

RESEARCH ARTICLE

APPLICATION OF PRINCIPAL COMPONENT ANALYSIS FOR THE EVALUATION OF PHYSICO-CHEMICAL PARAMETERS AND HEAVY METALS IN BERRECHID GROUNDWATER MOROCCO.

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Abstract

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*Keywords:-*Berrechid plain, groundwater, physicochemical analyzes, heavy metals, water pollution, ACP. This work is part of a program to study the Berrechid groundwater by conducting physico-chemical and heavy metal analyzes of seven samples. Indeed samples of water samples were taken during January 2018. The results of the analysis presented in this work, showed that the pH is close to the neutrality and the values found in ions potassium, calcium, chlorides and iron meet the standards defined by the W.H.O. On the other hand, the recorded values of electrical conductivity, sodium, nickel and lead remain high at certain measurement points and far exceed the guideline value set by Moroccan standards and also do not comply with the standards defined by the World Health Organization (WHO). So the waters of the Berrechid aquifer are contaminated by these elements. The application of the principal component analysis on these results, shows that we have two groups of wells: - A first group of wells in the positive part of the F1 axis, with waters with high concentrations of (Na, Cl, Co and Ca) and high values of electrical conductivity at wells P1 and P2. A second group of wells is in the negative part of the F1 axis, characterized by waters with high concentrations (Fe and Ni) at the stations (P5, P6 and P7). The correlation circle shows that the F1 axis which represents 55.67% of the variance is positively determined by (CE, Cl, Ca, and Na), this axis shows that Na, Cl, Ca and the electrical conductivity are closely related and evolve in the same sense and this axis opposes these elements and pH and iron. Finally, Co and K are opposite on axis II, which expresses (16.56%) of the variance.

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Introduction:-

The Berrechid Basin is located in the south of Casablanca, between the Atlantic Ocean and the Phosphate Plateau (Figure 1), its area is about 1500 km2. The Berrechid groundwater is the source of the drinking water of a large part of the rural areas of the Berrechid province and a part of Settat city. Berrechid groundwater is generally of a very bad quality for the whole of the sampling points, because of its strong mineralization, elevated chloride and nitrate [1]. The prevention of groundwater pollution is an important step, to which scientists must deploy more effort. This work aims to determine the water quality of the Berrechid aquifer by carrying out the physico-chemical and heavy metal analyzes of seven wells of the four samples.

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Presentation of the study area

The Berrechid plain, for a total surface area adjacent to 1500 km², is located to the south of Casablanca. It has the form of a broad cup, limited to the south and the South-East by the plateau of Settat, to the East and North is by the Oued Mellah, to the West and North West by the Primary outcrops and on the North by the coastal Chaouia [2, 3] (Fig.1). It is composed of sedimentary rocks formed Cretaceous limestone (Cenomanian) with intercalations of clays and marls and sedimentary rocks formed of calcareous sandstone to cemented conglomerates toward the base. The whole is surmounted by coverage of clayey silts of the recent quaternary. This part of the low Chaouia, receives of the upstream varied erosion elements from the high Chaouia (Plateau of Settat - Ben Ahmed) from which it is separated by the flexure of Settat) [4, 5].

The temperature varies from the summer to the winter with 24.9°C as average of the maxima and 9.6°C as an average of the minima. The annual precipitations average in Berrechid plain varies between 280 and 310mm/year.



Fig.1:-Study area

Results and Discussions:-

Sampling stations

To evaluate the physico-chemical quality and the heavy metals content of the Berrechid groundwater, the samples were taken from all seven stations in January 2018. The choice of stations was made in a way in order to have a good estimation of the water quality of the groundwater. These stations are as follows (**Table.1** and **Fig.2**):

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Stations	Location
P1	Derwa city
P2	Between de Derwa City and Berrechid City
P3	Berrechid City
P4	Jaqma 6 km south east of Berrechid
P5	16 Km south east of Berrechid between Jaqma and El Gara
P6	the rural commune of Sidi El Mekki
P7	the rural commune of Sidi El Aydi

Table	1·-sam	nling	stations
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Fig.2:-Sampling wells (January 2018)

pН

The determination of the pH consists in measuring the concentration of hydrogen ions H^+ contained in water; it is an indispensable parameter for most physicochemical and biological processes. PH is also influenced by acid precipitation, biological activity and some industrial discharges. The values of the quality criterion for raw water of supply are between 6.5 and 8.5 and between 6.5 and 9.0 for the protection of aquatic life [6]. Examination of the results obtained (FIG. 3a) shows that the average value of the pH at the level of the Berrechid groundwater is of the order of 7.24, it oscillates between a minimum of 6.9 and a maximum of 7.41. The maximum value is recorded at the No. 7 well located in the rural commune of Sidi El Aydi. These results show that the pH of the waters of the Berrechid groundwater is relatively stable and close to neutral. According to the Moroccan standards of portability, the pH values of the water of the seven wells studied are acceptable. They generally remain between 6.5 and 8.5 and 8.5 and 8.5 and 8.5 and 8.5 and 8.5 to neutral.





Fig.3:-Spatial variation of pH, electrical conductivity, Na⁺, K⁺, Ca²⁺ and chloride in Berrechid groundwater in wet season 2018

Electrical conductivity

The electrical conductivity informs us with a good approximation on the salinity of the water. It expresses the global mineralization; it translates the ionic charge of the water [7]. The results (**Fig. 3b**) show that the electrical conductivity of the water of the studied wells is of the order of 2190μ s/cm as a minimum value marked at the well No. 7 and 5300μ s/cm as a maximum value noted at the well No. 1. With the exception of the wells of the wells No. 4 and No. 7, (71.98%) of the studied waters of well in the Berrechid groundwater shows mineralization above the thresholds. Indeed, the Moroccan standards of the quality of the waters of supply require a maximum admissible value of 2700μ s / cm. on the other hand, the directives of the council of the human communities indicate for the electrical conductivity a guide level of 2500μ s / cm at 20 ° C. The average electrical conductivity at the wells of the Berrechid aquifer is 3975.71μ s / cm, it remains lower than that of groundwater in the Breanne region (11500\mus / cm) [8].

Sodium

Sodium is a mineral salt present at varying levels in all types of water, whether groundwater or surface water. The analysis of the results (**Fig.3c**) shows that the sodium concentrations vary between 186mg/l and 297mg/l with an average of 247.14mg/l. the highest levels (209 to 297 mg/l) of poor quality are observed in all the points studied except sampling point No. 7, considered of good quality (below 200 mg/l). The increase of sodium in groundwater at concentrations above the W.H.O standards of 200mg/l may be due to the presence of pollutants or saltwater invasion, in our case, agricultural, domestic and industrial pollutants are suspect. The figure 5a shows the distribution map of sodium obtained by interpolation of the sodium concentration values at the level of the seven wells.

Potassium (K⁺)

Potassium is the least common element in groundwater; it is naturally present in water but can also come from human activity. It is essential to life and especially to the growth of plants in agriculture. It is used as fertilizer in the form of potassium sulphates [9]. It results from the dissolution of chemical fertilizers (N P K) which are used massively by farmers. The presence of this element may also be related Potassium is a very common element in nature and can be derived from the leaching of sandstones, clays, pesticides and to the infiltration of domestic wastewater [10]. The observed values (**Fig. 3d**) show that potassium concentrations vary between 2.1 mg/l as a minimum value recorded at well N° 2 and 7.1mg/l as the maximum value recorded at well N° 1. Recorded average is 5.186mg/l. in all analyzed samples the Berrechid aquifer displays levels below the limit of potability (12 mg/l) set by the W.H.O. The figure 5b shows the distribution map of potassium obtained by interpolation of the potassium concentration values at the level of the seven wells.

Calcium

Calcium is a very common element in nature. It is found in almost all natural waters. Calcium is well known for its major role in the growth and maintenance of bones. It is very important for children, but also for pregnant women and the elderly. The concentration of calcium ion is directly related to the geological nature of the lands crossed by the water. Calcium ions result from attack by carbon dioxide-laden water from limestone rocks or the simple

dissolution of sulphates such as gypsum [11]. It is in the form of calcium carbonate and calcium bicarbonate responsible for the hardness of the water (17). Examination of the results (**Fig. 3e**) shows that the minimum concentration is 43mg/l recorded at the level of the well No. 4, while the maximum level is observed at the level of the well No. 1, it is of the order of 208mg/l. the average calcium concentration is recorded at the level of the seven wells is 153.71mg/l, this is closely related to the evolution of the electrical conductivity. All the points studied are lower than the guide value legally authorized by the W.H.O (270 mg/l). The figure 5c shows the distribution map of calcium obtained by interpolation of the calcium concentration values at the level of the seven wells.

Chlorides

Chlorides are widespread in nature, usually in the form of sodium (NaCl), potassium (KCl) and calcium (CaCl2) salts. The largest part is in the oceans constitutes about 0.05% of the lithosphere. Chlorine is present in all waters at different concentrations. The concentration of chloride in water may be higher or lower depending on the geology of the soil and their exposure to pollution. In groundwater concentrations of chloride ions can reach a few grams per liter in contact with certain geological formations. Waters rich in Chloride are laxative and corrosive, the values observed (**Fig. 3f**) show that the chloride concentrations are between 43 mg/l as a minimum value recorded at the well No. 7 and 183.2 mg/l as the maximum value recorded at the well No. 1. The recorded average is 115.8mg/l. these chloride values are considered normal since the Moroccan standard for the quality of human food water (N M, 2006) is set at 750 mg/l. The figure 5d shows the distribution map of chlorides obtained by interpolation of the chlorides concentration values at the level of the seven wells.

Heavy metals

In order to evaluate the metallic quality of the Berrechid groundwater, a study was conducted on the sampling of seven wells during the high-water season (January 2018). The obtained results are shown in Figure.4.





Fig.4:-Spatial variation of heavy metals

Cobalt

Cobalt is a heavy metal that has certain benefits for humans, it is one of the components of vitamin B12, and it stimulates the production of red blood cells. However, too high concentrations of cobalt can be harmful. Cobalt does not exist in the native state, it is found in various silicate minerals (biotite, olivine ...). It is mainly present in basic and ultra basic magmatic rocks (Gabbros and peridotites). In the studied points (**Fig. 4a**); the cobalt content does not show significant variations. The average is 0.262mg/l. all the analyzed wells show concentrations that do not exceed the Moroccan standards of potability. Therefore the Berrechid groundwater is not contaminated with cobalt. The figure 5e shows the distribution map of cobalt obtained by interpolation of the cobalt concentration values at the level of the seven wells.

Iron

Among the sources of iron are industrial, agricultural and domestic wastewaters, which are rich in organic matter that acts as a support for the precipitation of Fe in sediments [12]. The analysis of the results (**Fig. 4b**) shows that the concentrations of this metal remain stable from one sampling point to another, with an average of 195 mg/l. all the points studied show levels lower than the limit value of water intended for the production of drinking water $300 \mu g / l$ (Moroccan norms) and lower than the imperative value of waters favorable to irrigation (5mg/l) (Moroccan norms). Indeed, these contents are considered as natural contents [13-14], which means that the Berrechid groundwater is not contaminated with iron. The figure 5f shows the distribution map of iron obtained by interpolation of the iron concentration values at the level of the seven wells.

Nickel

In its natural state, nickel is present in the environment in very small quantities. It is widely used in the world of industry, especially for the production of metal objects. Nickel can also end up in surface water when it is present in wastewater. The largest portion of nickel released into the environment is adsorbed by sediment and soil particles and therefore becomes immobile. However, in acid soils, nickel becomes more mobile and can reach groundwater [15]. The concentrations mentioned in **Figure 4c** are between 0.29mg/l (wells of 1 to 5) and 0.3mg/l (wells 6 and 7). Moreover, these concentrations are both superior to the legal standards of potability $(20\mu g / l)$ and the imperative value of waters favorable to irrigation (0.2mg / l). The high concentrations are found in all the points studied, therefore, these wells are considered to be contaminated by nickel. The figure 5g shows the distribution map of nickel obtained by interpolation of the nickel concentration values at the level of the seven wells.

The Lead

It is a fairly widespread element in the globe. The main lead ore is galena (PbS) and is also found in the form of Anglesite (PbSO4) and Cerusite (PbCO3) [16]. It is also associated with other metalloid metals, for example in the form of lead chromate (PbCrO4), wulfenite or vanadinite. Its presence at high levels is toxic. Lead prevents the synthesis of hemoglobin and changes the composition of blood; it also acts on the central nervous system and causes lead poisoning. In the study area the recorded Lead concentrations (**Fig.4d**) are between 0.725mg/l as the minimum

value observed at the well No. 7 and 0.772mg/l as the maximum value recorded at the well No. 2 the average concentration is 0.747mg/l, these values are higher than the W.H.O standards recommending 0.01 mg / l as guide value. We can conclude that all studied sites are polluted by lead. The figure 5h shows the distribution map of the lead obtained by interpolation of the lead concentration values at the level of the seven wells.







Statistic study

Data processing methods

To release an overall synthesis of the different results we have submitted all the collected data to a Principal Component Analysis (PCA), although PCA is an exploratory and descriptive method [17]. The purpose of this treatment is to determine the main factors that control the chemistry of these waters. This statistical method has been widely applied to investigate environmental phenomena and hydro-geochemical processes around the world [18 - 19]. The PCA allows the analysis of quantitative numeric data tables to reduce dimensionality. The principal components are obtained by diagonalization of the matrix of bi-varied correlations. This diagonalization defines a set of eigen-values whose observation for each component makes it possible to determine the number of graphs to be examined [20]. The PCA makes it possible to explain the structure of correlations or covariances using linear combinations of the original data. Thus, its use makes it possible to reduce and interpret the data in a small space

[21]. We start from Table 2 consisting of the concentration values of the physicochemical and heavy metals parameters of the seven wells of the Berrechid aquifer (**Table.2** and **Fig.6**).

	CE	Na	Κ	Ca	Cl	pН	Ni	Fe	Со	Pb
P1	5300	284	7,1	208	183,2	6,9	0,2961	0,1942	0,2624	0,7491
P2	5110	297	2,1	169	151,6	6,98	0,2944	0,1947	0,2627	0,7724
P3	4460	256	5,3	181	138,1	7,3	0,2916	0,1945	0,2615	0,7511
P4	2610	209	6,9	104	50,6	7,36	0,2943	0,1952	0,26	0,7553
P5	3630	239	4,9	114	96,7	7,38	0,2939	0,1954	0,2632	0,7421
P6	4530	259	5	193	147,4	7,37	0,305	0,1954	0,2615	0,7308
P7	2190	186	5	107	43	7,41	0,3055	0,1952	0,2623	0,7255

 Table 2:-Average concentrations in mg / l of some elements and metals in the waters of the Berrechid aquifer

Results:-

Correlation matrix between variables

In our example, some variables are positively correlated and others are negatively correlated. Therefore, heavy metals that are positively correlated vary in the same direction; that is, the increase of one influences the increase of the other, so the variables which are negatively correlated vary in opposite directions; that is to say, the increase of one leads to the diminution of the other.

Variables	CE	Na	Κ	Ca	Cl	pН	Ni	Fe	Со	Pb
CE	1	0,981	-0,245	0,904	0,988	-0,759	-0,313	-0,635	0,339	0,468
Na	0,981	1	-0,349	0,818	0,942	-0,793	-0,382	-0,598	0,351	0,599
Κ	-0,245	-0,349	1	-0,029	-0,146	0,129	-0,020	-0,116	-0,498	-0,330
Ca	0,904	0,818	-0,029	1	0,948	-0,630	-0,041	-0,644	0,132	0,183
Cl	0,988	0,942	-0,146	0,948	1	-0,733	-0,224	-0,643	0,327	0,346
pН	-0,759	-0,793	0,129	-0,630	-0,733	1	0,335	0,810	-0,325	-0,630
Ni	-0,313	-0,382	-0,020	-0,041	-0,224	0,335	1	0,463	0,024	-0,772
Fe	-0,635	-0,598	-0,116	-0,644	-0,643	0,810	0,463	1	-0,121	-0,503
Со	0,339	0,351	-0,498	0,132	0,327	-0,325	0,024	-0,121	1	-0,044
Pb	0,468	0,599	-0,330	0,183	0,346	-0,630	-0,772	-0,503	-0,044	1

Table 3:-The correlation matrix between the variables studied during the present study

Positive correlation

Positive correlations (variation in concentrations of metals in the same direction) and high correlations between the variables studied can be classified into four groups as a result (**Table 4**):

Correlation degree	0,810 to 0,988	0,463 to 0,599	0,327 to 0,351	0,024 to 0,183
Variables	Fe/pH	Ni /Fe	Co/Cl	Ni /Co
	Na/Ca	CE/Pb	Ni / pH	K/ pH
	Na/Cl	Na/Pb	Co /CE	Ca/Co
	Ca/CE		Cl / Pb	Ca/Pb
	CE/Cl		Na/Co	
	Ca/Cl			
	CE/Na			

Table 4:-Positive correlation ranking of some heavy metals studied during this study

Negative correlation

Negative correlations that vary in two opposite directions, where one of the increasing variables leads to the decrease of the other and to the low correlations between the groups of variables studied, can be classified as follows (**Table 5**):

Correlation degree	-0.044 to -	-0.325 to -0.116	-0.330 to - 0.630	-0.635 to -0.793
	0,020	- , , -	- , ,	- , ,
Variables	Co/Pb	Co/pH	K /Pb	CE/Fe
	Ni/Ca	CE/K	Na/Ni	Cl/Fe
	Ca/K	Ni/CE	Na/K	Ca/Fe
	K/Ni	Co/Fe	K/Co	Cl/pH
		Cl/Ni	Fe/Pb	pH/CE
		K/Fe	Na/Fe	pH/Na
		K/Cl	Ca/pH	Ni/Pb
			Pb/pH	

Table 5:-Ranking of the negative correlation of some heavy metals studied during the present study

Diagonalization of the correlation matrix

Table 6 and Figure 6 show the diagonalization of the correlation matrix. The second line shows the eigenvalues of the correlation matrix. The third line tells us the percentage explained by each eigenvalue.

Table 6:-Diagonalisation of the correlation matrix of the studied variables

	F1	F2	F3	F4	F5	F6
Eigen-value	5,567	1,656	1,452	0,677	0,440	0,209
Variability (%)	55,668	16,564	14,517	6,769	4,396	2,087
% cumulated	55,668	72,231	86,748	93,517	97,913	100,000



Figure 6:-Graphical representation of eigenvalue and cumulative variability

Variables representation and variables circle

The coordinates of the variables vis-à-vis the axial planes F1, F2, ..., F9 shown in Table 6 show the representation of the variables in the plane (factor 1, factor 2) explaining 72.23% of the initial inertia.

For each variable, we associate a point whose coordinate on a factorial axis is a measure of the correlation between this variable and the factor (Axis F1 or Axis F2) example. The coordinate on axis 1 of the variable concentration of Sodium is 0.410 and that on axis 2 are 0.084 (**Table 7**). By projection on a factorial plane, the variables fit in a circle of radius 1. So to facilitate the visualization of the clouds of the points, they were projected in a space with 2 dimensions. According to Kaiser's criterion, only two factors have been retained (F1 and F2) which represent 72.23% of the total variance (**Fig.6**), which is good enough and can be used to identify the main variations in hydrochemistry [22]. These two axes are taken into account for the description of the distribution of variables on the main plane. The first and the second axis account respectively for 55.67% and 16.56% of total inertia. Axis F1

represents 55.67% of the variance determined positively by (CE, Cl, Ca, and Na). F2, which represents 16.56% of the total variance, is marked only by an opposition between Co and K. The axis I expresses 55.67% of the variance, showing that Na, Cl, Ca and electrical conductivity are closely related and evolve in the same direction and this axis contrasts these elements with pH and iron. Finally, Co and K are opposite on axis II, which expresses (16.56%) of the variance.

	F1	F2	F3	F4	F5	F6
CE	0,407	0,135	0,068	-0,167	-0,205	0,073
Na	0,410	0,084	-0,061	-0,208	-0,131	0,236
Κ	-0,104	-0,299	0,666	0,339	-0,270	0,422
Ca	0,351	0,210	0,362	-0,223	-0,029	-0,269
Cl	0,395	0,183	0,177	-0,116	-0,218	0,036
pН	-0,373	0,068	-0,003	-0,300	-0,502	-0,470
Ni	-0,189	0,576	0,244	-0,117	0,583	0,176
Fe	-0,331	0,223	-0,201	-0,420	-0,327	0,625
Со	0,143	0,453	-0,391	0,655	-0,268	0,068
Pb	0,266	-0,465	-0,363	-0,203	0,221	0,200

Table 7:-Correlations between variables and factors



Fig.7:-Correlation circle represents the F1-F2 factorial projection of the variables

The variables projection on the plane I-II shows The axis I expresses 55.67% of the variance shows that Na, Cl, Ca and the electrical conductivity are closely related and evolve in the same direction and this axis opposes (Na, Cl, Ca and electrical conductivity) and (pH and iron). Finally, Co and K are opposite on axis II, which expresses (16.56%) of the variance (**Fig.7**). In conclusion, the circle of correlations allows seeing, among the old variables, the groups of variables highly correlated with each other. So his study is simpler and more informative than the direct analysis of the correlation matrix.

	F1	F2	F3	F4	F5	F6
P1	25,263	0,077	25,906	25,407	0,915	8,146
P2	22,650	0,037	41,921	4,448	16,357	0,300
P3	3,258	6,997	1,483	0,817	8,787	64,374
P4	15,101	50,590	1,274	6,578	2,010	10,161
P5	2,954	1,105	16,973	8,454	49,037	7,191
P6	0,209	30,528	12,319	39,176	1,225	2,258
P7	30,565	10,667	0,124	15,120	21,670	7,569

Table8:-Coordinates of observations from the seven stations

Observation F1 F2 F3 F4 F5 F6 4,488 -0,299 0,252 0,084 1,842 0,001 1 2 0,312 -0,579 2,402 -0,563 0,063 0,023 3 -1,610 1,783 -0,548 -0,356 -0,276 0,162 4 -2,979 -0,005 -0,127 1,966 0,263 0,241 5 0,449 -1,566 -1,337 -0,890 -0,023 -0,119 -1,261 0,399 -0,087 6 -0,106 0,825 -0,357 7 -0,553 -2,186 -0,611 0,469 0,269 0,148

Station representation

Individuals study

The arrangement of the wells of the Berrechid aquifer in the plane defined by the first and second axis (Figure 8) showed that:

- 1. A first group of wells in the positive part of the F1 axis, with waters with high concentrations (Na, Cl, Co and Ca) and high values of the electrical conductivity at the wells P1 and P2.
- 2. A second group of wells in the negative part of the F1 axis, characterized by waters with high concentrations (Fe and Ni) at the wells (P5, P6 and P7).



Fig.8:-Projection of the stations and parameters studied on the factorial plane defined by the first two main components F1 and F2)

Conclusion:-

The present work is part of the study of the Berrechid groundwater. From the obtained results, it is interesting to note that the pH values are relatively neutral. Indeed, the values found in potassium, calcium, chloride and iron ions meet the standards defined by the W.H.O. On the other hand, the recorded values of electrical conductivity, sodium, nickel and lead remain high at certain measurement points and far exceed the guideline value set by Moroccan standards and also do not comply with the standards defined by the World Health Organization (WHO). So the Berrechid are contaminated by these elements. Indeed, domestic and industrial pollution, as well as the misuse of fertilizers of fertilizers and pesticides in the agricultural sector, affect the quality of the Berrechid groundwater.

The ACP has allowed us to highlight similarities or oppositions between stations and heavy metals. Indeed, the application of the principal component analysis on these results, shows that we have two groups of wells: - A first group of wells in the positive part of the F1 axis, with waters with high concentrations of (Na, Cl, Co and Ca) and high values of electrical conductivity at wells P1 and P2. A second group of wells is in the negative part of the F1 axis, characterized by waters with high concentrations (Fe and Ni) at the stations (P5, P6 and P7).

The correlation circle shows that the F1 axis which represents 55.67% of the variance is positively determined by (CE, Cl, Ca, and Na), this axis shows that Na, Cl, Ca and the electrical conductivity are closely related and evolve in the same sense and this axis opposes these elements and pH and iron. Finally, Co and K are opposite on axis II, which expresses (16.56%) of the variance.

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