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Hydro-Chemical Characterization of the Source Ain Moulay Yacoub Hamma of Sidi Slimane, Morocco

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ABSTRACT

The source Ain Moulay Yacoub Hamma located upstream of Oued Hamma (Outita : pre-rifaine ride) 18 km southeast of the city Sidi Slimane, presents non-permanent flows during the three months February, March and April of the year 2017. The objective of this study is to evaluate the quality of the natural waters of Ain Moulay Yacoub Hamma, the hydro-chemical facies and the origin of their mineralization.Sampling is carried out at the source of these natural waters in order to carry out physico-chemical analyses in our specialised laboratory. As a result, the study showed that the waters of the Ain Moulay Yacoub Hamma spring are meso-thermal waters (42°C), with a poor quality sulphurous odour loaded with mineral salts (chlorides, sodium and sulphates). In the results presented in the Piper, Schoeller and Stiff diagrams, show that these waters are characterized by a chloride sodium chemical facies.

Keywords: Source moulay yacoub hamma; Oued hamma; Physico-chemistry; Hydro-chemical facies; Sidi Slimane; Morocco

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INTRODUCTION

The river Hamma near the city Sidi Slimane, tributary of the river R'dom, is a non-permanent stream. It is fed by a set of freshwater sources upstream in the Outita pre-Riparian ride.

The discharge of thermal waters from the Ain Hamma Moulay Yacoub spring in the city of Sidi Slimane into the river could modify the quality of the latter's waters. The physico-chemical characteristics of thermal water are linked to its underground course, its depth (temperature) and the mineral constitution of the rocks. At depth, water can also be enriched with gas (CO_2, H_2S) depending on the nature of the rock [1]. Thermal waters have been the subject of several scientific studies [2].

They have particular physico-chemical characteristics that may undoubtedly modify the quality of the receiving environment.

In this context, the study of the quality of natural resources Ain Hamma Moulay Yacoub of Sidi Slimane is included. A follow-up of the physico-chemical parameters is done during the three months February, March and April in 2017. The main objective is on the one hand to study the quality of the spring water and to determine the hydro-chemical facies and the origin of the mineralization of these waters.

MATERIAL ET MÉTHODES

Presentation of the Study Area

The city of Sidi Slimane is located on the Gharb plain, in north-west Morocco, and belongs to the Rabat-Salé-Kénitra region.

The thermal spring of El Hamma-Outita emerges on the outskirts of the pre-rifain mountain range, 12 km from the town of Sidi Slimane, on the road that leads to Meknes, and is very close to the marabout of Sidi Moulay Yacoub, at the bottom of the N-S cluse of Oued El Hamma, and its coordinates are Lambert, X=459,60, Y=392,7 and Z=120m, with a scale of 1/50000 from the map of El Kansera.

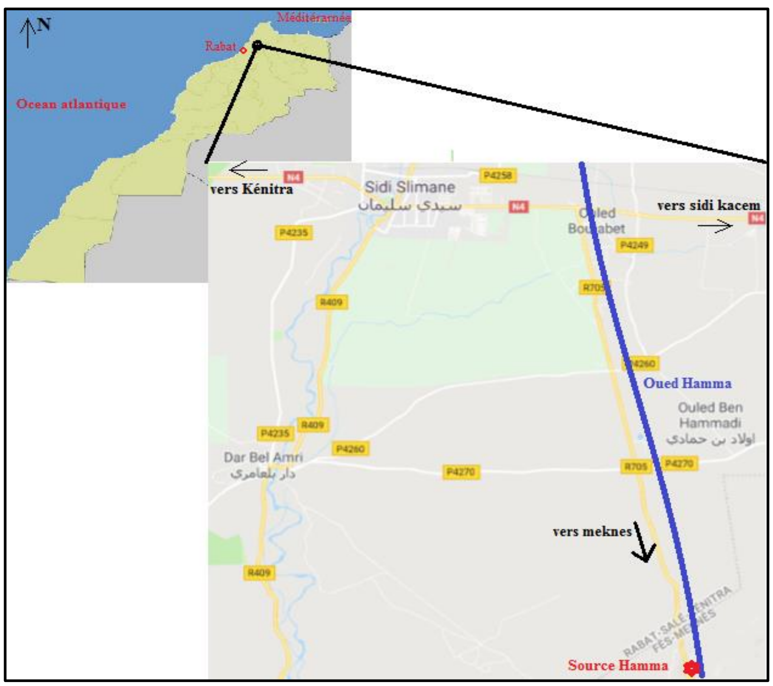

Figure 1. Geographic location of the study area

SAMPLING ET ANALYSIS

Sample Collection

The sampling campaign was carried out monthly over the period from February to May 2017, because of the flow of the source that is very important during this period on the other hand the other months of the year or this flow is very low to nil. Concerning the sampling method, plastic bottles were used which were rinsed several times with tap water beforehand, then allowed to dry, and before filling the bottles they were rinsed three times with water to be analysed, filled until overflowing to avoid any water-air reaction. Each bottle was labelled with the number, location and date of sampling.

Physico-Chemical Analyses

The analyses concerned the major elements expressed in cations (Ca^{2+}, Mg^{2+}, Na^{+} and K^{+}) and anions (Cl^{-}, HCO^{3-}, SO_4^{2-}), overall hardness, full alkali content, dry residue and heavy metals (Pb, Cd, and Ni).

The analyses were carried out in the laboratory of the Institut Nationale de Recherche Agronomique (Rabat). The pH and temperature measurements were made in situ by a portable instrument.

Evaluation of Analyses

The results of the physico-chemical analyses were used in the Avignon Hydrochemistry (L.H.A.) software version 4.2008, which enabled us to classify the waters into chemical facies and drinking and irrigation water classes, and in particular to construct the Piper, Schoeller-Berkaloff and Stiff diagrams [3].

RESULT AND DISCUSSION

Results

Results presentation: The different results of the physico-chemical analyses are average values of three months of analysis (February, March and April), represented in the following table.

Table 1. Presentation of physicochemical results from the Hamma natural source

	Parameter	Unit	February	March	April	Average
	Temperature	°C	42	41	43	42
	pH	-	6,77	7,06	6,92	6,91
	Electrical Conductivity	(µS/cm)	8837	8878	9240	8985
	Dry residue at 180°C	(mg/l)	701	638,24	651,12	663,45
	Hardness	(°F)	63,1	59,02	49,03	57,05
	TAC (Full Alkalimetric Title)	(°F)	41	30	37,9	36,3
	TA (Alkalimetric Title)	(°F)	0	0	0	0
	Sulphates	(mg/l)	633,89	772,88	560,89	655,88
	Chlorides	(mg/l)	1105,7	1016,67	1238,34	1120,23
	Calcium	(mg/l)	144,25	115,8	189,96	150
	Magnesium	(mg/l)	51,7	60	36,34	49,34
	Sodium	(mg/l)	557,58	735,8	815,7	703,02
	Potassium	(mg /l)	27,35	55,8	34,78	39,31
Trace	**Cadmium**	(mg/l)	0,015			

elements	**Lead**	(mg/l)	0,12			
	Nickel	(mg/l)	0,02			

Interpretation of measurement data and analysis results: Organoleptic characteristics of the waters of Hamma Outita Spring

Color: Water is clear, i.e., colorless.

Odour: Water has a sulphurous odour.

The physico-chemical characteristics of the water studied

(a) Physical parameters:

Temperature: The water temperature studied varies between 41°C and 43°C, so we can say that this water is ortho-thermal.

Hydrogen potential (pH): The pH varies according to the concentration of HCO_3^- or H_3O^+ ions, the pH of water measured at Hamma Outita source is neutral, varies between 6.89 and 7.06.

Electrical conductivity: The Table 2, shows the relationship between conductivity and mineralization and allows us to evaluate the overall mineralization of the water for this natural source.

Table 2. Presentation of electrical conductivity classes and mineralization levels

Conductivity (µS/cm)	**Mineralization**
- **Conductivity<100**	- Très faible
- **100<Conductivity<200**	- Faible
- **200<Conductivity<333**	- Moyenne
- **333<Conductivity <666**	- Moyenne accentuée
- **666<Conductivity <1000**	- Importante
- 1000>Conductivity	- Elevée

The electrical conductivity values are very high for the natural waters studied, varying between 8000 and 10000 µS/cm. The latter result from the high mineralization of the waters of the Ain Moulay Yacoub Hamma spring.

(b) Chemical parameters

The major elements

The cations

The calcium ion Ca^{2+}:

Calcium is introduced into the water system by the weathering of rocks, particularly limestone rocks, and by leaching and runoff from the ground into infiltrating waters. The concentration of calcium in water depends on the residence time of the water in calcium-rich geological formations.

The waters of the Hamma Outita spring have an average calcium concentration of around 150 mg/l. We estimate that this is linked to the importance of the liasic formations (limestone and dolomite) of the main karstic aquifer in the supply of this spring.

Moroccan standards recommend a concentration between 75 mg/l and 200 mg/l, which explains why these waters comply with national standards.

The Magnesium ion Mg^{2+}:

The magnesium content of the water is extremely varied and mainly related to the nature of the terrain crossed. In areas rich in magnesic rocks, water can contain concentrations of 10 to 50 mg/l of this element [4].

The water from the Hamma Outita spring has a magnesium concentration significantly lower than that of calcium, with an average of 49.34 mg/l. Therefore these waters are of good quality in comparison with the Moroccan standard requiring a maximum concentration of 150 mg/l in Mg^{2+}.

The hardness of the water is due to dissolved polyvalent metal ions. Mainly calcium and magnesium ions. In the water samples from the Hamma Outita spring the hardness reaches a value of 57.05 °F, this would be related to the lithological nature of the aquifer formation and in particular to its composition in calcium and magnesium.

Good quality drinking water has a hydrotimetric degree of less than 15 °F, they are acceptable up to 50 °F, but if they exceed 60°F their use will cause problems either with consumption or with certain domestic uses according to the W.H.O.

The sodium ion Na^{+}:

The sodium is a so-called conservative element because once in solution, no reaction makes it possible to extract it from groundwater. Precipitation brings a minimal amount of sodium to groundwater; abnormally high levels can come from salt leaching, or percolation through saline soils or brackish water infiltration. In unpolluted groundwater without contact with evaporates, the sodium content is between 1 and 20 mg/l [5,6].

Analysis of the data showed that the average sodium value of 713.02 mg/l, in the waters of the Hamma Outita spring, is very high, exceeding the Moroccan standard of 200 mg/l.

The potassium ion K^{+}:

Potassium is generally the least abundant major element in water after sodium, calcium and magnesium; it only exceptionally ranks third among cations [7,8]. Potassium occurs as double chlorides in many minerals such as corrollite and sylvinite. It is also found in plant ashes as carbonate. Potassium is an essential element for life and especially for plant growth.

Potassium content is almost constant in natural waters. This usually does not exceed 10 to 15 mg/l. Its concentration in the Hamma Outita spring is high and reaches an average value of around 39.31 mg/l.

The anions:

Chlorides Cl^{-} :

Chlorides are widely distributed in nature, usually in the form of calcium and potassium salts; they represent about 0.05 of the lithosphere, they are naturally present in groundwater due to weathering and leaching of sedimentary rocks and soils, and dissolution of salt deposits .

The average chloride value for the water source studied (Hamma Outita) is very high, reaching 1120.23 mg/l. This high value could be due to water contact with triasic saline deposits. The admissible concentration set by the Moroccan standard is 200 mg/l.

Sulphates SO_4^{2-} :

Under natural conditions, sulphates, the most responsive form of dissolved sulphur in natural waters, have essentially two origins: geochemical and atmospheric.

Due to the high solubility of sulphates, groundwater under normal conditions can contain up to 1.5 g/l. Oxidation of sulphides and degradation of biomass in soil are other possible sources. Many human and natural activities can generate sulphate inputs to groundwater: application of sulphate fertilizers, precipitation loaded with sulphur dioxide, etc.

The average value of sulphates in the waters studied (Hamma Outita) is about 655.88 mg/l. This high content seems to be linked to the triasic saline formation brought into contact with the aquifer reservoir through major faults that dominate the Outita wrinkle structure (Figure 1). The results obtained exceed the Moroccan standard of between 200 mg/l and 400 mg/l in sulphates.

Complete alkalimetric title:

The complete alkalimetric titre (TAC) in the water samples analyzed is mainly due to the presence of bicarbonates (HCO^{3-}). Is the Water Buffer Index, it is closely related to hardness, although many species of solutes can contribute to it. Alkalinity is expressed in equivalent amount of carbonate or in French degrees °F.

The bicarbonate content of groundwater not subject to human influences varies between 50 and 400 mg/l. The median values of bicarbonate contents are around 302 mg/l in the usual range of unpolluted groundwater. The high average bicarbonate value of the waters studied is of the order of 467.8 mg/l, seems to be due to the circulation of these waters in the aquifer of calcaro-dolomitic nature.

Trace elements:

The presence of minor elements or trace elements in thermo-mineral waters is of great interest, because it makes it possible to specify the characteristics of the waters and the mineral deposits through which they pass.

For the thermo-mineral waters of our study site, we performed atomic absorption analyses to determine the concentrations in (mg/l) of certain trace elements which are: Lead (Pb), Cadmium (Cd) and Nickel (Ni).

Lead (Pb)

According to the results obtained, during this campaign and by comparison with the maximum admissible values (MAV) (25 µg/l) for drinking water according to the Moroccan standard [9].

The results obtained do not exceed the MAV in the waters of the Hamma spring, which is in the order of 0.0015 mg/l.

Cadmium (Cd)

The water from the source analysed has an average value of about 0.015 mg/l, higher than the MAV (3 µg/l) according to the standard for drinking water supply.

Nickel (Ni)

The average Nickel value of 0.02 mg/l recorded in natural waters from the Hamma source actually exceeds the MAV of drinking water, which is in the order of 500 µg/L.

Study of relative values:

Basic Exchange Index (B.E.I.):

During its underground journey, water comes into contact with different substances that have the property of exchanging their ions against those contained in the water, among these substances, we have clay minerals: ferric hydroxide and organic substances.

Schoeller in 1934 specified that the basic exchange index (B.E.I.) as being the ratio between the exchanged ions and ions of the same nature primitively existing, when there is exchange of Na+ and K+ of water, against the then calcarino-earthly clays :

If I.E.B<0: The water is of crystalline origin (Ca^{2+} and Mg^{2+} are exchanged by Na^+ and K^+);

If I.E.B>0: The water is of sedimentary origin (Na^+ and K^+ are exchanged by Ca^{2+} and Mg^{2+});

If I.E.B=0: No ionic exchange between the water and the surrounding soil.

With;

- I.E.B=r Cl- - r (Na+ + K+)/r Cl- ;

In our case, this index is in the order of - 0.005, so we can see that the Ca^{2+} and Mg^{2+} ions of the water are exchanged slightly against the K^+ and Na^+ ions of the surrounding formations.

II-1-3-2- Characteristic reports

The characteristic ratio is defined as the ratio of certain chemical elements expressed in milliequivalents per litre (meq/l). The reports studied are:

- r Mg2+/r Ca2+ ;
- r (Na+, K+)/r Cl- ;
- r SO42-/r Cl-.

The study of variations in these ratios provides valuable information on groundwater recharge and circulation and sometimes allows the detection of other non-outcropping deep formations.

Report r Mg^{2+}/r Ca^{2+}:

When this ratio is higher than 1, it reflects the predominance of Magnesium, and when it is lower than 1 Calcium predominates and this is the case of our study (the ratio Mg2+/r Ca2+ is equal to 0.54), this can be explained by the solubility of limestones richer in Calcium than in Magnesium [10].

Report r $SO_4{}^{2-}$/r Cl^-:

When this ratio is greater than 1, Sulphates predominate, which are essentially linked to leaching of gypsum soils and oxidation of sulphides (pyrites).

When the ratio r SO4 2-/r Cl- is less than 1 there is predominance of Chlorides, this is the case of our study (r SO4 2-/r Cl- equal to 0.43).

Report r(Na^+ + K^+)/ r Cl^-:

When the ratio r(Na+ + K+)/r Cl- is less than 1, it reflects the predominance of Chlorides which are linked to saline soils.

When this ratio is greater than 1, it reflects the predominance of Sodium [11].

In our case, this ratio is equal to 1, which explains the existence of a balance between chlorides, potassium and sodium.

Sodium absorption ratio (SAR):

$$SAR = \frac{Na^{+}}{\sqrt{\frac{Ca^{2+} + Mg^{2+}}{2}}}$$

Chemical classification of spring water: The values of the chemical analyses can be plotted on diagrams to classify the waters into chemical families in order to determine the facies of these waters from the Hamma spring.

To determine the different facies crossed by water (source Hamma Outita) and classify them into chemical families, we used the Piper, Stiff and Schoeller Berkaloff diagrams that will be reviewed.

Piper's diagram: In this type of diagram, the representation of the chemical analyses makes it possible to have an approach of the chemical composition of well determined water, starting from the quantities in reaction expressed in percentage.

The results were represented on the Piper diagram, with the position of the representative points of the anions and cations that characterize the chemical composition of the water from the Hamma Outita thermal spring.

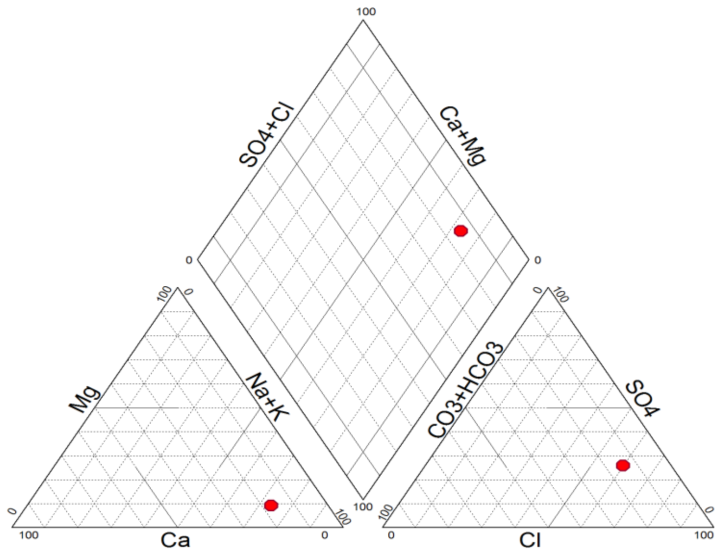

Figure 3. Hydro-chemical facies of Ain Hamma Moulay Yacoube Sidi Slimane spring

According to the Piper diagram (Figure 3), the hydro-chemical facies of these waters is: Chloro-sodium.

Schoeller Berkaloff diagram: The Schoeller-Berkaloff diagram is a semi-logarithmic graphic representation: the different ions are represented on the abscissa axes. For each of the major ions, the actual mg/l content is plotted on the ordinate axis; the points obtained are linked by line segments. The graphical appearance obtained (Figure 4) shows the facies of the mineral water concerned. The analysis of Schoeller Berkaloff's diagram allows us to conclude that the waters of the spring Hamma Outita rich in chlorides, sodium and sulphates. They are due to the existence of a source of saline sediments [12,13].

The important values of chlorides, sodium and sulphates indicate a relationship of evaporite rocks formed mainly by chlorinated and sulphated minerals.

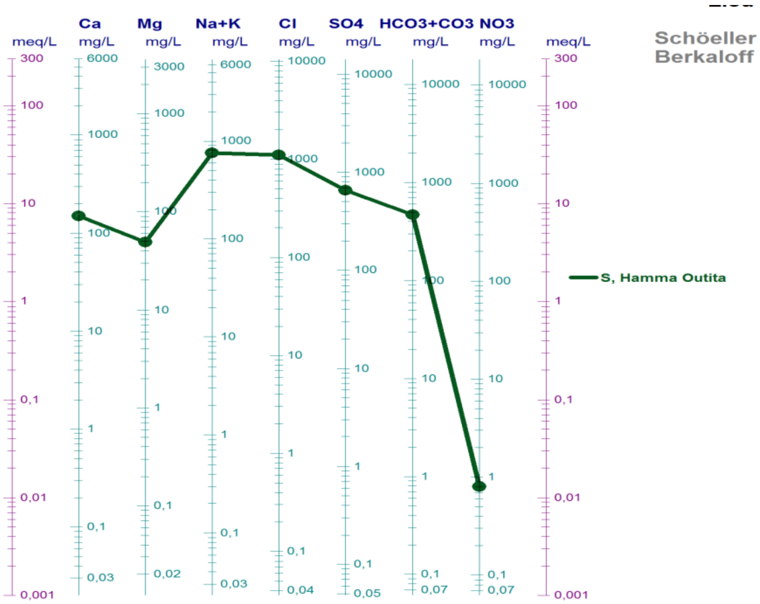

Figure 4. Ain Hamma Moulay Yacoube Sidi Slimane spring hydro-chemical facies (Schoeller diagram)

Stiff Diagram: It is a simple diagram and one can read directly on the diagram the ionic formula and the chemical facies.

The cations represented to the left of the vertical axis are the ions of (Na^+, K^+), Ca^{2+}, Mg^{2+} and Fe^{2+}. As well as the anions represented to the right of the vertical axis are: Cl^-, HCO^{3-}, SO^{4-} and CO^{3-}. As a result, the last line of iron and carbonate is often not included in the diagram due to the scarcity of these ions.

The horizontal axis expresses the concentrations in meq/l and the polygon is drawn by connecting the points corresponding to the different concentrations.

For balanced water, the area of the right part (anions) should equal that of the left part (cations).

In the Stiff diagram, analyses can be represented in sequences (one next to or below the other), facilitating graphical archiving of data.

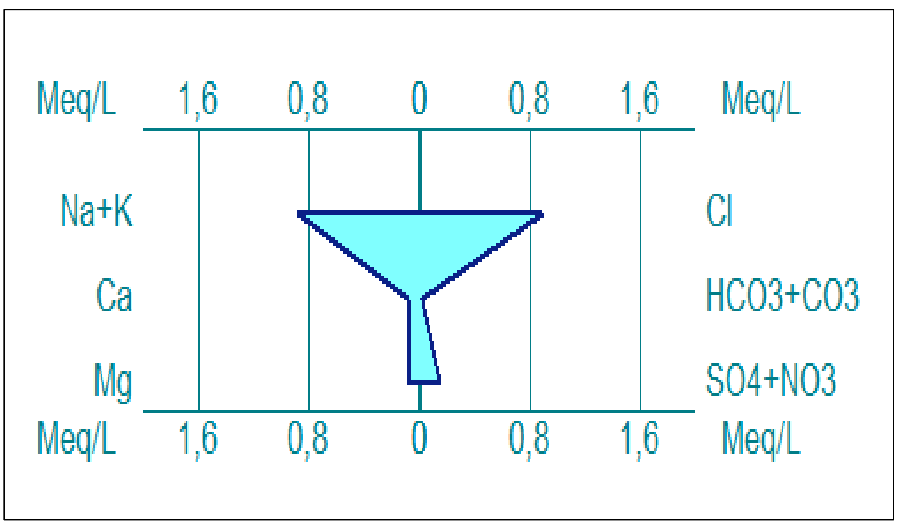

Figure 5. Hydro-chemical facies of the Hamma Moulay thermal spring Yacoube Sidi Slimane (StiffDiagram)

The representation of the analysis results on the Stiff diagram (Figure 5), clearly shows the hydro-chemical facies mentioned above which is: Chloride-sodium, with the following chemical formula:

$rCl^- > rSO4^{2-} > rHCO3^- \approx r(Na^+ + K^+) > rCa^{2+} > rMg^{2+}$

CONCLUSION

The study of the chemistry of the water of the Hamma Moulay Yacoube thermal spring using hydro-chemical and hydrogeochemical tools made it possible to determine its typological characteristics:

The waters of the spring are classified in ortho-thermal family because they have a temperature of order 42°C (37°C<T=42°C<45°C).

The chemical facies is chloride-sodium, which shows that the waters of the source having circulated through saliferous formations of the Triassic.

A study of the relative values of the characteristic ratios of the mineral elements in these waters shows that :

• The Ca^{2+} and Mg^{2+} ions are changed against the Na+ and K+ ions of the surrounding formations;

• The predominance of calcium in relation to magnesium, this can be explained by the solubility of limestones richer in calcium than in magnesium.

• The predominance of chloride in relation to sulphate may be due to the solubility of evaporites rich in chloride rather than sulphates.

• The existence of a balance between chloride, potassium and sodium.

The physico-chemical quality of the source is poor, because its chemical composition in different elements does not respect the maximum admissible values for the Moroccan standards of drinking water.

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