

Statistical Analysis of Forms of Phosphorus in Aquatic Sediments -Case of the Main Rivers in the area of Meknes (Morocco)-

Hind Omari ¹, Adil Lammini ¹, Ali Dehbi ¹, Abdelaziz Abdallaoui ^{2*}

PhD Student, Analytical Chemistry and Environment Team, Department of Chemistry, Faculty of Sciences, Moulay Ismail University, Meknes, Morocco ¹

Professor, Analytical Chemistry and Environment Team, Department of Chemistry, Faculty of Sciences, Moulay Ismail University, Meknes, Morocco ²

ABSTRACT: For a contribution to the study of the water quality of the Meknes region, we realized samples of surficial sediments at the level of the main wadis of this region in four different seasons.

The results of the study of different phosphorus fractions of studied sediments have been the subject of a principal component analysis (PCA). This statistical method allowed us to identify the principal relationships between forms of phosphorus and showed that the increase in total phosphorus content (P_{tot}) of the studied sediments is primarily caused by increased levels of inorganic forms of phosphorus {Fe (OOH)-P} and CaCO₃-P}.

Furthermore, for having the relationship between the sampling periods, sampling stations and forms of phosphorus, we performed a factorial correspondence analysis (FCA), as well as the hierarchical ascendant analysis (HAC), which helped to classify the individuals with similar behaviour in three different classes.

Indeed, the factorial correspondence analysis is a method that can be combined to the HAC because they use the same distance between individuals. The FCA has not only allows to classify individuals but has allows us also the identification of the homogeneous groups. The HAC using the same distance as that the FCA allows us to clarify the contours of homogeneous classes.

KEYWORDS: Sediment, Forms of phosphorus, Statistical analysis, PCA, FCA, HAC.

I. INTRODUCTION

The city of Meknes is situated in the northern part of Morocco; it is the second city of the plain Sais after the city of Fez. It is one of the most important agriculture regions of the Kingdom and is home every year since 2006, "The International Agriculture Show in Morocco". The intensification of industrial and agricultural activities as well as the rapid increase in the population of this city, leads to serious problems in the natural environment [1], and generate pollutants such as phosphorus that can affect the physicochemical and biological quality from the aquatic environment.

Furthermore, the sediment has the ability to store phosphorus in abundance in different forms. This sediment load can be put into solution under specific physicochemical conditions such as pH and redox potential which affect the mobility of phosphorus [2]. That sometimes poses serious problems with regard the waters quality of these rivers.

The main objectives of this study are the determination of the main correlations that might exist between the forms of phosphorus, and the establishment of relations between the stations (space), and forms of phosphorus (variables), and also the identification of homogeneous groups (individuals classes).

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II. MATERIAL AND METHODS

II.1 Study sites

This study was done on three rivers of Meknes region, Oued Boufekrane, Oued Ouislane and Oued Toulal. The first two streams have attracted the interest of many researchers [3] [4].

The Oued Boufekrane is a permanent watercourse of the Middle Atlas; it rises to the west of El Hajeb, in the Middle-Atlas, 750 meters above the sea level [5]: Ain Maârouf which flows in the agricultural plain of the plateau of Meknes and passes through the town of Boufekrane to which it owns its name to 10 km from the source. 34 km downstream the wadi crosses the valley separating the old town and the new town of the city of Meknes. At its middle course, it receives domestic and industrial discharges not treated in the city of Meknes [6].

Oued Boufekrane joined the two other streams to form Oued R'dom, first Oued Toulal which crosses the commune of Toulal, then Oued Ouislane which belongs to the superficial hydrographic network of the region of Meknes, starting from the south-east of the village of Boufekrane.

II.2 Sampling

Sediment samples were collected during four different seasons (Autumn, Winter, Spring and Summer) at nine stations, upstream, downstream, and at the confluences of three wadis (36 samples) (Table 1).

Table. 1 Location of sampling stations

Stations	Watercourse	Situation of the point from the rivers
S1	Ouislane	upstream
S2	Ouislane	In the middle
S3	Ouislane	Just before the confluence of the Oued Ouislane with the Oued Boufekrane
S4	Boufekrane	upstream
S5	Boufekrane	Just before the confluence of the Oued Ouislane with the Oued Toulal
S6	Toulal	upstream
S7	Toulal	Just before the confluence of the Oued Toulal with the Oued Boufekrane
S8	R'dom	Just after the confluence of the Oued Toulal with the Oued Boufekrane
S9	R'dom	Just after the confluence of the Oued Ouislane with the Oued Boufekrane

Sediment samples were taken using an Eckman grab to pick the top 5 cm of sediment. These samples have been preserved in plastic bags during their transport to the laboratory, where they will be processed in 24 hours. The fraction less than 200 μm has been preserved for analysis, after drying, and soft grinding to homogenize the sample. Figure 1 shows the location of sampling stations on the map.

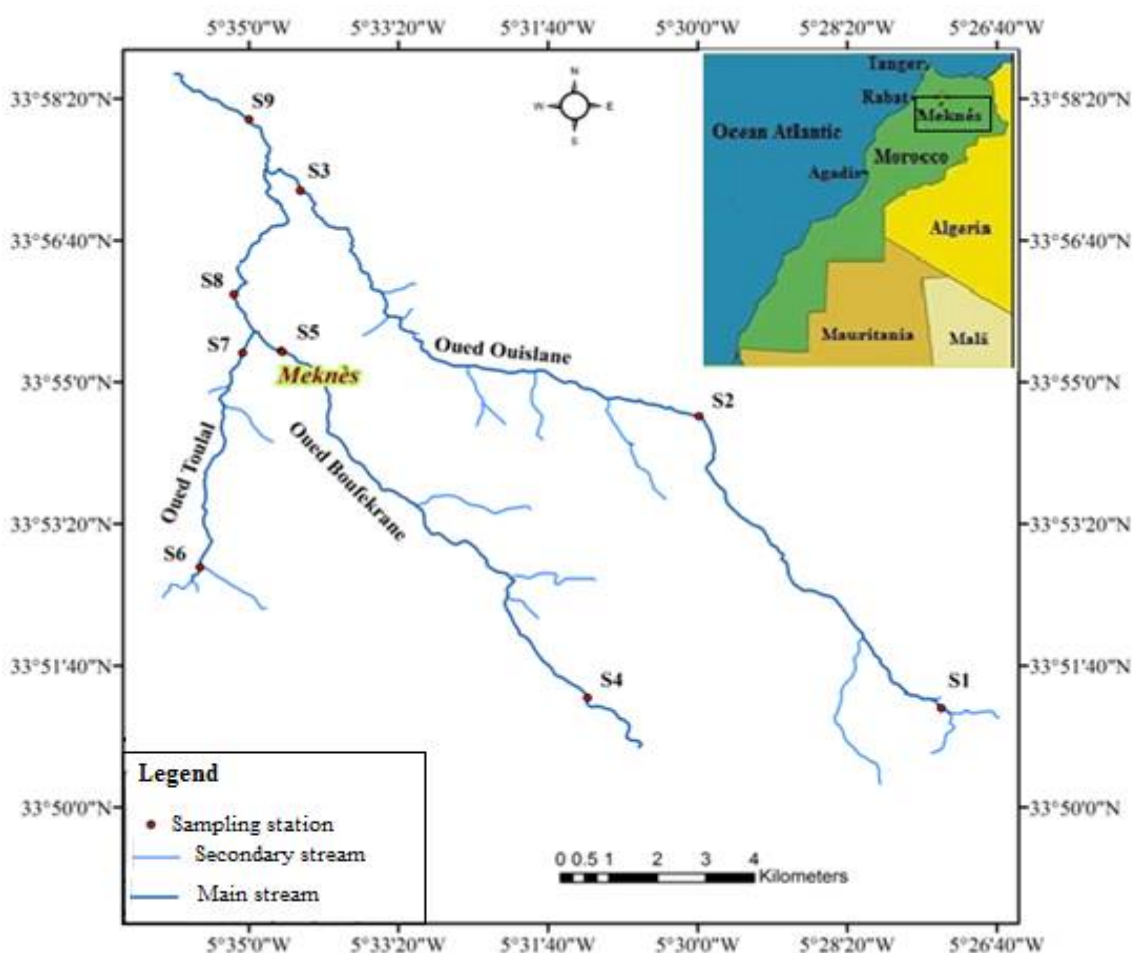


Fig. 1 Location map of sampling stations

Phosphorus is often present in sediments in organic form (P_{org}) and inorganic form (P_{inorg}). The inorganic fractions constituted of complexes of phosphorus with iron or calcium [7].

The different fractions of phosphorus in the studied sediments were determined following the scheme of splitting of Golterman [8], which was chosen because it uses specific chelators designed to extract the mineral phosphorus without disrupting organic phosphorus by adjusting the pH of the extractant solutions to the sediment [9]. This scheme allowed us to sequentially extract the phosphorus in several forms:

Fe (OOH)-P:	Phosphorus bound to iron,
CaCO₃-P:	Phosphorus bound to calcium,
ASOP:	Organic phosphorus soluble in acid,
ROP:	Residual organic phosphorus,
P_{inorg}:	Inorganic phosphorus: {Fe (OOH)-P + CaCO ₃ -P},
P_{org}:	Organic phosphorus: {POSA + POR},
P_{tot}:	Total phosphorus.

To get more information on the correlations that may exist between the forms of phosphorus in the studied sediments, we conducted a principal components analysis of all the data collected on these parameters.

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The application of this method of statistical analysis in the field of environmental study was the subject of many studies [10] [11] [12] [13]. This method of statistical processing allows regrouping of heterogeneous data (different units) in a simple graphical representation.

To perform this analysis, the raw data have been introduced into a double-entry matrix: observations x variables (samples x analytical data). This matrix is considered such as a data table centered and reduced, which is processed by principal component analysis to determine its factorial axes. The scatter of points corresponding to the matrix is then projected on a plane defined by two main axes. This graphic representation serves as a support to the interpretation of the results.

After establishing important correlations between the different forms of phosphorus, we have sought to highlight the relationship between the sampling periods, sampling stations, as well as forms of phosphorus, for this we conducted the factorial correspondence analysis (FCA), complemented by hierarchical ascendant classification (HAC) [14].

The complementarities of these two methods is the fact that the FCA introduces the elements studied as a continuous space and allows characterize the homogeneous groups, while the HAC made clear divisions or partitions between these same elements specifying the contours.

Table 2 summarizes the symbols used in this study associated with each sampling station during the four seasons (Winter, Spring, Summer, and Autumn).

Table. 2 Symbols of sediment sampling stations studied during the four seasons

Stations/ Winter	Stations/Spring	Stations/Summer	Station/ Autumn
SH1	SP1	SE1	SA1
SH2	SP2	SE2	SA2
SH3	SP3	SE3	SA3
SH4	SP4	SE4	SA4
SH5	SP5	SE5	SA5
SH6	SP6	SE6	SA6
SH7	SP7	SE7	SA7
SH8	SP8	SE8	SA8
SH9	SP9	SE9	SA9

III. RESULTS AND DISCUSSION

The principal components analysis which allows the description of the data contained in a table of individuals /quantitative variables (observation/forms of phosphorus), is the basic method of data statistical analysis. This technique allows study the forms of phosphorus in terms of correlation. Its main advantage lies in its ability to analyse simultaneously a large database. It also allows determining the interrelations between forms of phosphorus, by reducing in a small number of principal components also called indicators or factors.

The application of the principal component analysis to our database which consists of 36 observations (sediments) and 5 variables (forms of phosphorus) gave results that are recorded in tables 3 and 4, and figure 2.

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Issue 7, July 2016

Note also that forms of P_{inorg} and P_{org} were used in the principal component analysis as additional variables, given the first was estimated by adding Fe (OOH)-P and $CaCO_3$ -P, and the second was estimated by summing the forms ASOP and ROP. Table 3 includes the values and variances of the first four components of the principal component analysis (F_1 , F_2 , F_3 and F_4) with respect to the total variance, as well as their cumulative percentage.

Table. 3 Percentage of inertia explained by the first four axes of the PCA

	F1	F2	F3	F4
Values	3.24	1.28	0.36	0.10
% variance	64.75	25.62	7.10	1.97
% cumulative	64.75	90.37	97.46	99.44

From this table we note that the first two components F_1 and F_2 respectively explain 64.75 % and 25.62 % of inertia. The other factorial axes (F_3 , F_4 ...) have a small contribution compared to the total inertia and will therefore not be considered in interpretations.

Figure 2 presents the projection of phosphorus forms of sediments on the plane formed by the axes F_1 and F_2 . This factorial explains almost 90 % of the total variance and shows clearly the important objective of principal components analysis which is the determination of a reduced dimensional space, and obtaining a more relevant summary possible of initial data [15].

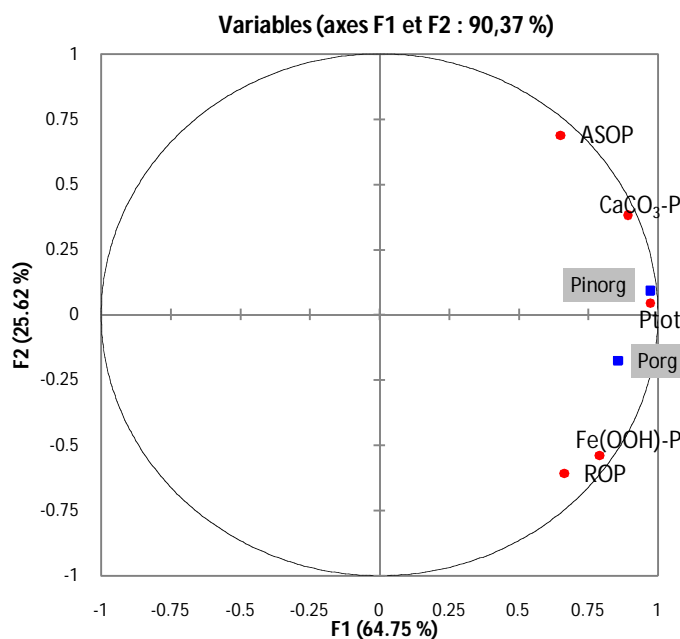


Fig. 2 Circle of correlation of the principal component analysis of forms of phosphorus of studied sediments

Table 4 represents the matrix of correlations between forms of phosphorus. We find that the majority of the correlation coefficients r values are above the critical value ($R_c = 0.33$), which is given by the usual tables found in the books specialized in the analysis of data and statistics (Saporta 1990). R_c values depend on the number of individuals n and desired confidence interval α_c . In our case $n = 36$ and $\alpha_c = 95\%$ therefore $R_c = 0.33$.

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Issue 7, July 2016

Table. 4 Correlation matrix between phosphorus forms in studied sediments

Variables	Fe(OOH)-P	CaCO ₃ -P	ASOP	ROP	P _{tot}	P _{org}	P _{inorg}
Fe(OOH)-P	1						
CaCO₃-P	0.50	1					
ASOP	0.11	0.78	1				
ROP	0.74	0.33	0.12	1			
P_{tot}	0.78	0.90	0.61	0.54	1		
P_{org}	0.67	0.64	0.57	0.88	0.74	1	
P_{inorg}	0.75	0.95	0.64	0.53	0.97	0.74	1

At first, it seems that in sediments of the studied wadis, an increase in the levels of total phosphorus (P_{tot}) is mainly caused by increased levels of forms inorganic phosphorus {Fe (OOH)-P and CaCO₃-P}. This result is confirmed if we consult the correlation matrix (table 4). Indeed, total phosphorus correlates more significantly with the phosphorus bound to iron (0.78), and with the phosphorus bound to calcium (0.90), more than the organic phosphorus : ASOP (0.61) et ROP (0.54).

Furthermore, the residual organic phosphorus (ROP) significantly correlates with the axis F₁, which shows that these two variables (ROP and P_{org}) correlate with each other in our sediments, with a correlation coefficient of the order of 0.88. While the organic phosphorus soluble in acid (ASOP) and the residual organic phosphorus (ROP), don't seem correlated (0.12).

The results of the correspondence analysis and hierarchical ascendant classification are shown in figures 3 and 4. Figure 3 shows the plane formed by the factorial axes F₁ and F₂. The axis F₁ explains 73.03% of the variance and the axis F₂ explains 16.43%, for both axes 89.46% of the total inertia.

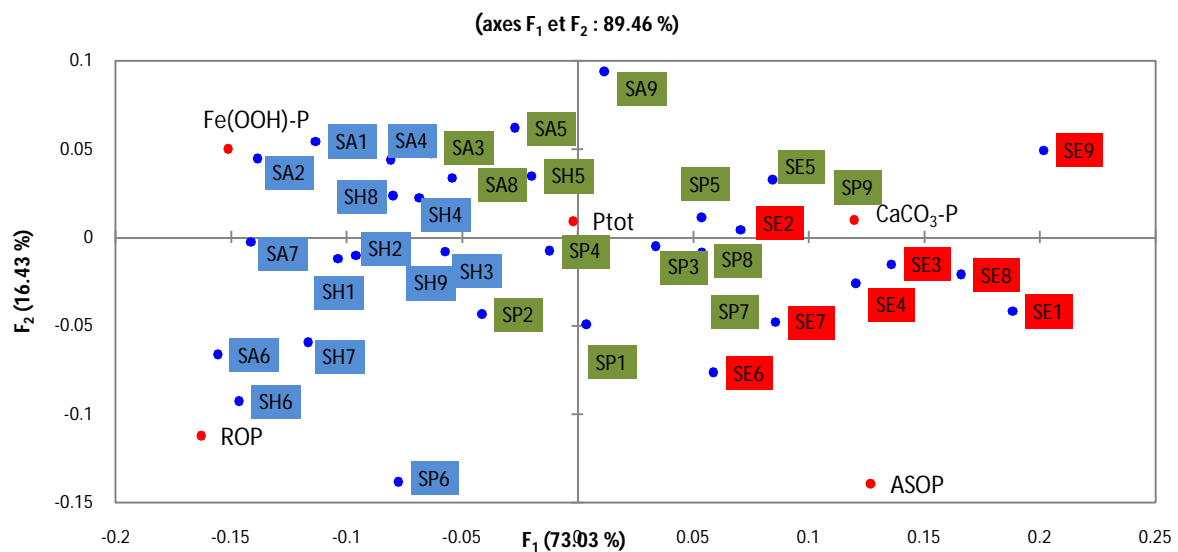


Fig. 3 Representation of the three groups of individuals in the first factorial, colored differently according to their class of membership. Class 1 in blue, class 2 in green and class 3 in red

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Issue 7, July 2016

Figure 4 shows the Hierarchical tree obtained by the Hierarchical Ascendant Classification, the main of this analysis is to represent homogeneous classes that represent similar values in all the variables analysed, where class 1 shown in blue, class 2 in green, and class 3 in red.

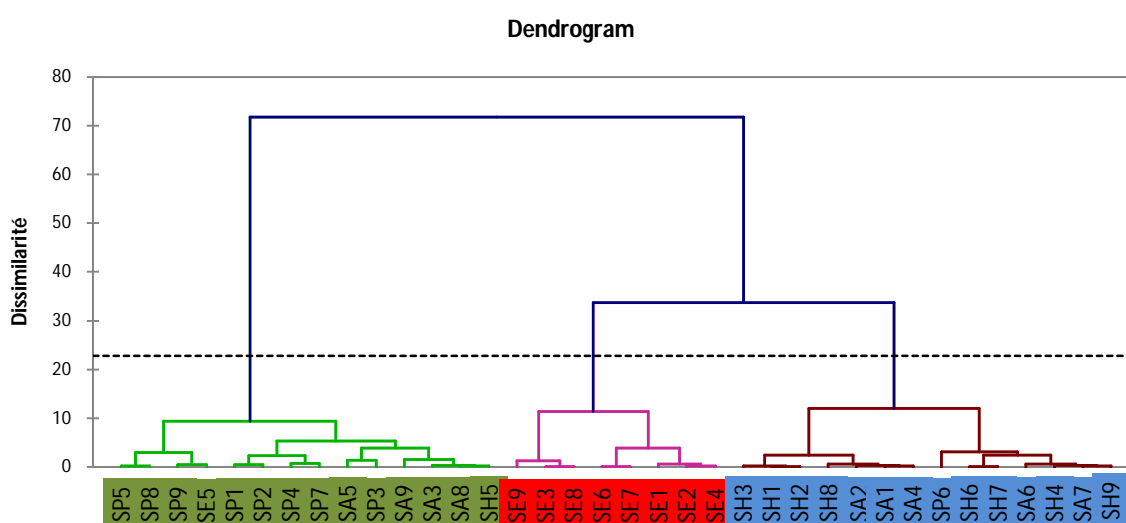


Fig. 4 Hierarchical tree obtained by the HAC. Class 1 in blue, class 2 in green, and class 3 in red

The application of these two complementary statistical techniques has identified three classes:

Class 1: Presented by sediments collected in autumn at the stations located upstream, and sediments collected in winter;

Class 2: Includes sediments collected in autumn at stations located downstream, and sediments where samples are taken in the spring;

Class 3: Presented by sediment collected in summer.

Indeed, we can interpret the high concentrations of $\text{CaCO}_3\text{-P}$ in spring and summer period, by the high values of pH in water column caused by photosynthetic activity which is responsible for the decrease of CO_2 in water, which decreases the adsorption capacity of phosphorus at the level of iron oxides by increasing competition between the hydroxide ion (OH^-) and phosphate [16] [17]. However, an increase in pH causes adsorption or co-precipitation of phosphorus with carbonates (CaCO_3) [18]. Conversely, acidic conditions cause the dissolution of carbonates and thus the release of phosphorus [19].

Maximum concentrations of Fe (OOH)-P in sediments recorded in autumn can be explained by elevated organic carbon levels, this can be explained by the formation of complex "Organic Matter-iron-phosphate". This explanation is suggested by several authors [20] [21].

Furthermore, a temperature rise in the surface sediment level is notably responsible for an increase in bacterial activity and mineralization of organic matter. In summer, the increased microbial activity causes a reduction of the redox potential in the sediment surface that can be responsible for a reduction of ferric ion into ferrous ion and phosphate release in the pore water [22] [23]. The result is a decrease in Fe (OOH) and Fe (OOH)-P in the sediment

IV. CONCLUSION

In this study, we realized a study on the correlation between the different forms of phosphorus in sediments studied by the application of the principal component analysis. Eigen value analysis allows us to retrain the first two axes; these express almost 90 % of the total inertia; that means that is 90 % of the data information is contained in the first two dimensions.

International Journal of Innovative Research in Science, Engineering and Technology

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Vol. 5, Issue 7, July 2016

The application of principal component analysis to our database of the phosphorus forms showed that the increase in total phosphorus (P_{tot}) is mainly caused by increased levels of inorganic phosphorus forms {Fe(OOH)-P et $CaCO_3$ -P}, with correlation coefficients respectively of the order of 0.78 et 0.90.

The combined application of a factorial method (factorial correspondence analysis, FCA) and hierarchical ascendant classification method, HAC), allowed us to identify three classes divided into the sampling stations as well as the periods of sampling. It also showed that the studied sediments are in spring and summer periods, richer in form $CaCO_3$ -P by cons into autumn period, these sediments are richer in Fe (OOH)-P.

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