated with Cu and As (Table 4). These correlations showed that Cu and As could be associated to TSM, which facilitated the transport and the distribution of metallic contamination through these urban discharges along the watercourse.

4. Conclusion

This study highlighted the multi-dimensional and multi-factorial aspects of Cheliff watershed pollution. Urban discharges (M2, C4) are a major source of water organic pollution, with high COD values largely exceeding the upper limit of guidelines. The inputs of untreated sewages were characterized by high concentrations of tryptophan-like and tyrosine-like compounds, confirming these amino acids as fingerprints of untreated urban discharges. A metallic contamination by Fe and Cr was also evidenced in C4 station, which may be correlated with local craft activities.

The synchronous monitoring and assessment of physicochemical parameters, fluorescent organic compounds and metallic elements of Cheliff river waters highlighted its global contamination, mainly in its downstream part (C3, C5 and C6).

Cheliff river was especially affected by organic pollution (COD) during the wet period, and by metallic contamination (Fe and Al) during dry period with concentrations greatly exceeding the guidelines.

During wet period, the water quality of Cheliff river (C3, C5 and C6) was affected by high concentrations of NO_3^- and Cu mainly related to intense agricultural activities. The influence of metallic elements (Zn, Mn, As, Pb, Cd) and fluorescent organic components (tryptophan-like) was greater during the dry period. This chronic contamination was related to untreated domestic sewages, agricultural effluents and technical landfill center discharges in this area. Diffuse pollutions were also evidenced, which made the identification of different contamination sources complicated.

Mina river was mostly affected by non-treated domestic sewages with high COD levels during wet period and high BOD_5 during dry period, exceeding the guideline limits. This tributary was also influenced by agricultural activities through NO_3^- inputs mainly during wet period, as a consequence of leaching. The presence of Li, Sr, SO_4^{2-} and Cl^- indicated the contribution of natural influence from saline soil of Mina valley, more specifically during dry period.

As illustrated in this report, untreated urban sewages combined to industrial and agricultural activities greatly contributed to the degradation of water quality of Cheliff and Mina rivers. Considering the rapid demographic growth, the improvement of water quality represents a real challenge for the Cheliff river which is used as the main water resource for irrigation and drinking water in the North-West region of Algeria.

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List of figure captions

Fig.1 Localisation of study area: the lower Cheliff and Mina basin located in the extreme northern part of the Cheliff basin **(a)**. Sampling stations along Cheliff and Mina rivers were indicated by green points **(b)**. Localisation of pollution inputs (urban discharges, technical landfill center, desalination plant) and distances between stations are notified **(c).**

Fig.2 Spatio-temporal variations of physicochemical parameters (conductivity, TSM, SO_4^{2-}, Cl^-, NO_2^-, NO^{3-}, COD, BOD_5) in urban discharges (M2 and C4), Mina river (M1 and M3) and Cheliff river (C1, C2, C3, C5 and C6). The dotted line corresponds to the Algerian guidelines for surface waters intended for production of drinking water.

Fig.3 Spatio-temporal variations of metal elements (Cu, Zn, Fe, Al, Mn, Cr, Ni, As, Cd, Pb) in urban discharges (M2 and C4), Mina river (M1 and M3) and Cheliff river (C1, C2, C3, C5 and C6). The dotted line corresponds to the Algerian guidelines for surface waters intended for production of drinking water. The continuous line corresponds to the French guidelines for surface waters intended for production of drinking water.

Fig.4 Relationships between Li and Sr concentrations ($\mu g.l^{-1}$) in urban discharges (M2 and C4), Mina river (M1 and M3) and Cheliff river (C1, C2, C3, C5 and C6) for both seasons. Rhombus corresponds to Mina river stations, square corresponds to Cheliff river stations. The full rhombus and square corresponds to the dry period, the empty rhombus and square corresponds to the wet period.

Fig.5 FEEMs characteristic from DOM in urban discharge (C4) and in waters of Cheliff river (C3, C5) at both seasons. Fluorescence intensity (F.I) in arbitrary units (a.u.).

Fig.6 Spatio-temporal variations of tryptophan-like and tyrosine-like in urban discharges (M2 and C4), Mina river (M1 and M3) and Cheliff river (C1, C2, C3, C5 and C6) for both seasons.

Fig.7 Results of PCA plotted according to axes 1-2. Distribution of physicochemical, fluorescent and metallic compounds **(a)**. Distribution of observations in urban discharges (M2 and C4), Mina river (M1 and M3) and Cheliff river (C1, C2, C3, C5 and C6) at both seasons **(b)**. Tryptophan-like was noted Tryptophan; Tyrosine-like was noted Tyrosine.

Figure 1

Figure 2
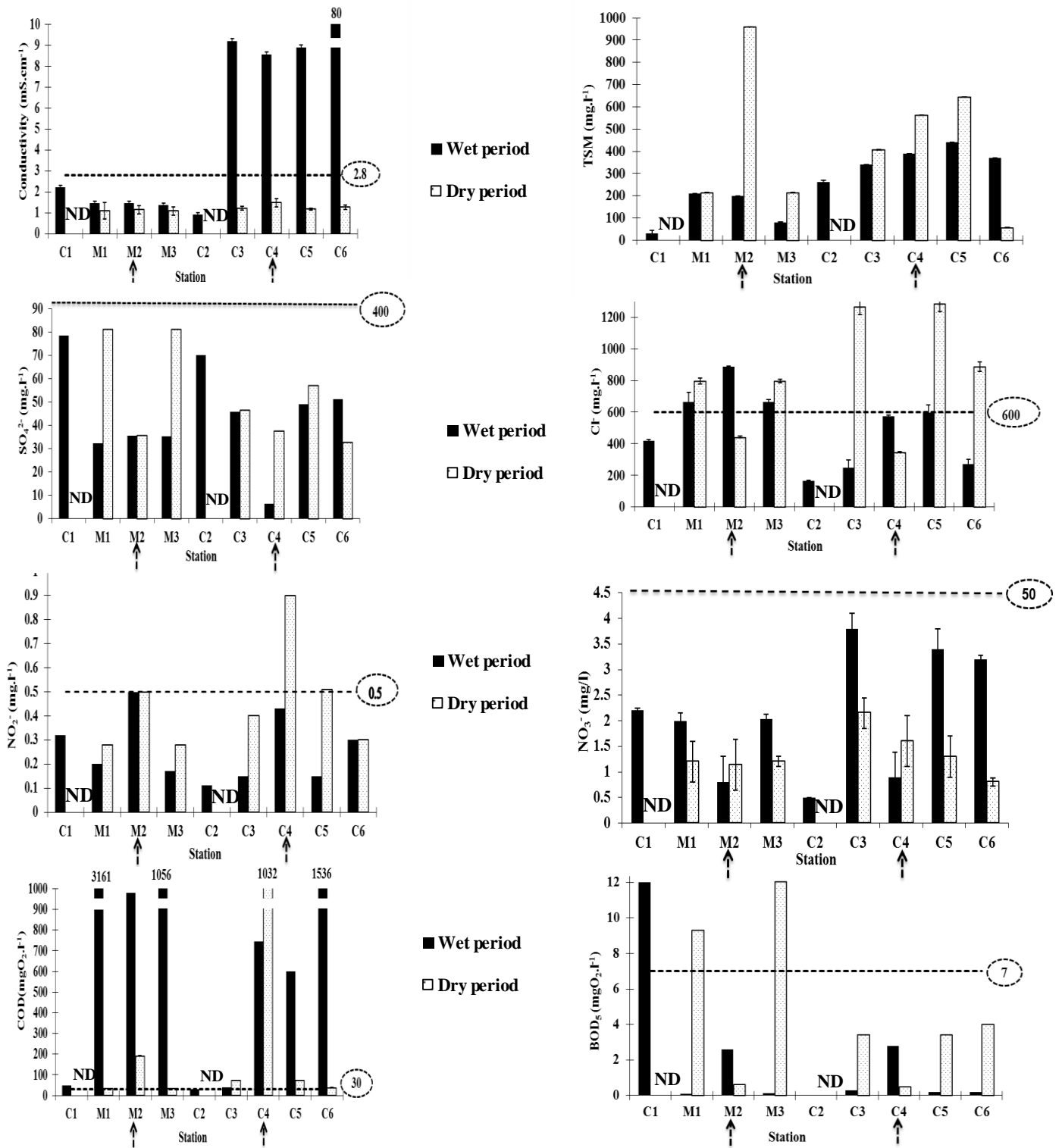
- - - - · Algerian guidelines for surface waters intended for production of drinking water

↑ Urban discharge **ND** no data

Figure 3

French guidelines for surface waters intended for production of drinking water
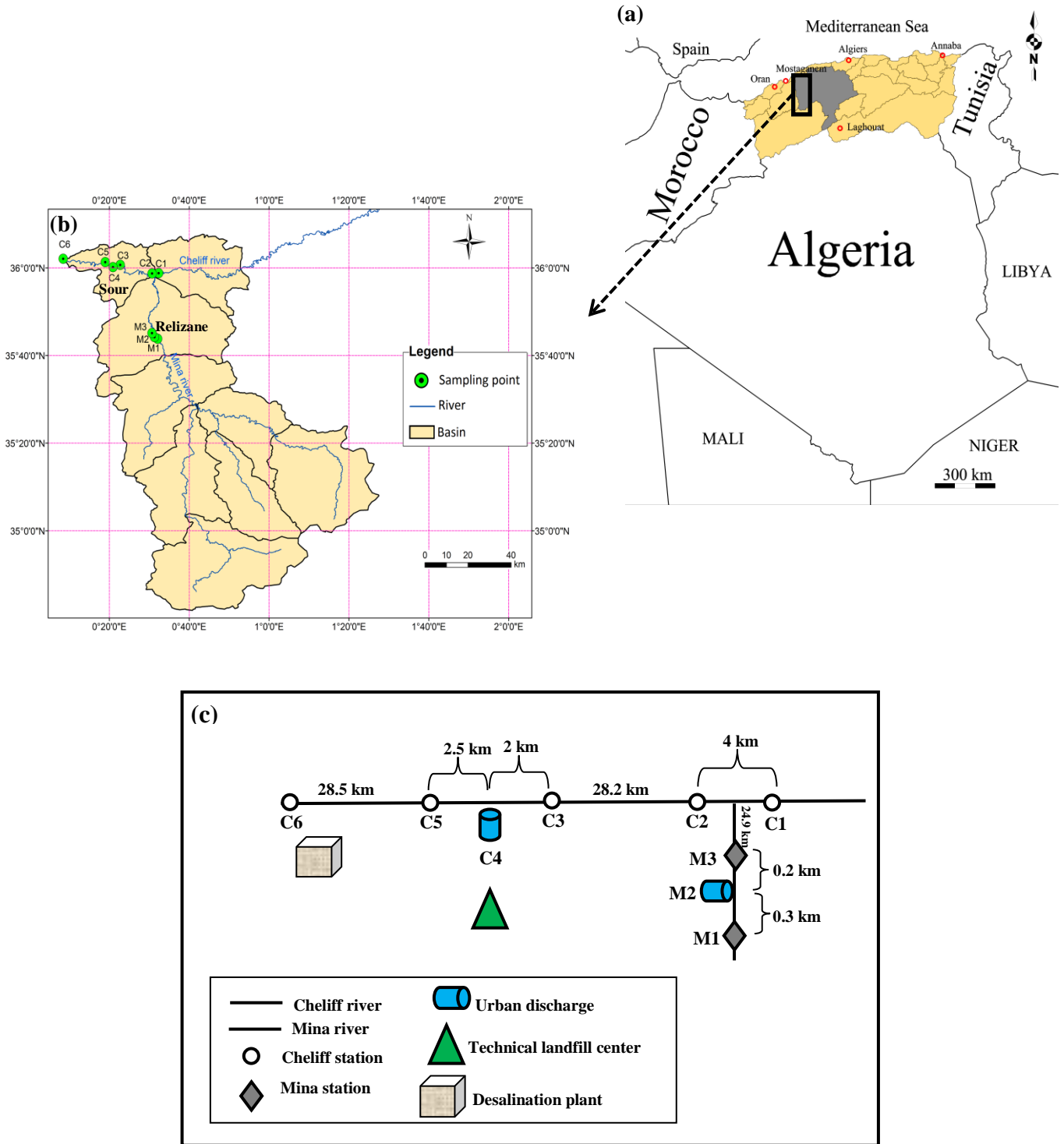
Algerian guidelines for surface waters intended for production of drinking water

Urban discharge **ND** no data
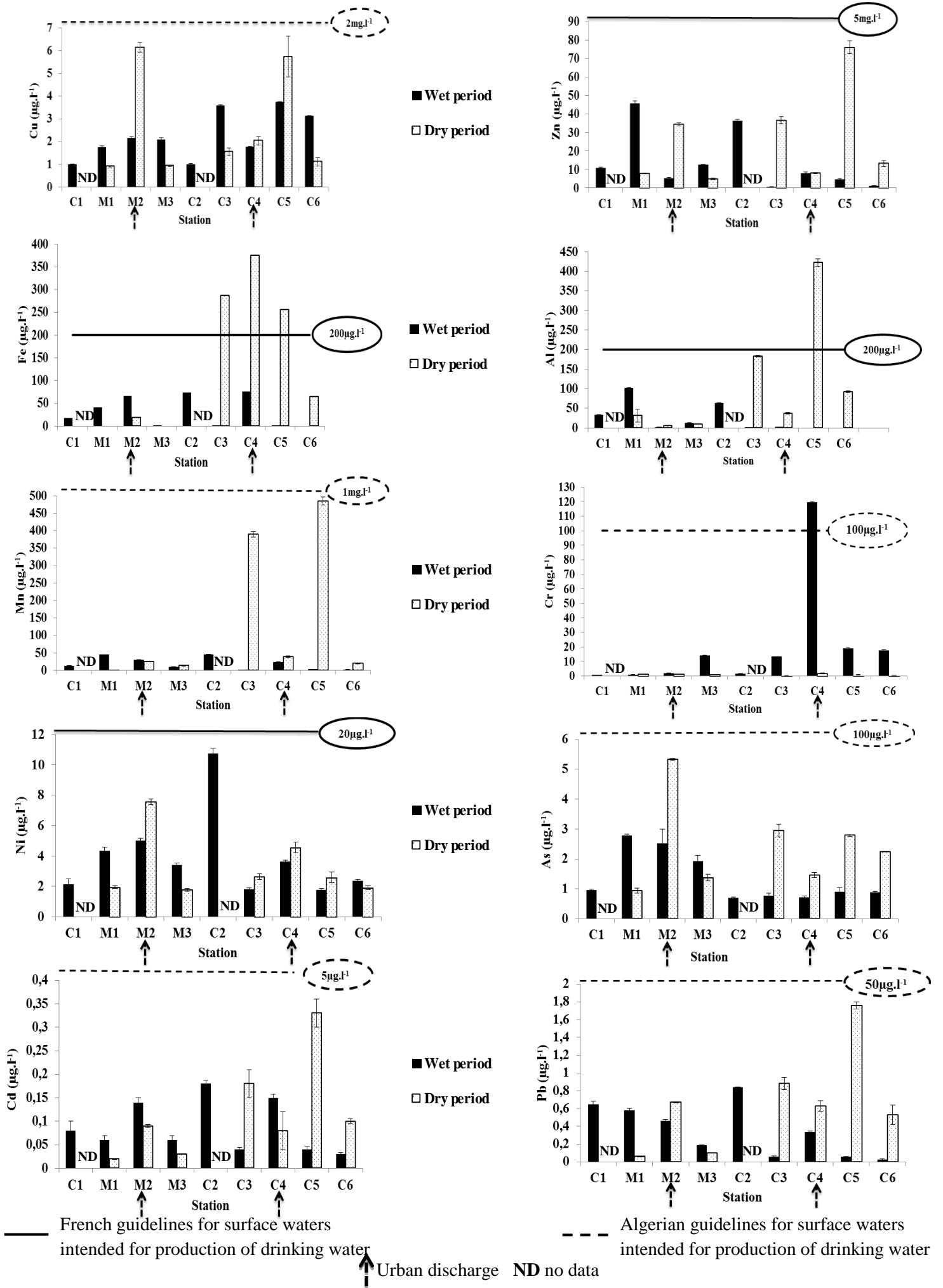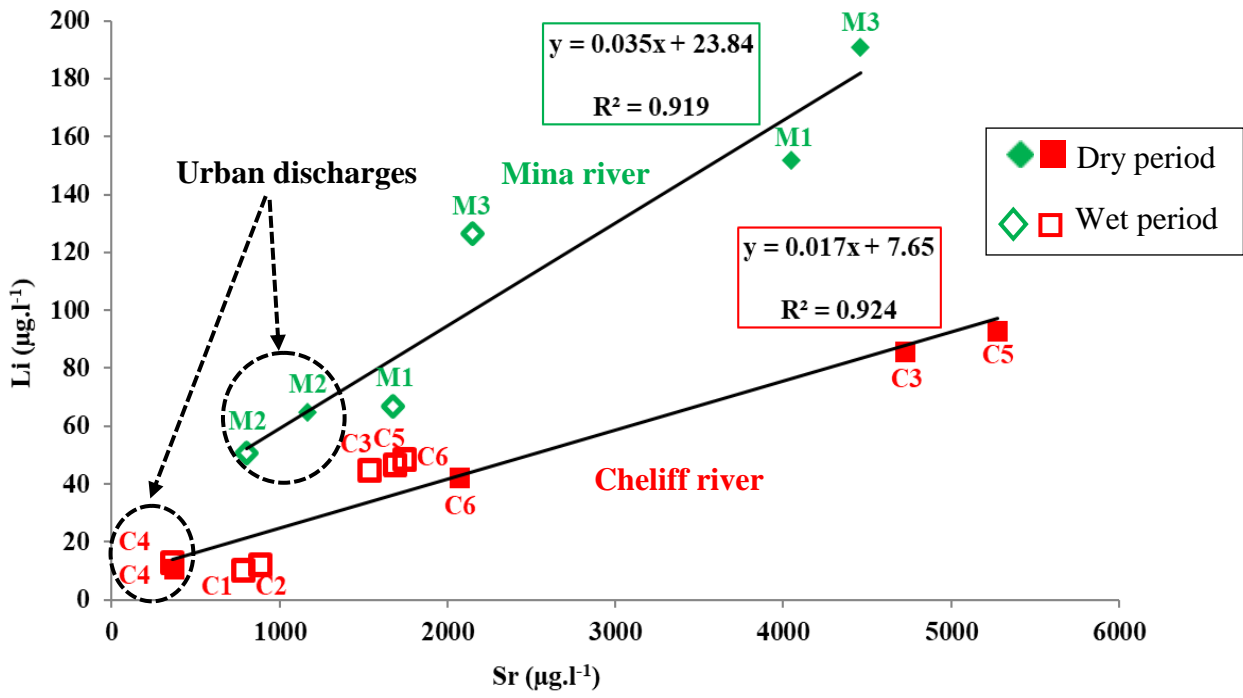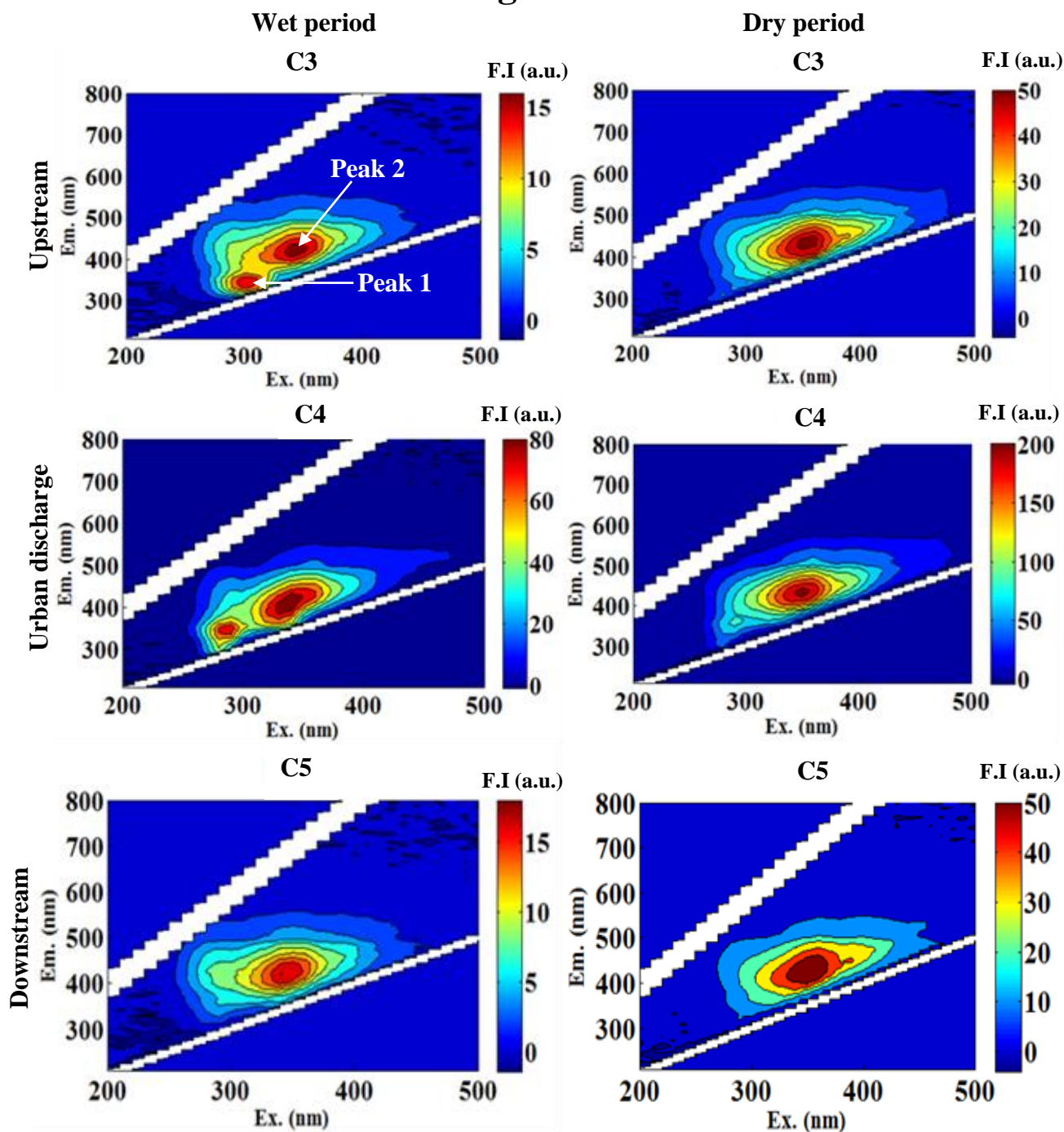
Figure 4

Figure 5

Peak	Excitation max (nm)	Emission max (nm)	Assignment and probable origin [1,2,3]
1	275-280	340-344	Aromatic amino acids
2	320-360	420-460	Terrestrial humic substances

([1] Chen et al.2003 ; [2] Osburn et al. 2012 ; [3] Yu et al. 2015)

Figure 6

Figure 7

(a) Variables (axes F1 et F2 : 55,72 %)

(b) Individual (axes F1 et F2 : 55,72 %)
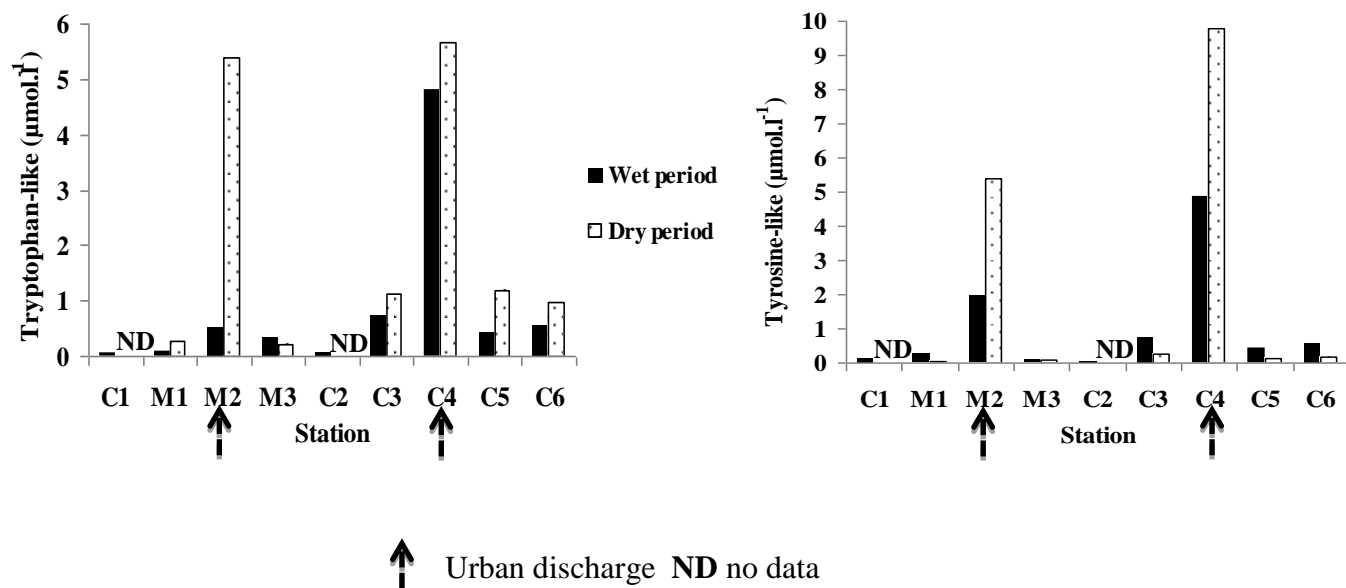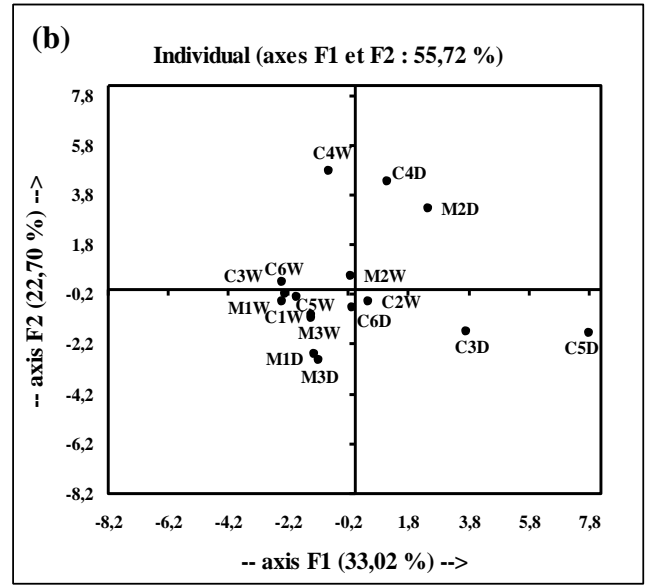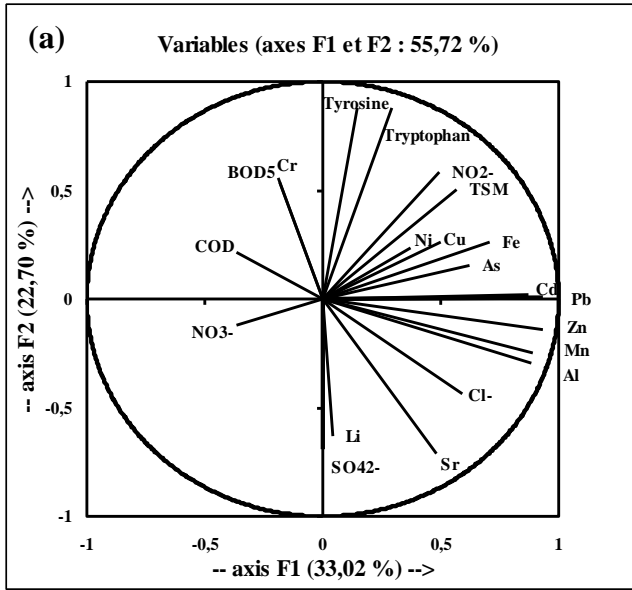
Table.1 The detection limits of instrument for each metal (Cu, Zn, Al, Fe, Mn, Cd, Pb, As, Ni, Cr, Sr and Li) were presented ($\mu g.g^{-1}$). The recovery percentages of metallic elements analysis were also notified.

Metallic elements	Detection limit ($\mu g.g^{-1}$)	Recovery (%)
Cu	0.1	100
Zn	0.1	103
Al	0.3	81
Fe	0.5	105
Mn	0.1	103
Cd	0.1	104
Pb	0.1	102
As	0.1	97
Ni	0.1	99
Cr	0.1	101
Sr	0.1	98
Li	0.1	105

Table.2 Comparison of some parameter concentrations (Cl⁻, BOD₅, SO₄²⁻ and Tryptophan) in waters from Cheliff river (present study) and others selected rivers.

Parameters	Concentrations in river water				
	Cheliff (Present study)	**Cheliff [1]** (Algeria)	**Sebou [2]** (Morocco)	**Nil [3]** (Egypt)	**Têt [4]** (France)
Cl^- (mg.l^{-1})	166-1287	100-1000	120-219	5	/
BOD_5 (mg O_2.l^{-1})	0.0-12.0	0.6-4.8	2.3	3.1	/
SO_4^{2-} (mg.l^{-1})	30.0-81.0	/	19.0-107.5	0.5	/
Tryptophan (µmol.l^{-1})	0.06-1.20	/	/	/	0.03-0.24

[1] Benson-Evans et al. (2006)

[2] Koukal et al. (2004)

[3] Elewa H (2010)

[4] Hammou (2012)

Table.3 Comparison of Trace metals concentrations (Cu, Zn, Mn, Ni, Cd and Pb) in waters from Cheliff river (present study) and others selected rivers.

Metals	Concentrations in river water (µg.l^{-1})				
	Cheliff (Present study)	**Moulouya** [1] (Morocco)	**Guadalquivir**[2] (Spain)	**Nil** [3] (Egypt)	**Rhône** [4] (France)
Cu	5.7	2.2	2.6	2.0	0.4
Zn	76.1	/	1.6	5.0	5.8
Mn	484.4	6.3	20.6	40.0	/
Ni	10.7	/	2.3	5.0	/
Cd	0.30	0.03	0.01	2.00	/
Pb	1.76	0.35	0.17	5.00	0.01

[1] Bouabdli et al. (2005)

[2] Mendiguichia et al. (2007)

[3] Elewa H (2010)

[4] Olivier et al. (2011)

Table.4 Pearson correlation matrix of physicochemical (TSM, SO_4^{2-}, Cl^-, NO_2^-, NO_3^-, COD and BOD_5), fluorescent (Tryptophan and Tyrosine) and metallic (Cu, Zn, Fe, Al, Mn, Cr, Ni, As, Cd, Pb, Li and Sr) parameters in waters from Cheliff and Mina rivers. Bold values: significant correlations

	COD	BOD$_5$	Cl$^-$	SO$_4^{2-}$	NO$_2^-$	NO$_3^-$	TSM	Li	Al	Cr	Mn	Fe	Ni	Cu	Zn	As	Sr	Cd	Pb	Tryptophan	Tyrosine
COD	-																				
BOD$_5$	0,103	-																			
Cl$^-$	-0,144	-0,142	-																		
SO$_4^{2-}$	-0,438	-0,490	-0,014	-																	
NO$_2^-$	-0,002	0,059	0,160	-0,268	-																
NO3-	0,185	-0,064	-0,274	0,031	-0,313	-															
TSM	-0,101	0,064	-0,012	-0,228	0,497	0,010	-														
Li	-0,121	-0,285	0,485	0,416	-0,211	-0,088	-0,109	-													
Al	-0,312	-0,186	**0,665**	0,139	0,241	-0,192	0,271	0,111	-												
Cr	0,085	**0,976**	-0,142	**-0,560**	0,021	-0,053	0,055	-0,279	-0,203	-											
Mn	-0,264	-0,136	**0,718**	0,058	0,276	-0,097	0,347	0,133	**0,932**	-0,150	-										
Fe	-0,125	-0,086	0,357	-0,151	**0,751**	-0,200	0,376	-0,213	**0,600**	-0,090	**0,670**	-									
Ni	-0,233	-0,057	-0,239	0,014	0,021	**-0,522**	0,350	-0,262	0,124	-0,037	0,100	0,072	-								
Cu	-0,138	-0,048	0,038	-0,203	0,227	0,237	**0,812**	-0,067	0,353	-0,028	0,341	0,102	0,249	-							
Zn	-0,371	-0,202	0,476	0,122	0,204	-0,342	0,482	0,050	**0,885**	-0,200	**0,842**	**0,500**	**0,512**	0,493	-						
As	-0,179	-0,303	0,391	-0,231	0,392	-0,305	**0,599**	0,144	0,304	-0,291	0,378	0,231	0,336	**0,579**	**0,521**	-					
Sr	-0,308	-0,294	**0,752**	0,448	-0,101	-0,029	0,042	**0,768**	**0,643**	-0,326	**0,666**	0,192	-0,242	0,078	0,484	0,191	-				
Cd	-0,261	0,070	0,491	-0,103	0,273	-0,400	0,326	-0,181	**0,870**	0,076	**0,840**	**0,599**	0,455	0,320	**0,896**	0,314	0,313	-			
Pb	-0,374	-0,174	0,440	0,061	0,429	-0,406	0,389	-0,180	**0,870**	-0,182	**0,814**	**0,669**	0,459	0,375	**0,921**	0,461	0,298	**0,927**	-		
Tryptophan	-0,023	0,389	-0,179	**-0,543**	**0,743**	-0,246	**0,692**	-0,341	-0,054	0,406	-0,001	0,454	0,197	0,368	0,102	0,406	-0,363	0,137	0,199	-	
Tyrosine	0,105	0,256	-0,297	-0,468	**0,817**	-0,198	**0,557**	-0,394	-0,187	0,273	-0,139	**0,501**	0,139	0,216	-0,080	0,239	-0,491	-0,011	0,092	**0,928**	-