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High-frequency monitoring of surface water quality at the outlet of the Ibrahim River (Lebanon): A multivariate assessment

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ABSTRACT

Surface water quality monitoring is essential to evaluate the quality of a water resource. The current study assesses the quality of the Ibrahim River, one of the main Lebanese rivers, exposed to considerable human activities. 285 samples were collected at the outlet of the river, between May 2016 and July 2017, covering one hydrological year. Twenty-three physico-chemical parameters (flow, pH, temperature, electrical conductivity, turbidity, total suspended solids, total dissolved solids, dissolved oxygen, dissolved organic carbon, biochemical oxygen demand, chemical oxygen demand, chemical oxygen demand/biochemical oxygen demand, specific ultraviolet absorbance, dissolved cations (Na^+ , K^+ , Ca^{2+} , Mg^{2+}), total alkalinity, dissolved anions (Cl^- , NO_3^- , NO_2^- , PO_4^{3-} and SO_4^{2-})) and five microbiological tests were assessed (total germs, total coliforms, fecal coliforms, *Escherichia coli* and *Enterococcus*). A Principal Component Analysis (PCA) was applied for data analysis. The first component showed high levels of anthropogenic characteristics mainly due to organic and bacteriological parameters, differentiating low and high river discharges (explaining around 35% of the total variance). The second component was mainly influenced by mineral variables showing a clear annual discrimination (explaining about 17% of the total variance). Moreover, this study led to variables reduction from twenty-eight to ten. The final shortlisted parameters are Q, pH, EC, NO_3^- , total coliforms, fecal coliforms, BOD_5 , K^+ , TA and Cl^- . A new PCA performed with the reduced matrix validated this selection. The water quality index (WQI) was then calculated in this study, using the shortlisted parameters characterizing the basin, excluding the flow since it cannot be considered as a quality indicator. Thus, the water was evaluated as « medium » to « good » with values ranging from 63.1 (August 2016) to 73.1 (November and December 2016) with an average of 69.0 ± 1.9 . The proposed WQI should be further tested for monitoring practices in the Ibrahim River basin or other similar basins of the region.

1. Introduction

Surface water is vulnerable to pollution from anthropogenic activities, mainly waste disposal and agricultural practices. Due to the accumulation and transport of pollutants, rivers are important vectors of pollution. With about 40 rivers, Lebanon is rich in surface and ground water as compared to neighboring countries of the Middle East and North Africa region (Assaf and Saadeh, 2008; Chamas et al., 2001). Despite this water richness, water availability and quality are significantly declining due to the lack of efficient management plans and the widespread pollution sources. Pollution mostly results from the growing population, the industrial development, the agricultural

activities, the uncontrolled discharges of industries and the solid waste mismanagement (Abu-Jawdeh et al., 2000; El-Fadel et al., 2000; Singh et al., 2004; SOER, 2001). Several studies on Lebanese rivers showed that their water quality has deteriorated due to many human activities (Assaf and Saadeh, 2008; Houri and El Jeblawi, 2007; Kabbara et al., 2008; Massoud, 2012). In addition, climate change and global warming are leading to significant disturbances of hydrological cycles and thus, are affecting water pollution (Fan et al., 2010; Giannakopoulos et al., 2009). All these problems have a direct impact on the functioning of ecosystems and biodiversity.

As rivers are the source of water used for most inland human activities, it is important to constantly control their quality taking into

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consideration temporal and spatial variations. For efficient monitoring, many physico-chemical, bacteriological and hydrological parameters should be studied. Such monitoring, if applied on every river in a country, would demand significant financial inputs. Thus, it is of utmost importance to optimize the monitoring activity by reducing the number of tested parameters without losing significant information (Singh et al., 2004). To do so, multivariate approaches such as Principal Component Analysis (PCA) can be used (Fan et al., 2010; Simeonov et al., 2003; Singh et al., 2004). In fact, PCA was largely used to evaluate the seasonal and particular variations, identify potential sources of pollution (Barakat et al., 2016; Sharma et al., 2015; Simeonov et al., 2003) and reduce the dimensionality of a data set while retaining most of the existing information and variability in the data (Alberto et al., 2001). Once the number of monitored parameters is reduced, water quality indexes (WQI) was calculated providing a single dimensionless number reflecting the influence of different water quality parameters (Ramakrishnaiah et al., 2009; Sutadian et al., 2018). It has been used worldwide to evaluate water quality and management effectiveness and is becoming one of the most effective tools of communication to citizens and policy makers (Sutadian et al., 2018).

Therefore, the main objective of this study is to evaluate the water quality of the Ibrahim coastal basin, one of the main Lebanese rivers, classified as World Heritage Site (Fitzpatrick et al., 2001) and propose a reduction of factors to monitor this river without losing information. By linking WQI and PCA methodologies, this work will help upcoming water strategies in Lebanon (Reza and Singh, 2010; Tyagi et al., 2013).

Water samples were collected at the outlet of the Ibrahim River with higher density during flood events. In fact, high fluxes of materials are exported to the outlet of rivers during these hydrological events (El Azzi et al., 2013; El Azzi et al., 2016; Taghavi et al., 2011). Both physico-chemical and microbiological parameters were then tested, and a multivariate study formed the basis for the development of an Ibrahim WQI (IWQI) which would reliably describe and rate the quality of the water in the future.

2. Materials and methods

2.1. Study site

The Ibrahim River is 28 km long and estimated as one of the largest rivers in Lebanon (Chamas et al., 2001; Fitzpatrick et al., 2001). It is located 20 km north of the Lebanese capital and has an annual average flow of 16,106 m³/year (Abboud, 2002; Chamas et al., 2001). Its source is located at the top of Mount Lebanon (Roueiss and Afqa) and flows westward discharging through the city of Jbeil, into the Mediterranean Sea (Papazian, 1981).

The Ibrahim watershed has a total area of 330 km² with a structure consisting mainly of Jurassic and Cretaceous limestones (El Amil and Oudwane, 2000; Papazian, 1981). It presents high flows during winter and autumn seasons, but low flow occurs in late summer (Fitzpatrick et al., 2001). Two perennial sources Roueiss and Afqa, located respectively at an altitude of 1300 and 1200 m, ensure the flow of the river all year through. In addition, other additional tributaries with about thirty different sources feed the main river (El Amil and Oudwane, 2000; Papazian, 1981). The industrial activities on the Ibrahim River are mainly referring to small firms such as marble and food factories, woodcraft industries and many repair workshops. The agricultural sector consumes the greatest part of water in the basin. It occupies only 7.8% of the basin's total surface and is largely concentrated at the river mouth. Agricultural fields are mainly occupied by fruit bearing trees, citrus and banana plantation (Fig. 1). The rest of the basin is occupied by non-fertile lands (43%), oak trees and mixed forests (37%) and herbaceous vegetation (10%). Hill dams occupy only 0.42% and are distributed throughout the basin (Assaker, 2016; Daou et al., 2013).

2.2. Sampling and pretreatment

From May 2016 to July 2017, water samples were collected at a predefined sampling station located at the Ibrahim River outlet (longitude is 34° 37'42 N and the latitude is 35° 38,724E). This station collects all the water drained by the river as well as all the materials transported to the sea (Fig. 2). It should be noted here that frequent measurements of water salinity were carried out at the beginning of the work, to locate the appropriate study site avoiding the mixing zone between freshwater and seawater. An automatic sampling device, equipped with a pump, was installed at the study site. Samples were then collected mechanically from the middle of the river, at an equal distance from the two shores (Hébert and Légaré, 2000).

Water was collected by an aspiration pump via a sterile exchangeable polyethylene pipe that is coated with a grey polypropylene protective tube. The mentioned sampling system pump is equipped with a small modifiable valve in the purpose to regulate the water flow rate required for our sampling. Basic precautions were considered to avoid any pump malfunction, especially during flood events. Thus, the sampling device was safely protected in a small shelter placed on a concrete slab.

A hydrometric station operated by the Litani River Authority (LRA) is already installed at this location. As a result, discharge measurements were available. During the entire study period, discharge fluctuated between 0.05 and 60.29 m³/s (Flow rate average of 36 ± 13.74 m³/s). 95 sampling points are represented on the hydrograph (Fig. 3). One sampling was scheduled per week except during flood events, when samples were collected every two hours.

Prior to water sampling, 1L polypropylene bottles were cleaned with a laboratory grade detergent (phosphate-free) and rinsed with distilled water and nitric acid 10% (Demirak et al., 2006; Rodier et al., 2009). These bottles were used for physico-chemical tests. In parallel, borosilicate amber glass bottles of 1 L capacity were prepared for microbiological tests. They were rinsed with distilled water to remove any detergent traces or residues and then sterilized by autoclaving at 120 °C for 15 min before each sampling.

Each sampling point represented on Fig. 3 corresponds to three polypropylene bottles and three borosilicate amber glass bottles (of 1L capacity each). In total, 285 samples were collected. All bottles were labeled with the sampling date and time, then stored at 4 °C in a portable refrigerator and directly transported to the laboratory, as recommended by the French standards organization AFNOR (NF T90-100). Once in the laboratory, all microbiological analysis tests were conducted on the borosilicate bottles within 24 h of the sampling.

Concerning the polypropylene bottles, 700 mL of each polypropylene bottle was filtered through a cellulose nitrate membrane filter (0.22 µm pore size) previously rinsed with ultrapure water. Half of the filtrates were then stabilized by acidification with few drops of high purity nitric acid. All samples were stored in a cold room at around 4 °C, in complete darkness. An accomplishment of the study within a period of 24 h up to few months after the sampling campaign is still possible, if the water samples are properly stored (Hébert and Légaré, 2000).

2.3. Physico-chemical analysis

Several chemical, physical or biological reactions may occur inside the sampling bottle and can directly affect the composition of the collected sample. Since some of these reactions are too fast, there may be a lot of changes and effects in the first few minutes after the collection. Therefore, these countless reactions can influence the concentrations of many elements and may have a vast impact on the tested parameters. Thus, in situ analysis, within 5 min after sampling, are necessary for some of the measured indicators (Ahoussi et al., 2012). The main parameters tested on site were pH, conductivity (µS/cm), temperature (°C), dissolved oxygen (mg/L) and turbidity (NTU). The accuracy of

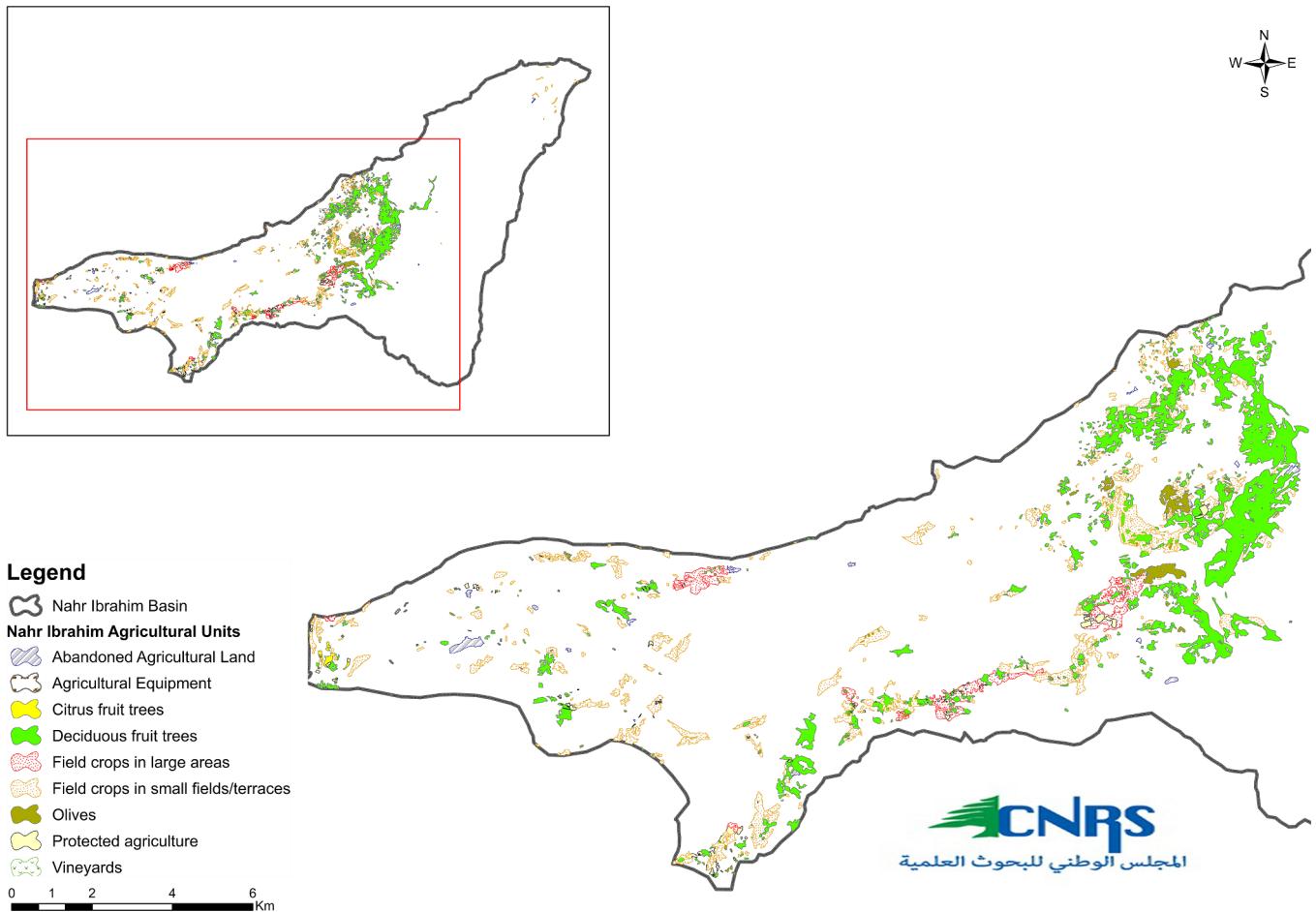


Fig. 1. Agricultural units of the Ibrahim basin area (Source: Lebanese National Council for Scientific Research – Lebanon CNRS).

each measurement was ensured by previous calibrations using appropriate buffer solutions (Lamizana-Diallo, 2008). Table 1 shows the studied parameters and the used analytical methods for each analysis.

2.4. Microbiological analysis

The water microbiological analysis was completed to detect and evaluate the existence of germs (Ouhmidou and Chahlaoui, 2015; Bou Saab et al., 2007; Daou et al., 2018). The presence of total germs (CFU/100 mL), total coliforms (CFU/100 mL), fecal coliforms (CFU/100 mL), *Escherichia coli* (CFU/100 mL) and *Enterococcus* (CFU/100 mL) was examined (Table 1).

The enumeration of culturable micro-organisms (total germs at 37 °C) was completed by inoculation in a nutrient agar culture medium followed by colony counting (ISO 6222:1999(E)). The used method for total coliforms, fecal coliforms, *Escherichia coli* and *Enterococcus* isolation is the membrane filtration technique by introducing water into a sterilized filtration unit containing a gridded sterile cellulose nitrate membrane filter of 0.45 µm diameter (NL ISO 9308-1:2012 and ISO 7899-2:2000(E)). After applying the vacuum, germs were retained on the filter that was then placed on the appropriate culture medium. Petri dishes were transferred to incubators at suitable temperature for 24–48 h and colonies were counted under a BOECO colony counting equipment. Results are expressed as the number of colony-forming units

per 100 mL (CFU/100 mL) of tested water.

2.5. Chemometric analysis: Principal Component Analysis (PCA)

PCA is an unsupervised exploratory method frequently used in surface water quality monitoring, for various purposes among which one could mention: modeling, outlier detection, variable selection and classification. Considering a set of n samples described by p variables, the data is gathered in a matrix X with n rows and p columns. In our case, a row of X corresponds to 28 physicochemical and microbiological measurements obtained from the analysis of a surface water sample, and a column of X to a variable for which the intensities have been measured for a total of 285 samples. Briefly, PCA produces a series of orthogonal axes (the Principal Components: PCs), a linear combination of the original variables, by decomposing the initial data matrix X into a matrix product $T.P^T$ (the “ T ” in P^T means “transposed matrix”). The T matrix is commonly named the “scores” matrix. The P matrix, the “loadings”, shows which variables are responsible for patterns found in the scores, T (Wold et al., 1987). PCA was performed on data matrix X (285×28) after column standardization (mean centering of each variable and dividing the resulting values by the column’s standard deviation). Data treatment was done using MATLAB version R2016a (The MathWorks, Natick, USA).



National Council for Scientific Research

Legend

- Point of Interest
- Tributaries
- Nahr Ibrahim River
- Streams and Tributaries
- Nahr Ibrahim Basin

0 15 30 60 90 120 Km

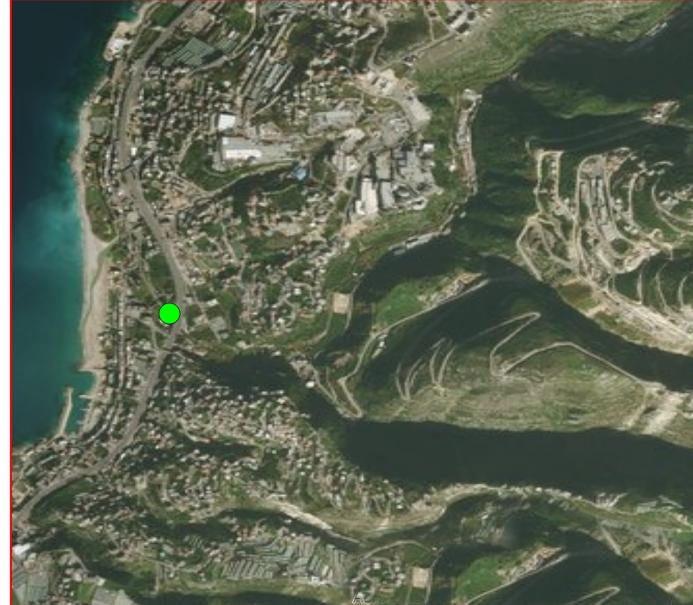
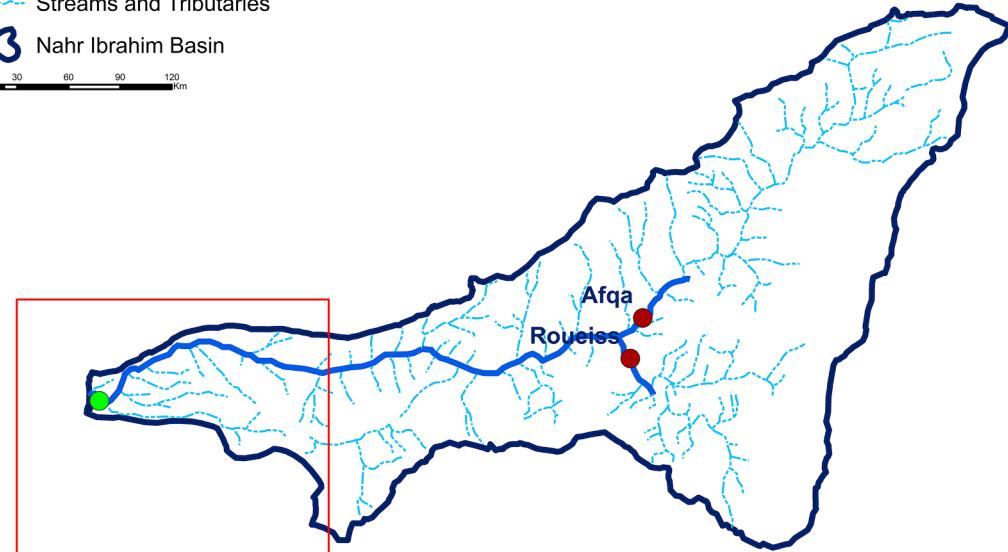


Fig. 2. The hydro-network of the Ibrahim basin locating the sampling station (Source: Lebanese National Council for Scientific Research – Lebanon CNRS).

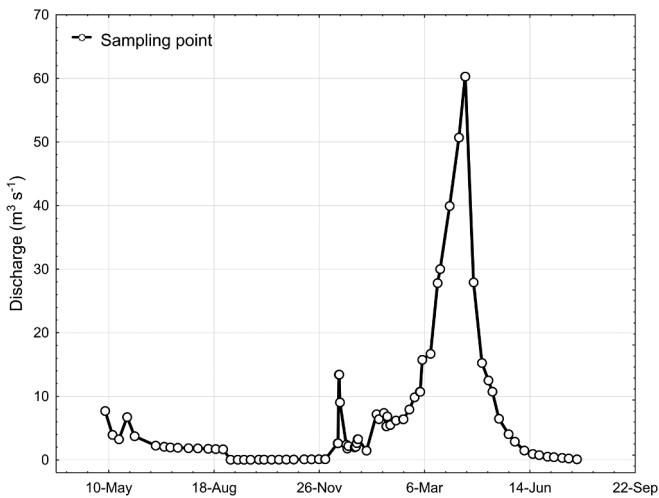


Fig. 3. Variations of the Ibrahim River discharge during the sampling campaign from May 2016 to July 2017. Sampling points are represented with the circles and were collected at the outlet during high flows (every two hours) and low flows (once a week).

2.6. Customized water quality index

Following the PCA, the proposed approach consisted in selecting the parameters that contributed the most to the highlighted trends; having loadings higher than 0.2, positively and negatively, on the first two PCs. After this first selection, Pearson correlations were computed, with statistical significance set at $p < 0.05$ and the least correlated parameters were retained. Moreover, when high correlations were obtained, a single parameter was selected as representative of the others. Parameters that can be simply calculated from other values were also removed.

The customized water quality index was then calculated, accounting only for the final shortlisted parameters, which characterize the Ibrahim watershed. The IWQI determination is assessed by applying the following equation:

$$WQI_{obj} = \frac{\sum_{i=1}^n CiPi}{\sum_{i=1}^n Pi}$$

where n is the total number of parameters, C_i is the value given to parameter i after normalization and P_i is the relative weight associated to each parameter. These values were adopted from multiple literatures (De La Mora-Orozco et al., 2017; Kannel et al., 2007; Koçer and Sevgili, 2014; Pesce and Wunderlin, 2000).

The WQI classification system transforms a set of measurements into a single number that simply reflects the quality of the studied surface water (Lumb et al., 2011; Srebotnjak et al., 2012). Values between 0 and 25 refer to “very bad” water quality, those between 26 and 50 to “bad” water quality, the ones between 51 and 70 to “medium” quality, those between 71 and 90 to “good” quality and values between 91 and 100 to an “excellent” water quality (Dojlido et al., 1994; Tyagi et al., 2013).

3. Results and discussion

Monitoring of the Ibrahim River at the outlet was conducted over a period of 15 months. All samples were analyzed for 28 parameters and their average and standard deviation values are presented in Table 1.

Principal Component Analysis was executed on the data matrix X (285×28) in the purpose of identifying temporal trends in the analyzed samples with regards to the 28 tested parameters. First, the data matrix was standardized to avoid any inappropriate discriminations that could be caused by vast variances in data measurements (Ringnér,

2008). Second, Kaiser-Meyer-Olkin (KMO) and Bartlett’s tests were done in order to check the appropriateness of this data for performing PCA. Data was recognized to be adequate for PCA ($KMO = 0.81$, indicating that PCA may be useful and significance level = 0, showing the presence of important relations between the variables) (Shrestha and Kazama, 2007).

PCA revealed that the first component (PC1) explained about 35%, while the second component (PC2) accounted for 17% of the total variance. The two sub-mentioned components explained jointly about 52% of the total variance and were therefore considered significant for our study. In each PC plot, the loadings (column chart) and the scores (plot) are presented. Loadings represent the contributions of the 28 variables to the different components, while scores plot illustrates the potential temporal trends within analyzed samples (red spots for samples collected in 2016 and blue spots for those collected in 2017).

Fig. 4 shows the scores of the 285 analyzed samples and the loadings referring to the 28 parameters on PC1. The anthropogenic (DOC, COD, NO_3^- and NO_2^-), physical (mainly T, DO, Turb, TSS), as well as all the bacteriological parameters, contribute basically to the construction of this PC. According to their locations on the scores plot, the 285 samples are mainly affected by the anthropogenic activities or not. In fact, samples collected during winter season and high overflow periods (from December 2016 to March 2017) present negative scores while samples collected during Low-Water periods (from May to November of 2016 and April to July of 2017) have positive scores with some variation between year 2016 and 2017.

The physical variables essentially implicated in this discrimination on PC1 are, water temperature (T) and dissolved oxygen (DO), which are considered as key water quality indicators (Sánchez et al., 2007), as well as turbidity (Turb) and total suspended solids (TSS) measurements. Checking the scores on PC1, a classical trend can be noticed on a temporal basis according to the water temperature. This temperature profile is reasonable where an increasing trend can be seen during summer period with decreasing scores during fall and winter seasons (Alberto et al., 2001). Concerning the DO levels, high scores are occurring from December 2016 to March 2017, while a decreasing trend is detected during summer time. In fact, such results are expected since these two parameters are inversely correlated and oxygen solubility shows a decrease as water temperature increases (Jung et al., 2016). In fact, the dissolved oxygen concentration is greater in high-water level and overflow periods due to water turbulence event (Daou et al., 2018). In addition, lower DO levels occur throughout Low-Water period since important anthropogenic inputs and low flow levels of the river contribute together in inhibiting natural oxygen dissolution.

When considering the scores of the 285 water samples, the contribution of organic components can be noticed. TSS and turbidity are influenced by the total discharge of the river and increase during flood event when higher erosion rates are observed (El Azzi et al., 2016). However, dissolved solids are more concentrated during summer season when only groundwater is contributing to the total discharge. In fact, the dissolved elements are diluted by surface and sub-surface runoffs during rain episodes and are therefore less concentrated during the winter season (Probst, 1992). This can explain the high levels of DOC during low-water periods. In addition, in-stream DOC production is important during low flow periods. In fact, the algal activity in spring as well as the leaf litter entering the stream in autumn can be responsible for DOC maxima during low flows (Mulholland and Hill, 1997). DOC has also been proven to increase during snowmelt periods (spring and summer) when runoff is mostly done via subsurface flow which activates new soil organic matter fluxes (Laudon et al., 2004).

Our results show high levels of nitrate during low-water periods. Previous studies stipulated that nitrate can enter streams through surface, subsurface and groundwater flow (El Azzi et al., 2016; Goolsby et al., 2000). Thus, its concentrations generally decrease in low flow, in the summer. In the Ibrahim River, an opposite pattern was observed. This can be explained by seasonal fluctuations in the number of bacteria

Table 1
Tested physico-chemical and microbiological parameters with mean values and standard deviations during the study period, at high flow and at low flow.

Parameter	Analytical Method	Mean ± Standard Deviation during the study period	Mean ± Standard Deviation during High-Water period	Mean ± Standard Deviation during Low-Water period
pH	pH Meter CyberScan pH11 part of ThermoFisherScientific Eutech NF T 90-008 Conductivity Meter CyberScan Con11 part of ThermoFisherScientific Eutech NF EN 27888 Checktemp1 Pocket Thermometer Hanna Oxygen meter Lutron DO5510 NF EN 25814 (March 1993) Turbidimeter TB1 Velp Scientifica NF EN ISO 7027 (March 2007)	8.04 ± 0.40 324.34 ± 72.37	7.96 ± 0.43 308.58 ± 79.56	8.20 ± 0.28 356.88 ± 37.92
Conductivity (EC, $\mu\text{S}/\text{cm}$)				
Temperature (T, °C)		15.85 ± 4.22	13.33 ± 2.39	21.05 ± 1.58
Dissolved Oxygen (DO, mg/L)		7.58 ± 1.26	8.23 ± 0.88	6.24 ± 0.76
Turbidity (Turb, NTU)		31.91 ± 38.13	42.44 ± 42.39	10.19 ± 7.33
Total Dissolved Solids (TDS, mg/L)	TDS meter (hold) HM digital AOAC 920.193 NF EN 872 (June 2005)	105.41 ± 22.86 32.39 ± 41.70	100.39 ± 24.85 43.54 ± 46.55	115.79 ± 13.00 9.36 ± 8.54
Total Suspended Solids (TSS, mg/L)	TOC-L SHIMADZU ISO 8245:1999	2.06 ± 0.77	1.71 ± 0.56	2.78 ± 0.63
Dissolved Organic Carbon (DOC, mg/L)	Lovibond OxidDirect NF EN 1899-2 (May 1998)	2.19 ± 0.57	2.28 ± 0.52	2.00 ± 0.63
Biochemical Oxygen Demand (BOD ₅ , mg/L)				
Chemical Oxygen Demand (COD, mg/L)	Spectrometry Helios Alpha Thermo Chemetrics Kits Titrimetry NF T 90-036 ISO 9963-1:1994	19.15 ± 6.88 130.81 ± 13.10	20.49 ± 7.32 131.87 ± 15.60	16.39 ± 4.83 128.62 ± 4.21
Total Alkalinity (TA, mg CaCO ₃ /L)	Spectrometry Helios Alpha Thermo 254 nm	1.74 ± 1.40	1.869 ± 1.18	1.50 ± 1.77
Specific Ultraviolet Absorbance (SUVA, L mg ⁻¹ m ⁻¹)				
Dissolved Sodium (Na ⁺ , mg/L)	Flame photometry M410 Sherwood Scientific NF T 90-019	3.88 ± 2.04	3.39 ± 2.11	4.90 ± 1.44
Dissolved Potassium (K ⁺ , mg/L)	Flame photometry M410 Sherwood Scientific NF T 90-019	1.02 ± 0.75	1.18 ± 0.86	0.69 ± 0.13
Dissolved Calcium (Ca ⁺⁺ , mg/L)	Titrimetry NF T 90-016 ISO 6058-1984	48.47 ± 6.92	50.65 ± 7.14	43.99 ± 3.40
Dissolved Magnesium (Mg ⁺⁺ , mg/L)	Titrimetry ISO 6059-1984	8.49 ± 4.09	7.46 ± 4.16	10.62 ± 2.98
Dissolved Chloride (Cl ⁻ , mg/L)	Titrimetry NF T 90-014 ISO 9297-1989	10.54 ± 3.10	11.25 ± 3.41	9.06 ± 1.47
Dissolved Nitrate (NO ₃ ⁻ , mg/L)	Spectrometry Helios Alpha Thermo NF T 90-045 ISO 7890-3:1988	0.82 ± 1.08	0.39 ± 0.54	1.70 ± 1.36
Dissolved Nitrite (NO ₂ ⁻ , mg/L)	Spectrometry Helios Alpha Thermo ISO 6777-1984	0.06 ± 0.05	0.07 ± 0.06	0.02 ± 0.02
Dissolved Phosphate (PO ₄ ³⁻ , mg/L)	Spectrometry Helios Alpha Thermo NF T 90-023	0.048 ± 0.05	0.03 ± 0.03	0.05 ± 0.06
Dissolved Sulfate (SO ₄ ²⁻ , mg/L)	Spectrometry Helios Alpha Thermo NF T 90-040	13.05 ± 6.85	11.64 ± 7.12	15.95 ± 5.19
Total Germs (CFU/100 mL)	ISO 6222:1999(E)	294.70 ± 1.03 10 ³	344.13 ± 0.82 10 ³	192.67 ± 0.53 10 ³
Total Coliforms	NL ISO 9308-1:2012 and ISO 7899-2:2000(E)	2.60 ± 0.78 10 ³	2.89 ± 0.75 10 ³	2.00 ± 0.38 10 ³
Fecal Coliforms		1.31 ± 0.56 10 ³	1.02 ± 0.34 10 ³	1.89 ± 0.45 10 ³
Escherichia coli		10.37 ± 11.06	4.20 ± 6.10	23.11 ± 7.53
Enterococcus (CFU/100 mL)		9.21 ± 8.78	4.35 ± 4.17	19.25 ± 7.12

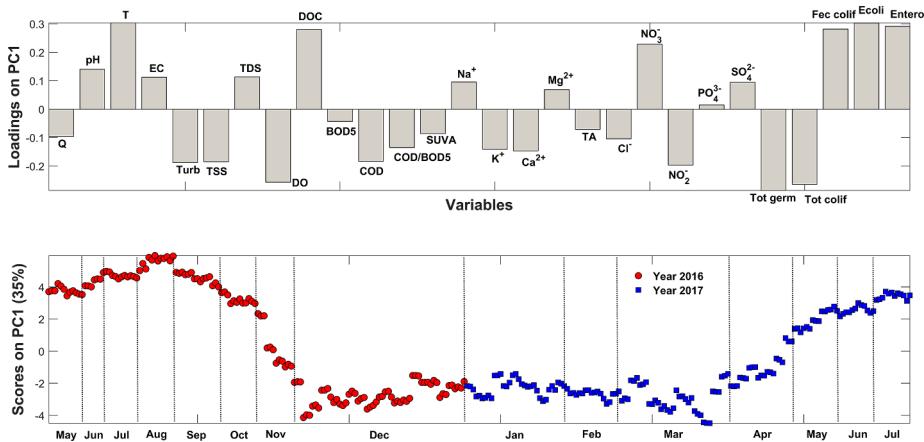


Fig. 4. Scores of the 285 samples on the Ibrahim River outlet (red spots for samples taken in 2016 and blue spots for samples taken in 2017) and loadings of the 28 tested parameters on PC1. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

and benthic microalgae colonizing the bed sediments and influencing the oxygen and nutrient levels at the sediment-water interface (Rysgaard et al., 1995). In summer, oxygen production by these populations increases the O₂ penetration in sediments improving the flux of inorganic nitrogen from sediments to overlying water (Rasmussen and Jørgensen, 1992; Rysgaard et al., 1995). Previous studies also proved that, during sunny days, O₂ from benthic photosynthesis reduces denitrification by more than 60% (Christensen et al., 1990). During winter season, nitrate arriving to the mainstream via surface, subsurface and groundwater flows was probably directed into the sediment by benthic assimilation in the surface layers and denitrification in the deeper sediment layers (Rysgaard et al., 1995).

The detected high rates of nitrite may originate from anthropogenic inputs and agricultural practices. In fact, fertilizer applications are common on the Ibrahim basin agricultural fields, particularly near the river mouth, as seen in Fig. 1 (Daou et al., 2016; Razmkhah et al., 2010). Nitrites present higher levels during autumn and winter seasons which confirms the important fluxes of organic material from the soil after rain events and their slow mineralization during these seasons (Heral et al., 1982).

These observations are endorsed by the bacteriological results. In fact, the low-water period is more affected by fecal contamination (the average mean values during the study period are as follow $1.31 \pm 0.56 \cdot 10^3$ CFU/100 mL for Fecal coliforms, 10.37 ± 11.06 CFU/100 mL for *Escherichia coli* and 9.21 ± 8.78 CFU/100 mL for *Enterococcus*) due to anthropogenic inputs and/or concentration factor as mentioned above.

Besides, the high-water period is marked by autochthonous germs (the mean values during the study period are as follow $294.70 \pm 1.03 \cdot 10^3$ CFU/100 mL for Total germs and $2.60 \pm 0.78 \cdot 10^3$ CFU/100 mL for Total coliforms) due to dilution factor and/or massive soil leaching. This bacterial profile does not only reveal the seasonal impact but also clarifies the anthropogenic evolution and consequently its effect on the water balance disturbance. Fig. 5 shows the scores of the 285 analyzed samples and the loadings referring to the 28 parameters on PC2. This second component is mainly described by mineral parameters (EC, TDS, Na⁺, TA, K⁺ and Cl⁻). Moreover, Q, pH and SUVA have also higher loadings than other parameters.

In this component, significant annual variation is detected when comparing 2016–2017. In fact, PC2 showed decreasing scores in 2017 as compared to 2016. This decrease can be explained by the higher precipitations in 2017 as compared to 2016 which might have led to different erosion and dilution patterns. It can also be related to the Ibrahim basin's structure consisting mainly of Jurassic and Cretaceous limestones leading to significant soil leaching during high-water seasons which can affect the mineral composition and pH of water, which is extremely influenced by the geological nature of the soil (Daou et al., 2013). This temporal variation is mainly perceptible in March and April 2017 when we witnessed the highest discharges (reaching $60.29 \text{ m}^3 \text{ s}^{-1}$) of the study period. The Ibrahim River is polluted by mineral discharges from industrial activities in its neighborhoods essentially marble industries, as well as by anthropogenic contaminants from surrounding areas. Moreover, the TDS measure, which refers mainly to

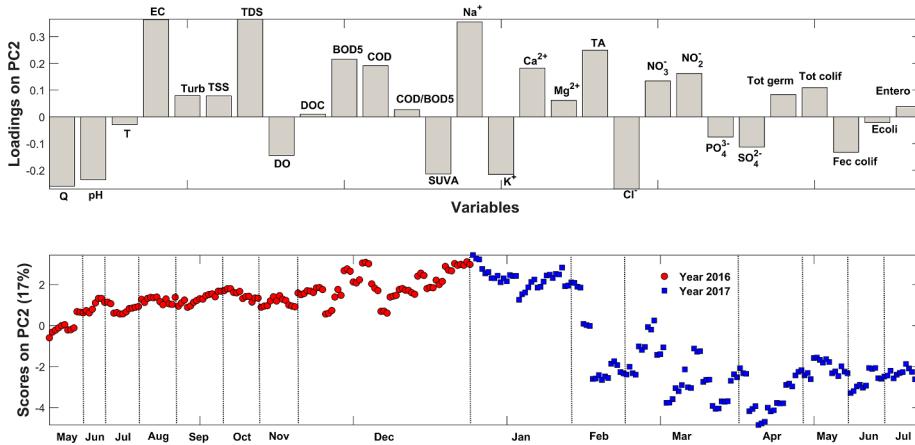


Fig. 5. Scores of the 285 samples on the Ibrahim River outlet (red spots for samples taken in 2016 and blue spots for samples taken in 2017) and loadings of the 28 tested parameters on PC2. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

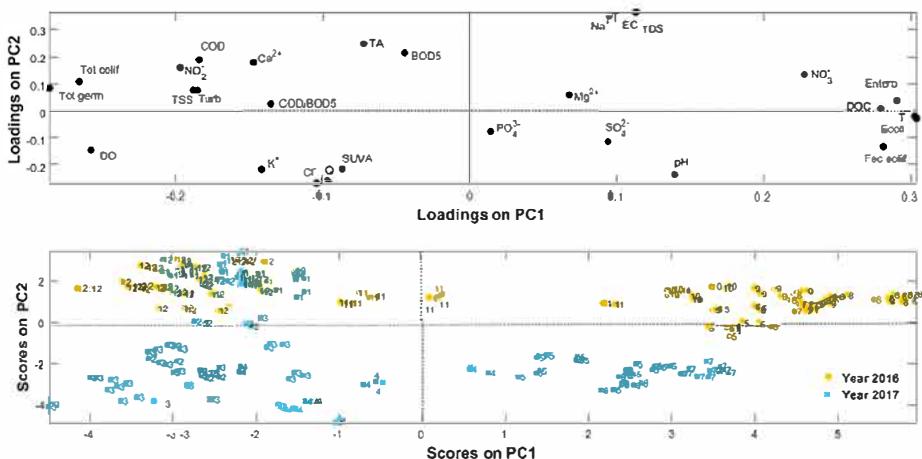


Fig. 6. Scores of the 285 samples on the Ibrahim River outlet (yellow spots for 2016 and blue spots for 2017; 1: January; 2: February; 3: March; 4: April; 5: May; 6: June; 7: July; 8: August; 9: September; 10: October; 11: November; 12: December) and loadings of the 28 tested parameters on PC1 vs PC2 plot. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 2
Correlation analysis between the nineteen shortlisted parameters.

	Q	pH	T	EC	TDS	DO	DOC	BOD5	SUVA	Na ⁺	K ⁺	TA	Cl ⁻	NO ₃ ⁻	Totgerms	Totcolif	Feccolif	Ecoli	Entero
Q	1																		
pH	0.03	1																	
T	-0.27	0.43	1																
EC	-0.45	-0.20	0.24	1															
TDS	-0.45	-0.20	0.24	0.99	1														
DO	0.28	-0.20	-0.83	-0.45	-0.45	1													
DOC	-0.36	0.48	0.82	0.32	0.32	-0.67	1												
BOD5	-0.15	-0.33	-0.15	0.13	0.13	-0.14	-0.07	1											
SUVA	0.21	0.22	-0.18	-0.42	-0.43	0.31	-0.20	-0.31	1										
Na ⁺	-0.48	-0.46	0.24	0.72	0.73	-0.42	0.24	0.19	-0.42	1									
K ⁺	0.29	-0.03	-0.43	-0.53	-0.52	0.67	-0.38	-0.26	0.14	-0.40	1								
TA	-0.40	-0.20	-0.32	0.48	0.49	0.21	-0.12	-0.01	-0.10	0.32	0.13	1							
Cl ⁻	0.60	0.11	-0.31	-0.39	-0.38	0.54	-0.28	-0.31	0.22	-0.44	0.46	-0.14	1						
NO ₃ ⁻	-0.27	0.14	0.64	0.38	0.40	-0.73	0.58	0.09	-0.44	0.46	-0.32	-0.07	-0.43	1					
Totgerms	0.09	-0.43	0.88	-0.12	-0.12	0.72	0.76	0.21	0.11	-0.16	0.39	0.33	0.26	0.58	1				
Totcolif	0.12	0.56	-0.79	-0.10	-0.11	0.61	0.70	0.16	0.06	0.01	0.40	0.32	0.18	-0.47	0.84	1			
Feccolif	-0.12	0.57	0.88	0.10	0.10	-0.61	0.85	-0.26	-0.04	0.03	-0.23	-0.31	-0.07	0.48	-0.82	-0.74	1		
Ecoli	-0.34	0.45	0.92	0.26	0.26	-0.74	0.85	-0.17	-0.16	0.25	-0.37	-0.19	-0.32	0.65	-0.88	-0.78	0.90	1	
Entero	-0.37	0.39	0.88	0.38	0.38	-0.77	0.85	-0.09	-0.21	0.32	-0.40	-0.10	-0.33	0.63	-0.79	-0.70	0.87	0.89	1

Shaded areas only point out the parameters that showed a correlation of $R > 0.7$.

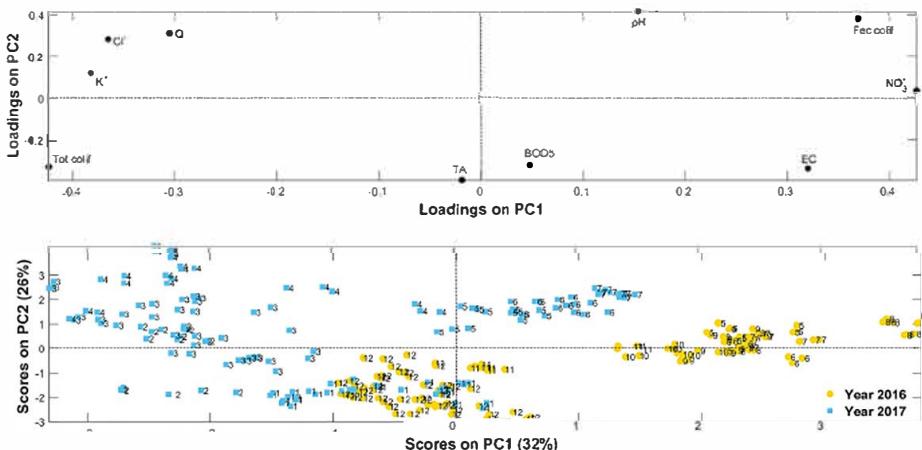


Fig. 7. Scores of the 285 samples on the Ibrahim River outlet (yellow spots for 2016 and blue spots for 2017; 1: January; 2: February; 3: March; 4: April; 5: May; 6: June; 7: July; 8: August; 9: September; 10: October; 11: November; 12: December) and loadings of the 10 shortlisted parameters on PC1 vs PC2 plot. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

various minerals, salts, metals, cations and anions present in water, besides organic substances contained in water (Weber-Scannell and Duffy, 2007), is a major parameter implicated in this PC2.

The specific ultraviolet absorbance index SUVA which is calculated through dividing the UV absorbance value at 254 nm (m^{-1}) by the dissolved organic carbon concentration (mg L^{-1}), indicates the source of organic compounds found in water (Westerhoff and Anning, 2000). Checking the scores on the PC2, lower SUVA levels are noticed during

year 2016, reaching $0.06 \text{ L mg}^{-1} \text{ m}^{-1}$ in September 2016, designating subsequently an anthropogenic hydrophilic organic matter source. On the other hand, mean values are obtained for the year 2017, fluctuating around the reference value of $4 \text{ L mg}^{-1} \text{ m}^{-1}$, which means that organic matter, during this period at the Ibrahim River outlet, originates from natural sources and is essentially composed by aromatic and humic substances (Hatt et al., 2013).

In order to attribute an appropriate trophic state for the Ibrahim

Table 3

Relative weight assigned to the 9 shortlisted parameters used for the evaluation process.

Parameter	Weight Pi
pH	2
EC	3
NO_3^-	1
Total coliforms	3
Fecal coliforms	3
BOD ₅	3
K ⁺	5
TA	3
Cl ⁻	3

River outlet station, the 285 samples were plotted according to PC1 and PC2 ([Fig. 6](#)).

This plot clearly demonstrates that the samples of the year 2016 form two well defined clusters, located in the negative quadrant of PC1 and in the positive quadrant of PC2 for the first cluster and corresponding to November and December 2016. While the second 2016 cluster is found in the positive quadrant of PC1 and in the positive one of PC2, referring to June, July, August, September and October 2016. However, May 2016 samples are not affected by PC2 since their scores are around 0. The discrimination between the two 2016 clusters is mainly due to bacterial indicators and organic parameters such as NO_2^- , NO_3^- and DOC. Concerning the samples of year 2017, three independent clusters are identified, classified as follow. The first cluster is situated in the negative quadrant of PC1 and in the positive quadrant of PC2, corresponding to January and February 2017. Regarding March and April 2017, scores are positioned in the negative quadrant of PC1 and PC2, essentially discriminated due to their DO, K⁺, Cl⁻, SUVA and Q values. Yet, the third cluster formed by samples collected on May, June and July 2017, scores are situated in the positive quadrant of PC1 and in the negative quadrant of PC2. This very-well discriminated cluster is mainly separated due to its SO_4^{2-} and pH parameters. According to the variable loadings responsible for the year 2017 discrimination, low-water level periods and high-water level ones are classified due to differences in some mineral components' levels, highlighting consequently a clear temporal discrimination.

3.1. Parameter selection using PCA and Pearson correlation

After performing PCA, a total of 19 parameters highly contributing to the first two principal components PC1 and PC2 were selected

(> 0.2 ; positively or negatively). This comprised 9 variables from PC1 (T, DO, DOC, NO_3^- , total germs, total coliforms, fecal coliforms, *Escherichia coli* and *Enterococcus*) and 10 variables from PC2 (Q, pH, EC, TDS, BOD₅, SUVA, Na⁺, K⁺, TA and Cl⁻). Then, Pearson correlations were computed ([Table 2](#)) and only parameters with low correlations were considered. For highly correlated parameters, a single parameter was selected as representative of the others.

In fact, water temperature was removed since it was highly correlated to all bacteriological parameters. Similarly, TDS and Na⁺ both demonstrated high correlations with EC and were removed. On another hand, DO and DOC measures, were excluded due to their high correlation with the NO_3^- as well as with all the bacteriological parameters. Furthermore, SUVA was removed since it is a calculated parameter. Finally, the total coliforms and the fecal coliforms' counting were selected among the bacteriological parameters.

This left us with 10 shortlisted variables to work with (Q, pH, EC, NO_3^- , total coliforms, fecal coliforms, BOD₅, K⁺, TA and Cl⁻).

Additionally, a new PCA was performed on the reduced matrix and the scores of the 285 analyzed samples and the loading referring to the 10 selected parameters were then plotted according to PC1 and PC2 as shown in [Fig. 7](#) (PC1 explained around 32% while the second component PC2 accounted for 26% of the total variance). This new plot leaves us with the same cluster distribution as the one previously shown in [Fig. 6](#), which consequently highlights the importance of the reduction of number of parameters while keeping the same classification. This will help maintain all the information and thus will allow more feasible and practicable monitoring of surface water quality ([Tripathi and Kumar Singal, 2019](#)).

9 of the parameters selected were used to apply the WQI approach for the first time on the Ibrahim River using relative weights according to [Table 3](#). The flow parameter was disregarded since it is not considered as a quality indicator.

While the average WQI is 69.037 ± 1.864 referring to a good quality range, the calculated values fluctuated between 63.125 and 73.125, as shown in [Fig. 8](#), which designates medium to good water quality ([Dojlido et al., 1994; Tyagi et al., 2013](#)). The monthly WQI average values are as follows: 69.2 ± 1.5 for May 2016, 68.8 ± 1.7 for June 2016, 68.2 ± 0.6 for July 2016, 65.3 ± 1.4 for August 2016, 67.3 ± 1.2 for September 2016, 67.8 ± 0.9 for October 2016, 70.8 ± 2.5 for November 2016, 70.6 ± 1.7 for December 2016, 69.9 ± 1.3 for January 2017, 69.1 ± 0.9 for February 2017, 68.2 ± 1.5 for March 2017, 68.7 ± 0.8 for April 2017, 68.0 ± 1.4 for May 2017, 68.9 ± 0.4 for June 2017 and 68.9 ± 0.9 for July 2017.

Comparably to the previous PCA results ([Fig. 4](#)), this trend shows a seasonal variation in the Ibrahim water quality, with a medium quality

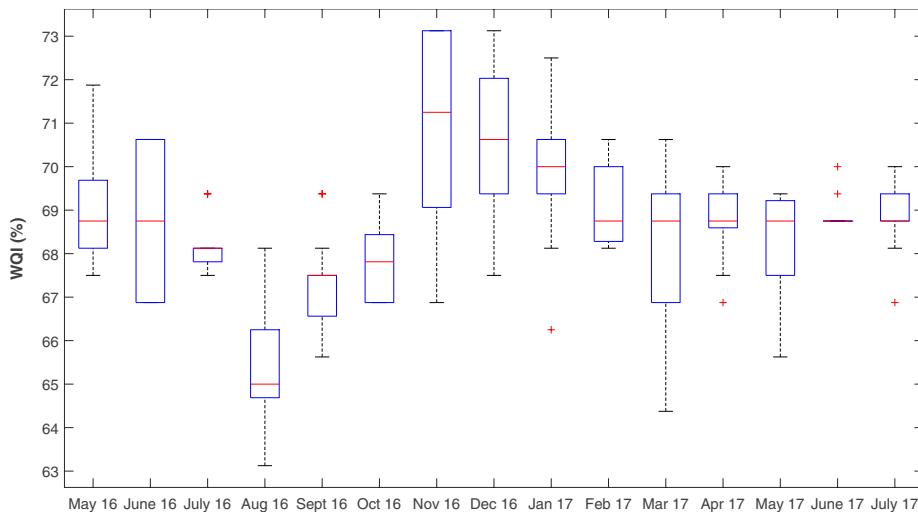


Fig. 8. Boxplot representation of the monthly variation of calculated WQI.

during low-water periods and a good one in high-water periods.

The IWQI should be further tested on the Ibrahim watershed. This technique can be extrapolated to other river basins, characterizing spatial and/or temporal variability. Such studies, reflecting the aggregate influence of multiple physico-chemical as well as microbiological parameters, integrating therefore several variables in a specific value, can be accomplished in forthcoming assessments to support the evaluation of various management strategies and monitoring decisions (Massoud, 2012).

4. Conclusion

The presented periodic assessment of the Ibrahim River water quality was based on a temporal measurement of various physico-chemical and bacteriological parameters. Sampling campaigns were executed on the river outlet for fifteen consecutive months, from May 2016 till July 2017. This monitoring generated complex multivariate data that needed interpretation using chemometric treatment coupled with flow dynamics and in-stream behavior knowledge. This analysis identified two principal components. The first one was characterized by organic and microbiological parameters and highlighted a temporal trend, differentiating low and high river discharges. Thus, it helped identifying the main factors responsible for the water quality variations, mainly related to anthropogenic inputs and flood events. The second component was mainly influenced by mineral variables and showed a clear annual discrimination. It is noticeable that mineral parameters implicated in this discrimination were not only due to natural events such as soil erosion and leaching but also to anthropogenic activities. To reduce the total number of parameters monitored in the future, influential quality indicators were identified. More specifically, PCA and Pearson correlations efficiently rendered important data reduction as it proposed only 10 parameters (Q , pH, EC, NO_3^- , total coliforms, fecal coliforms, BOD_5 , K^+ , TA and Cl^-) to assess temporal variations in the Ibrahim river water quality. These shortlisted parameters, excluding the flow Q , were then used to calculate the water quality index of the Ibrahim River outlet. With an average of 69.0 ± 1.9 , the IWQI values ranged between 63.1 and 73.1 referring to medium to good water quality thus showing a temporal quality variation. This study conducted on the Ibrahim River outlet can lead to future assessments of this river. Moreover, this methodology could be extended to the monitoring of the water quality in similar rivers.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ecolind.2019.04.061>.

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pH values	Ci	Pi	EC values	Ci	Pi	NO ₃ ⁻ values	Ci	Pi	Total coliforms values	Ci	Pi	Fecal coliforms values	Ci	Pi	BOD5 values	Ci	Pi	K ⁺ values	Ci	Pi	TA values	Ci	Pi	Cl ⁻ values	Ci	Pi	WQI
8,3	80	2	315	100	3	1,97	100	1	1070	70	3	1480	0	3	2	90	3	0,27	100	5	123	70	3	7,81	100	3	78,8461538
8,27	80	2	322	100	3	2,02	100	1	900	80	3	1370	10	3	2	90	3	0,32	100	5	130	70	3	7,7	100	3	81,1538462
8,32	80	2	325	100	3	2,07	100	1	1150	70	3	1540	0	3	2	90	3	0,3	100	5	132	70	3	8,02	100	3	78,8461538
8,5	80	2	343	100	3	3,05	100	1	1200	70	3	1430	0	3	2	90	3	0,31	100	5	122	70	3	7,21	100	3	78,8461538
8,44	80	2	349	100	3	2,94	100	1	1280	70	3	1480	0	3	2	90	3	0,27	100	5	130	70	3	7,53	100	3	78,8461538
8,48	80	2	353	100	3	2,87	100	1	1340	70	3	1450	0	3	2	90	3	0,32	100	5	130	70	3	7,3	100	3	78,8461538
8,25	80	2	314	100	3	2,51	100	1	1170	70	3	1460	0	3	2	90	3	0,38	100	5	133	70	3	7,11	100	3	78,8461538
8,18	80	2	309	100	3	2,71	100	1	950	80	3	1380	10	3	2	90	3	0,36	100	5	132	70	3	7,25	100	3	81,1538462
8,19	80	2	319	100	3	2,48	100	1	930	80	3	1430	0	3	2	90	3	0,41	100	5	134	70	3	7,09	100	3	80
8,37	80	2	352	100	3	1,82	100	1	1310	70	3	1360	10	3	3	80	3	0,39	100	5	130	70	3	7,01	100	3	78,8461538
8,31	80	2	347	100	3	1,93	100	1	1280	70	3	1450	0	3	3	80	3	0,38	100	5	129	70	3	7	100	3	77,6923077
8,29	80	2	355	100	3	1,77	100	1	1260	70	3	1330	10	3	3	80	3	0,41	100	5	128	70	3	7,03	100	3	78,8461538
8	90	2	344	100	3	2,71	100	1	1540	70	3	1290	10	3	2	90	3	0,62	100	5	125	70	3	7,34	100	3	80,7692308
7,92	90	2	339	100	3	2,94	100	1	1590	70	3	1370	10	3	2	90	3	0,58	100	5	124	70	3	7,55	100	3	80,7692308
7,89	90	2	349	100	3	3,01	100	1	1470	70	3	1410	0	3	2	90	3	0,63	100	5	126	70	3	7,22	100	3	79,6153846
7,98	90	2	350	100	3	3,49	100	1	1500	70	3	1380	10	3	3	80	3	0,6	100	5	125	70	3	7	100	3	79,6153846
7,78	90	2	354	100	3	3,55	100	1	1550	70	3	1490	0	3	3	80	3	0,56	100	5	127	70	3	6,89	100	3	78,4615385
7,83	90	2	348	100	3	3,67	100	1	1480	70	3	1550	0	3	3	80	3	0,57	100	5	125	70	3	6,97	100	3	78,4615385
8,07	80	2	365	100	3	3,37	100	1	1590	70	3	1570	0	3	2	90	3	0,61	100	5	128	70	3	7,04	100	3	78,8461538
8,01	80	2	359	100	3	3,88	100	1	1630	70	3	1620	0	3	2	90	3	0,63	100	5	125	70	3	6,91	100	3	78,8461538
8,04	80	2	367	100	3	3,56	100	1	1550	70	3	1660	0	3	2	90	3	0,59	100	5	125	70	3	6,9	100	3	78,8461538
8,13	80	2	355	100	3	2,58	100	1	1660	70	3	1730	0	3	2	90	3	0,63	100	5	128	70	3	7,14	100	3	78,8461538
8,01	80	2	348	100	3	2,19	100	1	1530	70	3	1770	0	3	2	90	3	0,57	100	5	130	70	3	7,07	100	3	78,8461538
8,05	80	2	359	100	3	2,22	100	1	1610	70	3	1830	0	3	2	90	3	0,64	100	5	128	70	3	7,21	100	3	78,8461538
8,08	80	2	352	100	3	2,09	100	1	1520	70	3	2020	0	3	2	90	3	0,66	100	5	128	70	3	7,05	100	3	78,8461538
8,11	80	2	347	100	3	1,97	100	1	1670	70	3	2100	0	3	2	90	3	0,66	100	5	131	70	3	6,96	100	3	78,8461538
8,05	80	2	356	100	3	1,89	100	1	1630	70	3	1950	0	3	2	90	3	0,71	100	5	130	70	3	6,91	100	3	78,8461538
8,12	80	2	360	100	3	1,55	100	1	1770	70	3	2130	0	3	3	80	3	0,56	100	5	130	70	3	8,01	100	3	77,6923077
8,07	80	2	355	100	3	1,69	100	1	1720	70	3	2200	0	3	3	80	3	0,62	100	5	132	70	3	7,88	100	3	77,6923077
8,13	80	2	362	100	3	1,60	100	1	1680	70	3	2070	0	3	3	80	3	0,58	100	5	131	70	3	7,92	100	3	77,6923077
7,95	90	2	355	100	3	1,48	100	1	2020	60	3	2240	0	3	3	80	3	0,64	100	5	130	70	3	7,31	100	3	77,3076923
7,9	90	2	351	100	3	1,53	100	1	1950	70	3	2380	0	3	3	80	3	0,58	100	5	132	70	3	7,44	100	3	78,4615385
7,91	90	2	359	100	3	1,54	100	1	2060	60	3	2330	0	3	3	80	3	0,63	100	5	130	70	3	7,57	100	3	77,3076923
8,36	80	2	399	100	3	4,06	100																				

7,98	90	2	400	100	3	3,07	100	1	1900	70	3	1810	0	3	2	90	3	0,57	100	5	134	70	3	10	90	3	78,4615385
8,15	80	2	388	100	3	2,58	100	1	1830	70	3	1590	0	3	2	90	3	0,59	100	5	137	70	3	9,09	100	3	78,8461538
8,03	80	2	391	100	3	2,77	100	1	1960	70	3	1660	0	3	2	90	3	0,62	100	5	135	70	3	10,09	80	3	76,5384615
8,07	80	2	390	100	3	2,49	100	1	1880	70	3	1550	0	3	2	90	3	0,56	100	5	135	70	3	9	100	3	78,8461538
8,29	80	2	385	100	3	2,72	100	1	1940	70	3	1380	10	3	2	90	3	0,62	100	5	131	70	3	10,09	80	3	77,6923077
8,2	80	2	382	100	3	2,82	100	1	1860	70	3	1470	0	3	2	90	3	0,6	100	5	130	70	3	10	90	3	77,6923077
8,19	80	2	389	100	3	3,05	100	1	1970	70	3	1440	0	3	2	90	3	0,66	100	5	133	70	3	10,01	80	3	76,5384615
8,3	80	2	391	100	3	2,47	100	1	1850	70	3	1490	0	3	2	90	3	0,49	100	5	125	70	3	10,02	80	3	76,5384615
7,99	90	2	389	100	3	2,55	100	1	1980	70	3	1330	10	3	2	90	3	0,53	100	5	126	70	3	10,17	80	3	78,4615385
8,01	80	2	393	100	3	2,21	100	1	2030	60	3	1300	10	3	2	90	3	0,55	100	5	127	70	3	10,1	80	3	76,5384615
8,24	80	2	384	100	3	2,64	100	1	2550	60	3	1260	10	3	2	90	3	0,68	100	5	120	70	3	10,01	80	3	76,5384615
8,17	80	2	380	100	3	2,25	100	1	2730	60	3	1310	10	3	2	90	3	0,72	100	5	121	70	3	10,13	80	3	76,5384615
8,14	80	2	388	100	3	2,17	100	1	2660	60	3	1220	10	3	2	90	3	0,66	100	5	122	70	3	10,27	80	3	76,5384615
7,57	90	2	346	100	3	0,18	100	1	2640	60	3	1110	10	3	2	90	3	0,54	100	5	126	70	3	9,64	100	3	79,6153846
7,68	90	2	349	100	3	0,18	100	1	2720	60	3	1230	10	3	2	90	3	0,58	100	5	130	70	3	8,23	100	3	79,6153846
7,72	90	2	349	100	3	0,18	100	1	2690	60	3	1190	10	3	2	90	3	0,61	100	5	130	70	3	8,93	100	3	79,6153846
7,75	90	2	330	100	3	0,27	100	1	2770	60	3	940	20	3	2	90	3	0,55	100	5	126	70	3	8,23	100	3	80,7692308
7,78	90	2	331	100	3	0,28	100	1	2650	60	3	1030	10	3	2	90	3	0,63	100	5	124	70	3	8,23	100	3	79,6153846
7,79	90	2	336	100	3	0,27	100	1	2700	60	3	1050	10	3	2	90	3	0,62	100	5	128	70	3	8,93	100	3	79,6153846
7,79	90	2	334	100	3	0,31	100	1	2730	60	3	820	20	3	2	90	3	0,6	100	5	122	70	3	6,81	100	3	80,7692308
7,8	90	2	333	100	3	0,32	100	1	2810	60	3	880	20	3	2	90	3	0,56	100	5	124	70	3	7,52	100	3	80,7692308
7,81	90	2	331	100	3	0,31	100	1	2780	60	3	930	20	3	2	90	3	0,54	100	5	128	70	3	7,52	100	3	80,7692308
7,21	90	2	295	100	3	0,41	100	1	2900	60	3	660	30	3	3	80	3	0,54	100	5	134	70	3	8,58	100	3	80,7692308
7,22	90	2	293	100	3	0,42	100	1	3100	50	3	740	20	3	3	80	3	0,55	100	5	130	70	3	8,93	100	3	78,4615385
7,24	90	2	297	100	3	0,42	100	1	3300	50	3	750	20	3	3	80	3	0,62	100	5	130	70	3	8,23	100	3	78,4615385
7,6	90	2	274	100	3	0,29	100	1	3700	50	3	620	30	3	3	80	3	0,65	100	5	130	70	3	8,93	100	3	79,6153846
7,57	90	2	274	100	3	0,29	100	1	3500	50	3	660	30	3	3	80	3	0,63	100	5	129	70	3	9,29	100	3	79,6153846
7,57	90	2	276	100	3	0,29	100	1	3300	50	3	630	30	3	3	80	3	0,66	100	5	126	70	3	8,93	100	3	79,6153846
7,46	90	2	279	100	3	0,54	100	1	3200	50	3	630	30	3	3	80	3	0,67	100	5	132	70	3	8,58	100	3	79,6153846
7,5	90	2	278	100	3	0,55	100	1	3000	60	3	680	30	3	3	80	3	0,59	100	5	136	70	3	8,23	100	3	80,7692308
7,49	90	2	276	100	3	0,54	100	1	3500	50	3	620	30	3	3	80	3	0,65	100	5	130	70	3	8,58	100	3	79,6153846
7,51	90	2	274	100	3	0,14	100	1	3700	50	3	660	30	3	3	80	3	0,53	100	5	108	70	3	8,93	100	3	79,6153846
7,53	90	2	272	100	3	0,15	100	1	3900	50	3	700	30	3	3	80	3	0,48	100	5	110	70	3	9,29	100	3	79,6153846
7,53	90	2	275	100	3	0,15	100	1	3500	50	3	620	30	3	3	80	3	0,55	100	5	116	70	3	8,93	100	3	79,6153846
7,49	90	2	261	100	3	0,18</																					

7,79	90	2	427	100	3	0,49	100	1	2570	60	3	810	20	3	2	90	3	0,48	100	5	150	70	3	9,29	100	3	80,7692308
7,8	90	2	428	100	3	0,50	100	1	2550	60	3	830	20	3	2	90	3	0,54	100	5	150	70	3	9,29	100	3	80,7692308
8,04	80	2	380	100	3	0,37	100	1	2490	60	3	880	20	3	2	90	3	0,71	100	5	140	70	3	8,93	100	3	80
8,04	80	2	387	100	3	0,37	100	1	2500	60	3	910	20	3	2	90	3	0,66	100	5	142	70	3	8,93	100	3	80
8,09	80	2	387	100	3	0,37	100	1	2430	60	3	860	20	3	2	90	3	0,65	100	5	146	70	3	8,93	100	3	80
7,85	90	2	379	100	3	0,36	100	1	2630	60	3	820	20	3	2	90	3	0,58	100	5	156	70	3	9,29	100	3	80,7692308
7,88	90	2	386	100	3	0,36	100	1	2520	60	3	850	20	3	2	90	3	0,67	100	5	150	70	3	8,93	100	3	80,7692308
7,9	90	2	385	100	3	0,36	100	1	2690	60	3	890	20	3	2	90	3	0,62	100	5	154	70	3	9,29	100	3	80,7692308
8,21	80	2	379	100	3	0,45	100	1	3300	50	3	830	20	3	3	80	3	0,63	100	5	164	70	3	8,23	100	3	77,6923077
8,26	80	2	380	100	3	0,46	100	1	3400	50	3	880	20	3	3	80	3	0,57	100	5	160	70	3	8,58	100	3	77,6923077
8,24	80	2	378	100	3	0,45	100	1	3000	60	3	890	20	3	3	80	3	0,55	100	5	160	70	3	8,58	100	3	78,8461538
8,22	80	2	381	100	3	0,41	100	1	3200	50	3	770	20	3	3	80	3	0,66	100	5	156	70	3	9,29	100	3	77,6923077
8,23	80	2	380	100	3	0,42	100	1	3000	60	3	800	20	3	3	80	3	0,59	100	5	150	70	3	8,93	100	3	78,8461538
8,23	80	2	383	100	3	0,41	100	1	3600	50	3	810	20	3	3	80	3	0,64	100	5	150	70	3	8,93	100	3	77,6923077
8,19	80	2	412	100	3	0,43	100	1	3300	50	3	780	20	3	3	80	3	0,5	100	5	138	70	3	11,77	80	3	75,3846154
8,2	80	2	413	100	3	0,44	100	1	3500	50	3	750	20	3	3	80	3	0,53	100	5	136	70	3	10,35	80	3	75,3846154
8,21	80	2	410	100	3	0,44	100	1	3000	60	3	770	20	3	3	80	3	0,48	100	5	134	70	3	10,35	80	3	76,5384615
8,18	80	2	413	100	3	0,48	100	1	3470	50	3	680	30	3	3	80	3	0,54	100	5	150	70	3	8,23	100	3	78,8461538
8,2	80	2	412	100	3	0,48	100	1	3550	50	3	730	20	3	3	80	3	0,55	100	5	150	70	3	8,93	100	3	77,6923077
8,22	80	2	410	100	3	0,48	100	1	3490	50	3	720	20	3	3	80	3	0,55	100	5	150	70	3	9,64	100	3	77,6923077
8,29	80	2	410	100	3	0,33	100	1	3560	50	3	710	20	3	2	90	3	0,66	100	5	154	70	3	8,93	100	3	78,8461538
8,3	80	2	412	100	3	0,33	100	1	3510	50	3	750	20	3	2	90	3	0,58	100	5	150	70	3	8,93	100	3	78,8461538
8,32	80	2	412	100	3	0,33	100	1	3490	50	3	720	20	3	2	90	3	0,67	100	5	150	70	3	8,23	100	3	78,8461538
8,33	80	2	414	100	3	0,32	100	1	3000	60	3	770	20	3	2	90	3	0,57	100	5	148	70	3	9,29	100	3	80
8,34	80	2	410	100	3	0,33	100	1	2900	60	3	760	20	3	2	90	3	0,6	100	5	148	70	3	9,64	100	3	80
8,34	80	2	412	100	3	0,32	100	1	3000	60	3	780	20	3	2	90	3	0,61	100	5	150	70	3	8,93	100	3	80
8,29	80	2	402	100	3	0,35	100	1	3100	50	3	800	20	3	2	90	3	0,48	100	5	150	70	3	11,77	80	3	76,5384615
8,28	80	2	405	100	3	0,36	100	1	3300	50	3	770	20	3	2	90	3	0,53	100	5	152	70	3	10,35	80	3	76,5384615
8,27	80	2	402	100	3	0,36	100	1	3200	50	3	740	20	3	2	90	3	0,47	100	5	150	70	3	10,35	80	3	76,5384615
7,92	90	2	393	100	3	0,34	100	1	3300	50	3	830	20	3	2	90	3	0,82	100	5	154	70	3	11,77	80	3	77,3076923
7,9	90	2	395	100	3	0,34	100	1	3100	50	3	840	20	3	2	90	3	0,82	100	5	150	70	3	11,77	80	3	77,3076923
7,79	90	2	395	100	3	0,34	100	1	3000	60	3	790	20	3	2	90	3	0,84	100	5	150	70	3	10,35	80	3	78,4615385
7,33	90	2	371	100	3	0,30	100	1	3500	50	3	810	20	3	2	90	3	0,96	100	5	130	70	3	11,77	80	3	77,3076923
7,21	90	2	386	100	3	0,30	100	1	3100	50	3	850	20	3	2	90	3	0,9	100	5	136	70	3	11,77	80	3	77,3076923
7,29	90	2	385	100	3	0,30	100	1	3900	50	3	800															

8,18	80	2	212,7	100	3	0,50	100	1	3400	50	3	800	20	3	2	90	3	2,81	80	5	132	70	3	11,77	80	3	72,6923077
8,24	80	2	212,2	100	3	0,49	100	1	4000	50	3	850	20	3	2	90	3	2,88	80	5	130	70	3	10,35	80	3	72,6923077
8,28	80	2	211,9	100	3	0,50	100	1	3700	50	3	850	20	3	2	90	3	2,9	80	5	135	70	3	12,12	80	3	72,6923077
8,27	80	2	213	100	3	0,34	100	1	3200	50	3	840	20	3	2	90	3	2,91	80	5	130	70	3	8,58	100	3	75
8,3	80	2	212,8	100	3	0,36	100	1	3200	50	3	880	20	3	2	90	3	2,94	80	5	134	70	3	8,93	100	3	75
8,23	80	2	213	100	3	0,36	100	1	3400	50	3	830	20	3	2	90	3	3,03	80	5	128	70	3	8,23	100	3	75
8,08	80	2	211,3	100	3	0,29	100	1	3300	50	3	870	20	3	2	90	3	2,91	80	5	136	70	3	9,64	100	3	75
8,17	80	2	212	100	3	0,30	100	1	3000	60	3	920	20	3	2	90	3	3,05	80	5	133	70	3	10,35	80	3	73,8461538
8,22	80	2	211,1	100	3	0,30	100	1	3100	50	3	960	20	3	2	90	3	2,98	80	5	134	70	3	11,42	80	3	72,6923077
8,15	80	2	360,5	100	3	0,01	100	1	2960	60	3	960	20	3	2	90	3	1,73	90	5	138	70	3	13,90	80	3	75,7692308
8,2	80	2	362,7	100	3	0,02	100	1	2890	60	3	1010	10	3	2	90	3	1,96	90	5	137	70	3	13,19	80	3	74,6153846
8,18	80	2	361,9	100	3	0,02	100	1	2910	60	3	930	20	3	2	90	3	1,83	90	5	135	70	3	13,54	80	3	75,7692308
8,01	80	2	417,8	100	3	0,07	100	1	2920	60	3	1000	20	3	2	90	3	1,92	90	5	144	70	3	16,73	80	3	75,7692308
8,13	80	2	418,6	100	3	0,08	100	1	2970	60	3	960	20	3	2	90	3	1,37	90	5	145	70	3	17,44	80	3	75,7692308
8,08	80	2	419,3	100	3	0,08	100	1	2880	60	3	1020	10	3	2	90	3	1,06	90	5	147	70	3	16,38	80	3	74,6153846
7,92	90	2	230,7	100	3	0,02	100	1	2980	60	3	1030	10	3	2	90	3	1,61	90	5	140	70	3	12,48	80	3	75,3846154
8,03	80	2	239,4	100	3	0,02	100	1	2930	60	3	970	20	3	2	90	3	1,73	90	5	142	70	3	13,19	80	3	75,7692308
8,09	80	2	286,4	100	3	0,02	100	1	2990	60	3	990	20	3	2	90	3	1,66	90	5	145	70	3	11,77	80	3	75,7692308
8,2	80	2	154,7	100	3	0,06	100	1	3100	50	3	1010	10	3	2	90	3	2,11	80	5	125	70	3	15,32	80	3	71,5384615
8,14	80	2	155,3	100	3	0,06	100	1	3500	50	3	1050	10	3	2	90	3	2,5	80	5	123	70	3	14,96	80	3	71,5384615
8,16	80	2	155,7	100	3	0,06	100	1	3300	50	3	1090	10	3	2	90	3	2,25	80	5	125	70	3	14,61	80	3	71,5384615
8,19	80	2	146	100	3	0,11	100	1	3800	50	3	1120	10	3	2	90	3	2,29	80	5	130	70	3	13,90	80	3	71,5384615
8,14	80	2	150,3	100	3	0,11	100	1	4100	40	3	1080	10	3	2	90	3	2,91	80	5	131	70	3	14,25	80	3	70,3846154
8,18	80	2	150,2	100	3	0,11	100	1	3600	50	3	1160	10	3	2	90	3	2,37	80	5	132	70	3	13,19	80	3	71,5384615
8,25	80	2	278,6	100	3	0,03	100	1	3300	50	3	1140	10	3	2	90	3	1,36	90	5	124	70	3	13,19	80	3	73,4615385
8,24	80	2	143,8	100	3	0,03	100	1	3000	60	3	1110	10	3	2	90	3	1,84	90	5	126	70	3	13,90	80	3	74,6153846
8,28	80	2	143,3	100	3	0,03	100	1	3500	50	3	1170	10	3	2	90	3	1,54	90	5	123	70	3	13,90	80	3	73,4615385
8,27	80	2	296,1	100	3	0,08	100	1	2930	60	3	1130	10	3	2	90	3	2,18	80	5	154	70	3	8,23	100	3	75
8,26	80	2	292,7	100	3	0,08	100	1	2860	60	3	1150	10	3	2	90	3	2,39	80	5	150	70	3	8,93	100	3	75
8,26	80	2	289,7	100	3	0,08	100	1	2880	60	3	1210	10	3	2	90	3	2,22	80	5	151	70	3	8,58	100	3	75
8,1	80	2	194	100	3	0,19	100	1	2820	60	3	1200	10	3	2	90	3	1,23	90	5	110	70	3	16,86	80	3	74,6153846
8,09	80	2	188	100	3	0,17	100	1	2910	60	3	1180	10	3	2	90	3	1,73	90	5	111	70	3	16,15	80	3	74,6153846
7,89	90	2	179,1	100	3	0,18	100	1	2870	60	3	1100	10	3	2	90	3	1,56	90	5	112	70	3	17,44	80	3	75,3846154
8,3	80	2	128,2	100	3	0,31	100	1	2740	60	3	1110	10	3	2	90	3	2,78	80	5	124	70	3	16,51	80	3	72,6923077
8,23	80	2	123,7	100	3	0,28	100</td																				

8,41	80	2	281	100	3	0,16	100	1	2020	60	3	1640	0	3	2	90	3	0,54	100	5	114	70	3	12,68	80	3	76,5384615
8,43	80	2	282,2	100	3	0,10	100	1	1590	70	3	1770	0	3	2	90	3	0,36	100	5	114	70	3	12,68	80	3	76,5384615
8,41	80	2	284,1	100	3	0,09	100	1	1620	70	3	1730	0	3	2	90	3	0,38	100	5	114	70	3	11,97	80	3	76,5384615
8,38	80	2	282,6	100	3	0,11	100	1	1660	70	3	1800	0	3	2	90	3	0,39	100	5	112	70	3	11,26	80	3	76,5384615
8,17	80	2	282,5	100	3	0,20	100	1	1380	70	3	1790	0	3	4	70	3	0,37	100	5	110	70	3	15,59	80	3	74,2307692
8,32	80	2	278	100	3	0,19	100	1	1440	70	3	1850	0	3	4	70	3	0,36	100	5	108	70	3	14,17	80	3	74,2307692
8,36	80	2	275,1	100	3	0,20	100	1	1520	70	3	1760	0	3	4	70	3	0,39	100	5	112	70	3	14,88	80	3	74,2307692
8,4	80	2	286,2	100	3	0,11	100	1	1410	70	3	1840	0	3	3	80	3	0,55	100	5	106	70	3	12,68	80	3	75,3846154
8,37	80	2	287,1	100	3	0,12	100	1	1370	70	3	1770	0	3	3	80	3	0,54	100	5	108	70	3	11,26	80	3	75,3846154
8,39	80	2	285,6	100	3	0,13	100	1	1480	70	3	1860	0	3	3	80	3	0,52	100	5	106	70	3	11,97	80	3	75,3846154
8,37	80	2	298,3	100	3	0,13	100	1	1370	70	3	1920	0	3	2	90	3	0,89	100	5	120	70	3	12,68	80	3	76,5384615
8,55	70	2	299,1	100	3	0,15	100	1	1420	70	3	1870	0	3	2	90	3	0,82	100	5	125	70	3	11,26	80	3	75,7692308
8,61	70	2	299,8	100	3	0,15	100	1	1430	70	3	1900	0	3	2	90	3	0,85	100	5	123	70	3	11,97	80	3	75,7692308
8,55	70	2	300,3	100	3	0,12	100	1	1480	70	3	1830	0	3	2	90	3	0,88	100	5	126	70	3	10,35	80	3	75,7692308
8,59	70	2	299,9	100	3	0,14	100	1	1350	70	3	1940	0	3	2	90	3	0,92	100	5	128	70	3	11,77	80	3	75,7692308
8,63	70	2	301,9	100	3	0,13	100	1	1370	70	3	1860	0	3	2	90	3	0,93	100	5	130	70	3	12,48	80	3	75,7692308
8,56	70	2	301,4	100	3	0,22	100	1	1520	70	3	1870	0	3	2	90	3	0,87	100	5	118	70	3	13,90	80	3	75,7692308
8,58	70	2	303,5	100	3	0,19	100	1	1490	70	3	2010	0	3	2	90	3	0,88	100	5	120	70	3	13,19	80	3	75,7692308
8,59	70	2	302,1	100	3	0,21	100	1	1550	70	3	1940	0	3	2	90	3	0,85	100	5	124	70	3	11,77	80	3	75,7692308
8,53	70	2	298,3	100	3	0,11	100	1	1580	70	3	1930	0	3	1	90	3	0,93	100	5	130	70	3	11,06	80	3	75,7692308
8,47	80	2	298,7	100	3	0,14	100	1	1550	70	3	2020	0	3	1	90	3	0,96	100	5	126	70	3	10,35	80	3	76,5384615
8,56	70	2	299,7	100	3	0,14	100	1	1630	70	3	2100	0	3	1	90	3	0,97	100	5	128	70	3	10,35	80	3	75,7692308
8,6	70	2	301,1	100	3	0,17	100	1	1660	70	3	2100	0	3	2	90	3	0,91	100	5	130	70	3	9,64	100	3	78,0769231
8,61	70	2	304,3	100	3	0,15	100	1	1720	70	3	1950	0	3	2	90	3	0,89	100	5	130	70	3	11,06	80	3	75,7692308
8,61	70	2	304,7	100	3	0,14	100	1	1600	70	3	2030	0	3	2	90	3	0,94	100	5	132	70	3	10,35	80	3	75,7692308
8,53	70	2	303	100	3	0,26	100	1	1770	70	3	2160	0	3	1	90	3	0,88	100	5	136	70	3	10,35	80	3	75,7692308
8,6	70	2	306,3	100	3	0,26	100	1	1740	70	3	1970	0	3	1	90	3	0,86	100	5	138	70	3	11,06	80	3	75,7692308
8,62	70	2	306,7	100	3	0,25	100	1	1810	70	3	2080	0	3	1	90	3	0,9	100	5	140	70	3	11,06	80	3	75,7692308
8,59	70	2	301,9	100	3	0,21	100	1	1780	70	3	2220	0	3	1	90	3	0,92	100	5	124	70	3	10,35	80	3	75,7692308
8,62	70	2	304,9	100	3	0,21	100	1	1830	70	3	2190	0	3	1	90	3	0,92	100	5	128	70	3	10,35	80	3	75,7692308
8,63	70	2	305,3	100	3	0,21	100	1	1850	70	3	2150	0	3	1	90	3	0,94	100	5	124	70	3	11,06	80	3	75,7692308
8,6	70	2	305,1	100	3	0,17	100	1	1930	70	3	2150	0	3	1	90	3	0,91	100	5	128	70	3	8,93	100	3	78,0769231
8,58	70	2	305,4	100	3	0,15	100	1	1890	70	3	2300	0	3	1	90	3	0,93	100	5	128	70	3	9,64	100	3	78,0769231
8,59	70	2	306	100	3	0,20	100	1	1940	70	3	2360	0	3	1	90	3	0,9	100	5	132	70	3	10,35	80	3	75,76