



Experimental research on water chemistry evolution in case of inadequate conservation protocols: application on surface and groundwater

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Abstract

The objective of this study conducted from October to December 2020 in the Natural Resources and Sensitive Environment Development Laboratory was to demonstrate the importance of conservation protocols respect throw evolution of water chemistry. Ninety-nine samples representing three water types (tap, spring and mineral water) were analyzed. Storage was at laboratory temperature with no conservation protocol. Studied parameters (temperature, pH, CE, dissolved oxygen, oxydo-reduction potential, total dissolved solids, HCO_3^- , Ca^{2+} , Mg^{2+} , SO_4^{2-} and Cl^-) were determined using standard methods. The data registered from physico-chemical parameters were subjected to different analytical methods to assess the time affect on their values compared with initial state. The results indicate that pH and alkalinity (exprimed in HCO_3^-) are the most vulnerable to evolution processes with highly significant time factor effect, while the concentrations of chlorides and sulfates with conductivity levels are statistically less evolved. PCA analysis accounting 71.43% of the total variance examines contribution of water type composition as a second variation factor. Projection through F1*F2 plan demonstrates clearly two groups with surface waters (tap water) which are excessively mineralized and groundwaters (spring and bottled waters) in which pH and magnesium parameters variations are the best illustrated.

Keywords Conservation protocols · PCA · Water chemistry · Surface water · Groundwater · Chemistry evolution

Introduction

Water chemistry deals with the fundamental chemical properties of water itself, the chemical properties of other constituents that dissolve in water, and the countless chemical reactions that take place in water (Theodore and Ryan Dupont 2019). Water chemistry is important because several

factors about water to be treated and then distributed or returned to the environment are determined through simple chemical analysis. Probably the most important determination that the water practitioner makes about water is its hardness (Spellman 2020).

Good interpretation of water sample analysis results requires strict adherence to sampling and conservation protocols. There are two types of elements: those that must be analyzed immediately (without delay) and others—with preservatives—which can be stored for months until their analysis. Passing storage precautions may lead to a modification of waters composition (increasing or decreasing contents).

If a water sample cannot be analyzed immediately after collection, it must be stabilized until analysis to prevent or slow down various chemical or biological processes. Preservation techniques include pH control, addition of preservatives, temperature control and protection from light (Lallemand-Barrès 1993).

Several investigations tried to determine the effect of sampling temperature, bottle cleanliness and analysis time on the representativeness of the characterization (Ferland

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2014). Using uncleaned bottles during sampling increase the Suspended solids and volatile suspended solids values and decrease the chemical demand of oxygen (COD), biological demand of oxygen (BOD_5), NH_4^+ and PO_4^{3-} values compared to samples taken with clean bottles according to standard recommendations (Muirhead et al. 2006). Wastewater acidification allows the conservation of COD and BOD_{5C} . Freezing wastewater allows the conservation of BOD_{5C} and COD (Henze et al. 2008). A study by Nopens et al. (2001) demonstrates that a pH maintained at 3 in wastewater allows total and soluble COD to be retained. The main objective of this study was to determine the effect of exceeding storage standards on some parameters over a long period for that daily monitoring of three types of natural water was based on electrochemical measurements and some major elements were carried out.

Materials and methods

Samples choice

This study has an essentially qualitative aim realized through quantitative analysis. The hypothesis of having different behavior of evolution of the studied parameters led to the choice of three types of natural waters: tap water as surface water (drinking water from dam waters), spring water and bottled mineral water (Texanna) as groundwaters. The tap water and the spring water came from the region of Oum el Bouaghi located in the north eastern Algeria and characterized by semi-arid conditions.

Sampling

Ninety-nine samples were taken on October 15, 2020 and collected in 500-ml polyethylene bottles completely filled to avoid contact with ambient air. Then, transported to the laboratory (The transport time was approximately 15 min), the first sample was immediately analyzed.

The rest of the samples were left at laboratory temperature and analyzed after every 48 h. In total, 33 analyses by water type were carried out at the Natural Resources and Sensitive Environment Development Laboratory (RNAMS) at Larbi ben m'hidi University, Oum el Bouaghi.

Parameters

Temperature, pH, electrical conductivity, dissolved oxygen, oxydo-reduction potential and total dissolved solid were determined using the potentiometric method using a multi-parameter HANNA HI9829 type.

Alkalinity was determined by the titrimetric method using 0.02 N hydrochloric acid. Calcium and magnesium are also

titrimetrically titrated with ethylene diamine tetra acetic acid (EDTA) in the presence of murexide and black erichrome, respectively, as color indicators. The chlorides were determined according to the Mohr method in the presence of silver nitrate solution at 0.0282 M (Rodier and Legube 2009).

UV-Visible spectrophotometry was used to determine sulfates in an acid solution with the presence of a combined reagent: barium chlorides and tween20 solution. Barium sulfates held in suspension are easily quantified at 420 nm wavelength (Rodier and Legube 2009). The results are expressed in milligrams per liter of each of the chemical parameters.

Data analysis

Statistical analyses were performed using XI-STAT software. The descriptive statistics concerned electrochemical measurements and major elements. All three types of water and storage time were considered to be factors with three replications.

Analysis of variance (ANOVA) was used to make multiple comparisons. The means were compared and the differences were considered significant at the odds threshold at $P < 0.05$.

Table 1 represents the conservation norms of water samples. Results obtained later will be compared to them.

Results and Discussion

ANOVA results

Analysis of variance (Table 2) revealed the presence of a non-significant time (day) effect on electrical conductivity and total dissolved solids (TDS) and significant to a very highly significant effect on the rest of the measured parameters of the water samples. It also showed a very highly significant effect of water type on all measured variables except dissolved oxygen, which represents relatively similar values in the three types of water (Table 2).

For the two parameters sulfate and chloride, the measurements are carried out weekly; therefore, they were separately exposed to an analysis of variance. This showed the absence of significant variations between the different weeks for two variables. On the other hand, it revealed the existence of a very highly significant effect of water nature on them.

Water chemistry evolution

Time effect on daily measured parameters

Electrochemical parameters *Temperature* Since the analyzed waters are exposed to ambient temperature, their

Table 1 Containers, techniques and storage time

Parameter	Container	Conservation agent	Maximum conservation time
pH	Polyethylene, Glass	Not necessary	Immediate analysis
Dissolved oxygen	Glass	Not necessary	Immediate analysis
Temperature	Polyethylene, Glass	Not necessary	Immediate analysis
Alkalinity	Polyethylene, Glass	Cold 4 °C	24 h
Calcium and Magnesium	Teflon, Polyethylene	Filtration and acidification (pH < 2 with HNO ₃)	6 months
Chlorides	Polyethylene, Glass	Not necessary	28 days
Sulfate	Polyethylene, Glass	Cold 4 °C, add zinc acetate and NaOH (pH > 9)	7 days

(Scaif et al. 1981; Barcelona et al. 1985)

temperature is strongly influenced by its changes. Days 71, 43, 36, 15, 34, 17, 72, 39, 67 and 41 are characterized by relatively high temperatures, dropping from $20.53 \pm 0.25^\circ\text{C}$ to $22.1 \pm 0.30^\circ\text{C}$, while the days 74 and 76 are characterized by low temperatures (15.47 ± 0.25 and $15.20 \pm 0.26^\circ\text{C}$, respectively) and the rest of the days record intermediate temperatures (between 16 and 20°C).

pH Water pH is an important chemical property that controls the distribution of chemical species in various forms. For example, the pH is buffered at precise values in animal cells to maintain the functionality of specific enzymes and proteins. It is important to measure water pH in situ because samples are susceptible to temperature variations (Larson 1975; Kohlmann 2003).

In closed systems, every change in sample temperature induces a change in hydrogen ion activity. A diminution of 0.45 was recorded in pure water if the temperature is raised to 25°C (Langelier 1946).

Water that is not in equilibrium with the atmosphere (groundwater) may change when exposed to the atmosphere; therefore, sample containers should be filled entirely without agitating and stirring and measured in a closed system if possible. Schock (2013) demonstrates the effect of CO₂ loss on pH when the sample is exposed to the atmosphere at 25°C .

pH registered values show that the water concerned by this study has increased significantly (Fig. 1b) compared with the initial state. It should be noted that there are no preservation methods for this parameter and the analysis must be carried out within 6 h after sampling.

In the first week, the pH values recorded of the waters are relatively low (7.36 ± 0.55 , 7.43 ± 0.56 , 7.40 ± 0.44 and 7.45 ± 0.54 which constitute the G group). In the second week, the values of this parameter increase and reach the maximum values (7.86 ± 0.53 , 7.90 ± 0.44 , 7.94 ± 0.50 and 7.93 ± 0.51 and form the homogeneous group A, the rest

of the weeks and until the end of the test the pH indicates intermediate values.

There are no agents that can stabilize alkalinity and acidity; these parameters are determined in the field immediately after sampling (Barcelona and Helfrich 1986; Barker and Dickhout 1988); for that, results showed significant variations in time.

Electrical conductivity Micro siemens per centimeter is the used unit for EC measurements. Water conductivity may be controlled by various factors like geology, atmospheric inputs, evaporation, some microbial metabolism, etc.

Depending on which electrolytes are present, the electrical conductivity increases $1\text{--}3\%/^\circ\text{C}$ (Robinson and Stokes 1965). Therefore, electrical conductivity is typically reported at 25°C to standardize the effect of temperature. The conductivity of natural water can be calculated from their chemical composition. Interpretation of results is based on temperature and TDS data.

Figure 1c explores the daily variation of conductivity in the three water types. No significant variations were noted over 78 days. Separately represented, EC values correlations with temperature are most illustrated for tap water. This is probably due to their excessive mineralization.

Dissolved oxygen Dissolved oxygen (DO) is a vital component in determining the health of aquatic systems. Its rates are highly dependent on temperature, atmospheric pressure and biota metabolism (respiration and photosynthesis).

In the current study, atmosphere-water surface exchange is canceled. The statistical data analysis reveals a tendency for a decrease in dissolved oxygen over time. Studied waters were driven to anoxic conditions, the highest values were detected at the start of the test; 17.13 ± 1.36 on the first day (group A) and 16.53 ± 3.07 on the thirteenth day (group C), while those lowest are recorded at the end of the test (9.2 ± 0.6 on the last day, 8.92 ± 0.28 on the 71st day and 8.91 ± 3.62 on the 64th day thus representing group D).

Table 2 Analysis of variance (mean squares of deviation) results

Variation source	ddl	T	pH	CE	DO	ORP	TDS	HCO ₃ ⁻	Ca ²⁺	Mg ²⁺	SO ₄ ²⁻	Cl ⁻
Time effect	31	9,02 ^{***}	0,06 ^{***}	1137,3 ^{ns}	10,9 ^{***}	2507,3 ^{***}	312,7 ^{ns}	748,1 ^{***}	582,6 [*]	2,6 ^{***}	1985,7 ^{ns}	431,9 ^{ns}
Water type effect	2	0,237 ^{***}	7,23 ^{***}	27,741,349,4 ^{***}	2,3 ^{ns}	2130,1 ^{***}	6,940,425 ^{***}	55,343,7 ^{***}	53,689,9 ^{***}	21,2 ^{***}	33,615,6 ^{***}	234,709,6 ^{***}
residual	62	0,03	0,01	769,3	1,95	34,1	199,8	115,3	350,4	220,4	1439,1	380,6

ns, *, **, ***: non significant et significant at 5%, 1% and 1%, respectively

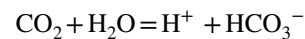
ORP Oxydo-reduction potential; TDS total dissolved solids

Major anions and cations Alkalinity (HCO₃⁻) The protocol for determining alkalinity by standard methodology is presented by Eaton et al. (2005). The traditional procedure for alkalinity is to measure how much H⁺ is required to titrate a sample in the presence of methyl orange to the endpoint (about pH 4.5). The pH at the titration endpoint corresponds approximately to the point where an amount of H⁺ has been added to react with all the OH⁻, CO₃²⁻, and HCO₃⁻ in the sample to produce CO₂ and H₂O. The milliequivalents of H⁺ used in the titration multiplied by 50.04 mg CaCO₃/meq is the alkalinity.

Limestone is a major source of alkalinity and hardness. This substance varies in composition ranging from CaCO₃ (calcite) to MgCO₃.CaCO₃ (dolomite), but most limestone is a mixture of CaCO₃ and MgCO₃ in which CaCO₃ is most abundant (Bowles 1956).

The discussion of alkalinity evolution is possible only in the case of comparison with the temperature evolution curve. Carbon dioxide enters the water from the atmosphere and the respiration of aquatic organisms.

The solubility of CO₂ in water depends on atmospheric pressure, the concentration of CO₂ in the atmosphere, water temperature and salinity, according to the following formula:



In Fig. 2, fluctuations in alkalinity expressed in HCO₃⁻ are a function only of temperature and salinity as the effect of atmospheric CO₂ and pressure are canceled. Variations are significant and the respect of sampling norms for this parameter is required (24 h).

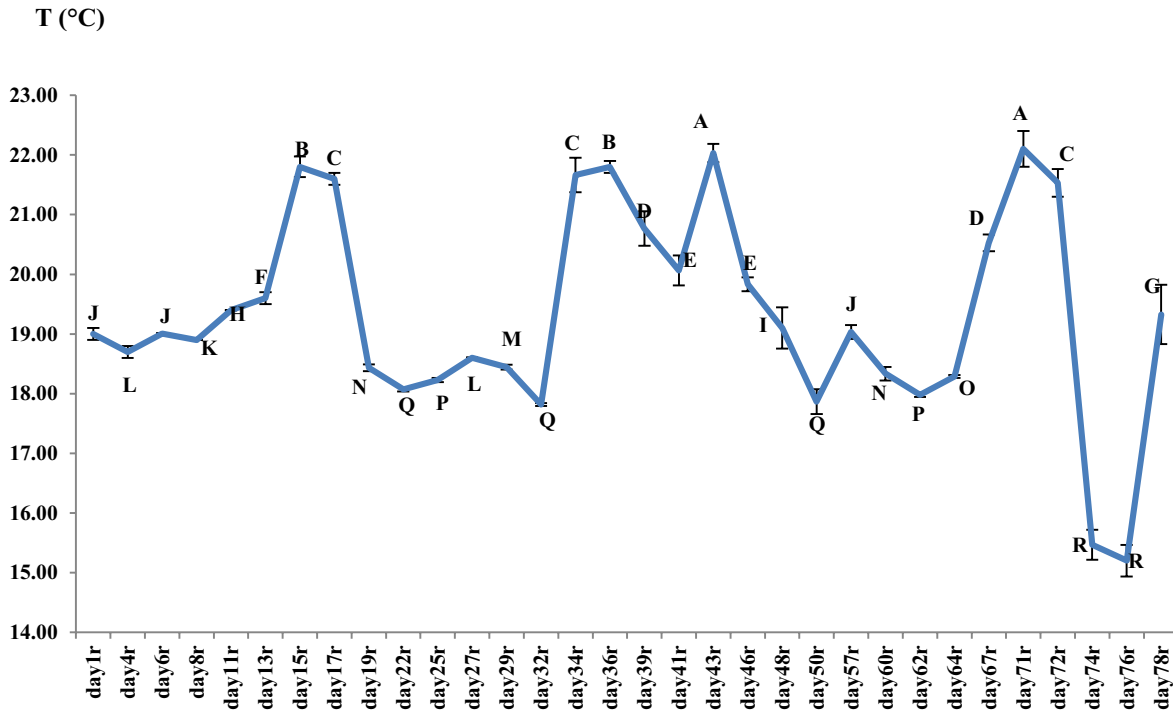
The bicarbonate values oscillate between 16.94 ± 8.64 mg/l. The value marked on the 11th day is 105.39 ± 51.36 mg/l., and the value recorded on the 62nd day, an increase of 88.45 mg /l indicates the instability of this element during water storage.

Chlorures The mean values of the chlorides of the studied samples pass from 95.56 mg / l; value recorded at the Third week at 133.33 mg / l; value marked at the 12th week. The contents of drinking water studied in this element represent values; statistically similar over the 12-week study.

Sulfate The average sulfate content of the three types of drinking water analyzed varies between 27.58 mg/l; value recorded at the 2nd week and 111.69 mg/l; value observed at the end of the test (12th week), i.e., a difference of 84.11 mg /l (Fig. 2.c). This increase remains statistically insignificant, which requires the hypothesis of the stability of sulfate concentrations during the period of water storage, at least during the three months of testing.

Calcium Ca²⁺ Calcium is an alkaline earth metal that is extremely common in nature especially, in calcareous rocks in the form of carbonates. A major component of water hardness, calcium is generally the dominant element in drinking water. Its levels vary essentially according to land geology.

a



b

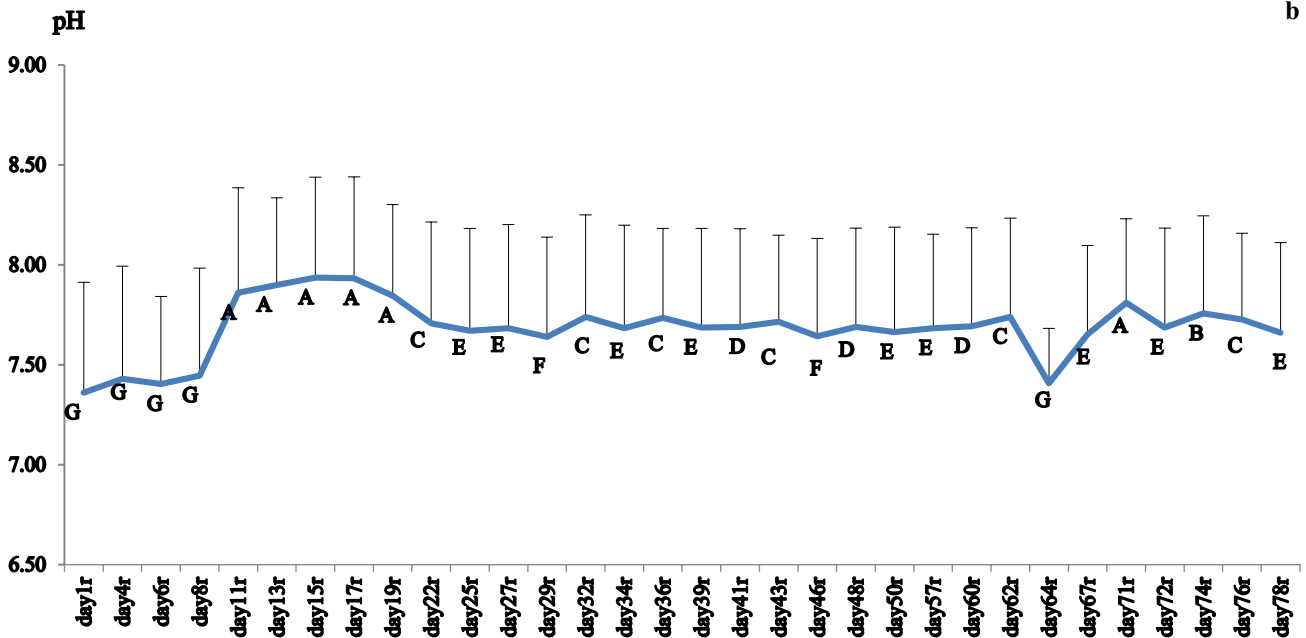


Fig. 1 Average effect of time on physico-chemical parameters: temperature in (a), pH in (b), CE in (c) and dissolved oxygen in (d)

Results revealed that initial calcium levels are relatively lower than final levels.

Magnesium Mg^{2+} The temporal variation of the magnesium content of the water studied indicates the presence

of an increasing trend over time with a correlation coefficient r equal to 0.67. This tendency has made it possible to highlight three homogeneous groups: groups A, B, and C.

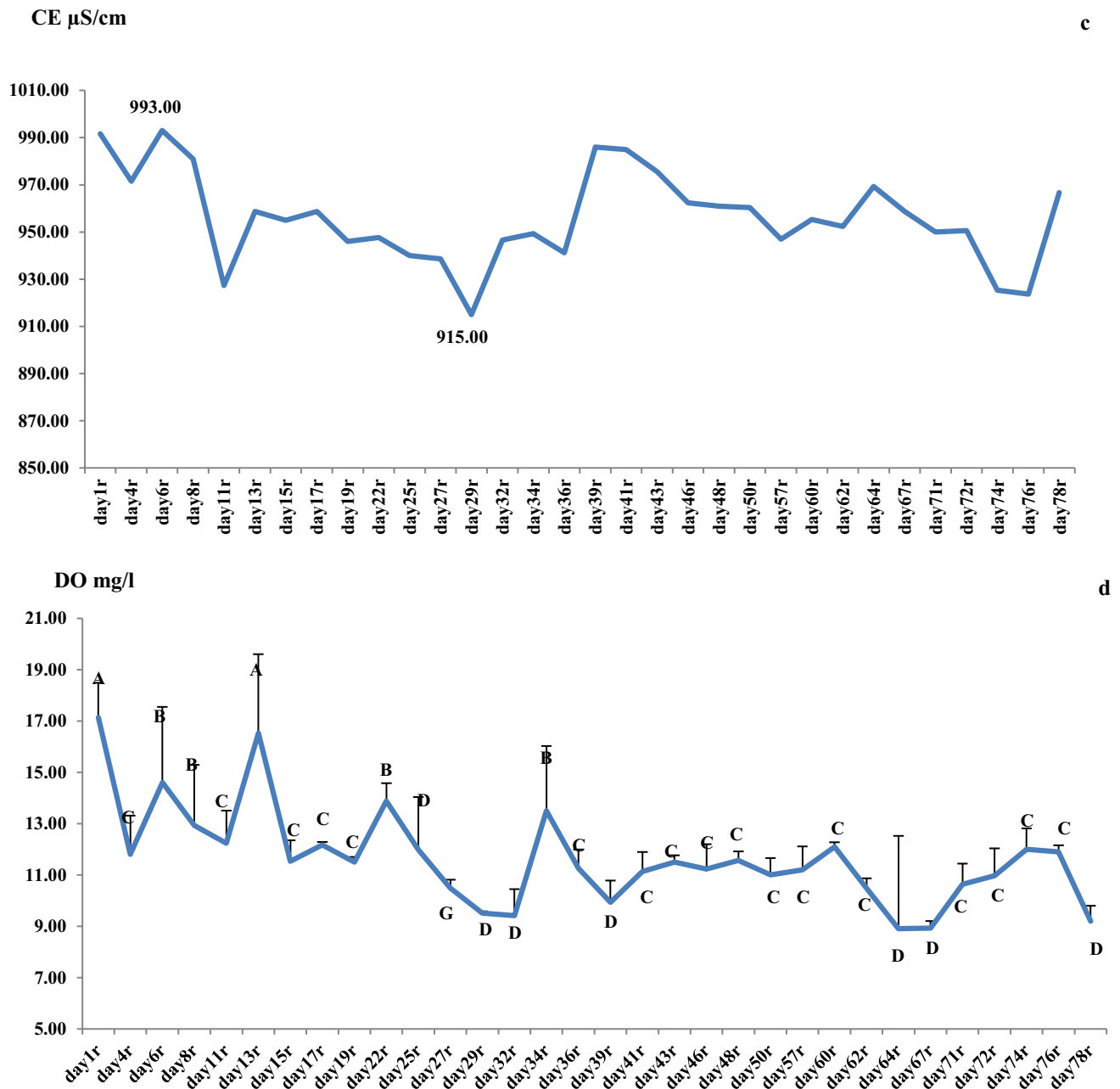


Fig. 1 (continued)

Water type effect on daily measured parameters

As was observed by the analysis of variance, the effect of the nature of drinking water is very highly significant on all the parameters measured except dissolved oxygen. This means that there are significant differences between all types of water studied (Table 3).

The comparison of the means of the variables measured on the three types of drinking water indicates that tap water represents the highest values for the majority of the

parameters measured (temperature, electrical conductivity, redox power, the level of dissolved salts, bicarbonate, calcium, magnesium, sulfate and chloride) compared to other types of water, thus building group A. This water, on the other hand, has a relatively lower pH. Mineral water shows average values of temperature and dissolved oxygen similar to tap water. For the rest of the parameters measured, its values seem closer to that of spring water except the pH, where each type of drinking water falls into a different group.

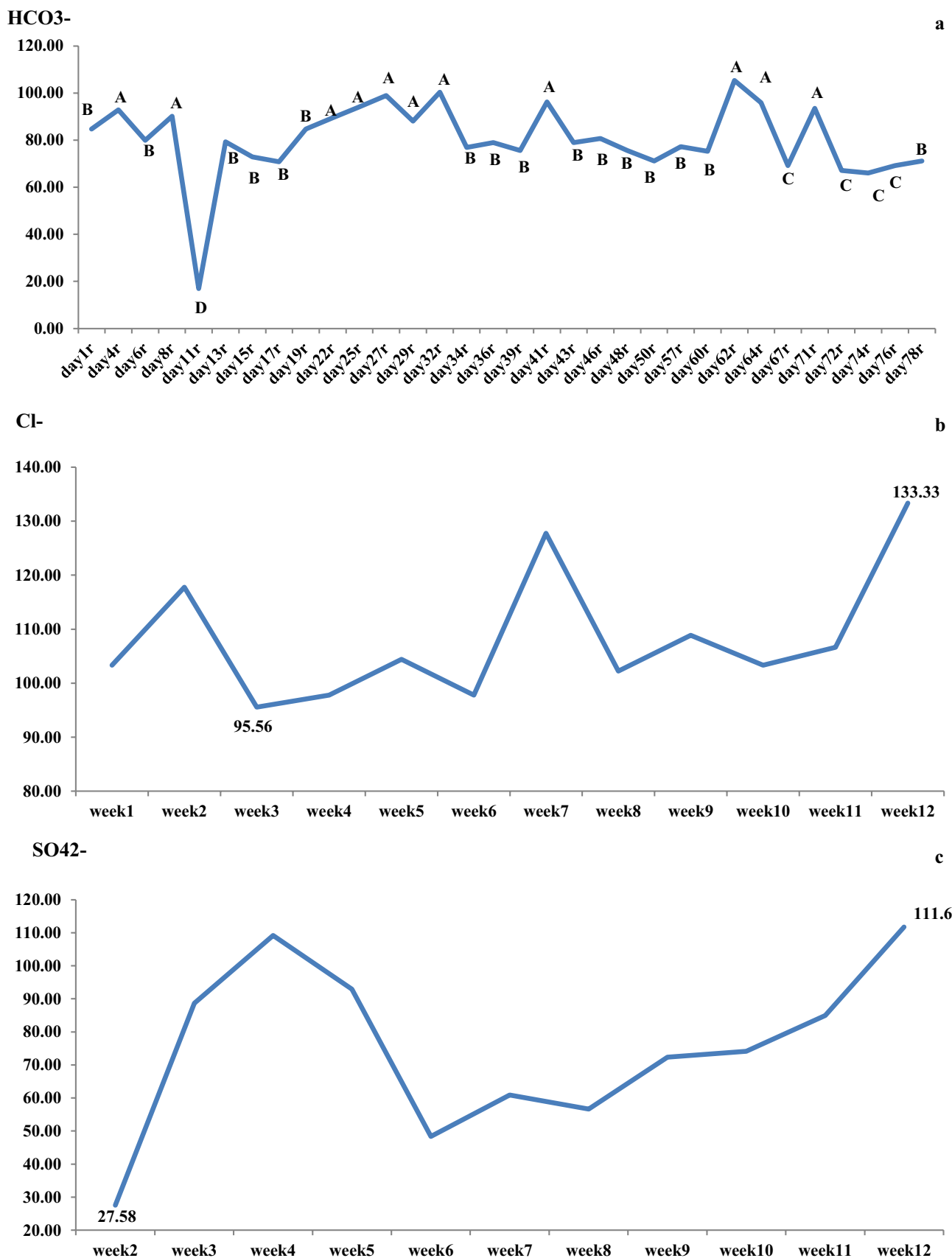


Fig. 2 Average effect of time on Anions in (a, b and c) and Cations in (d and e)

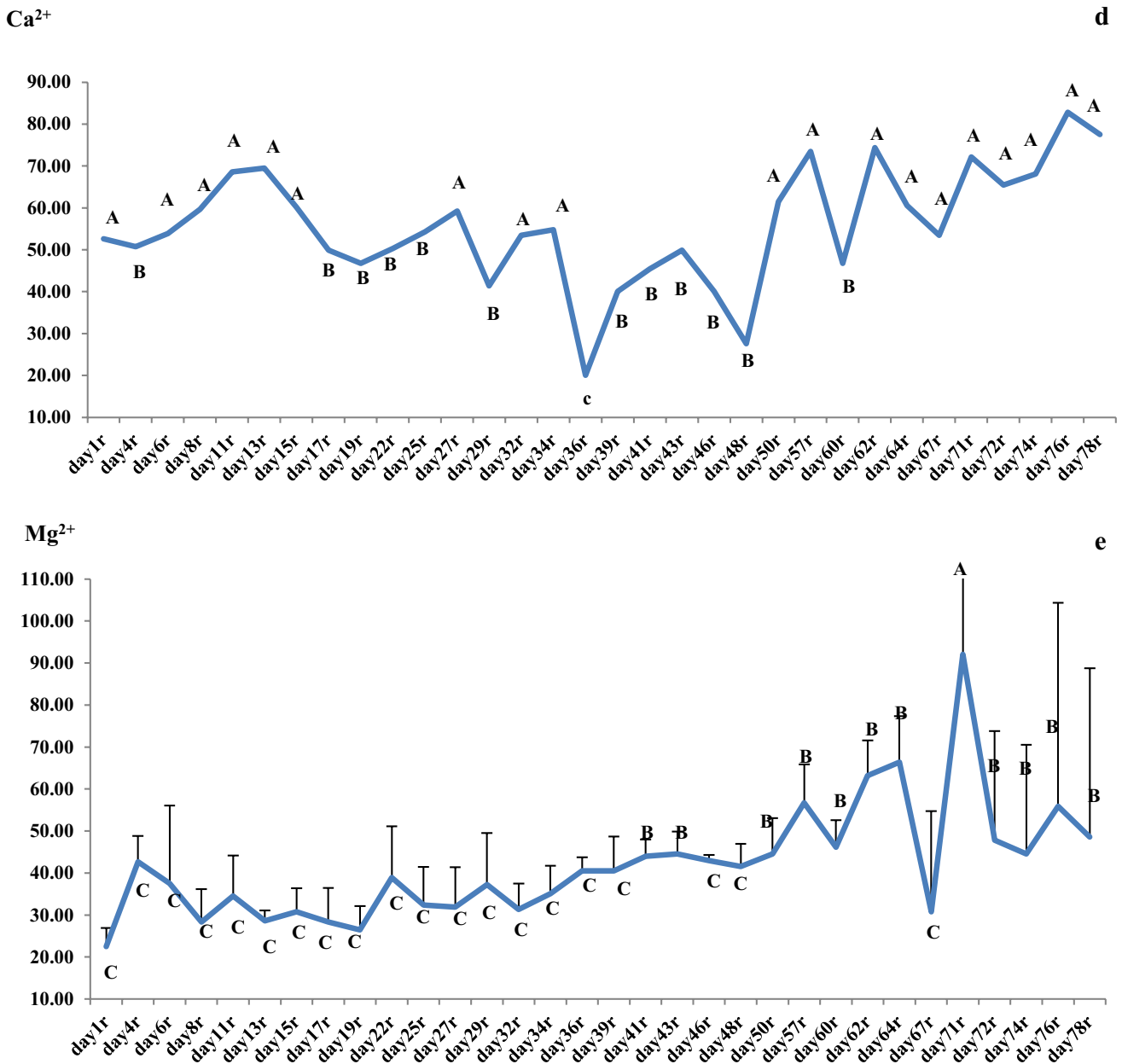
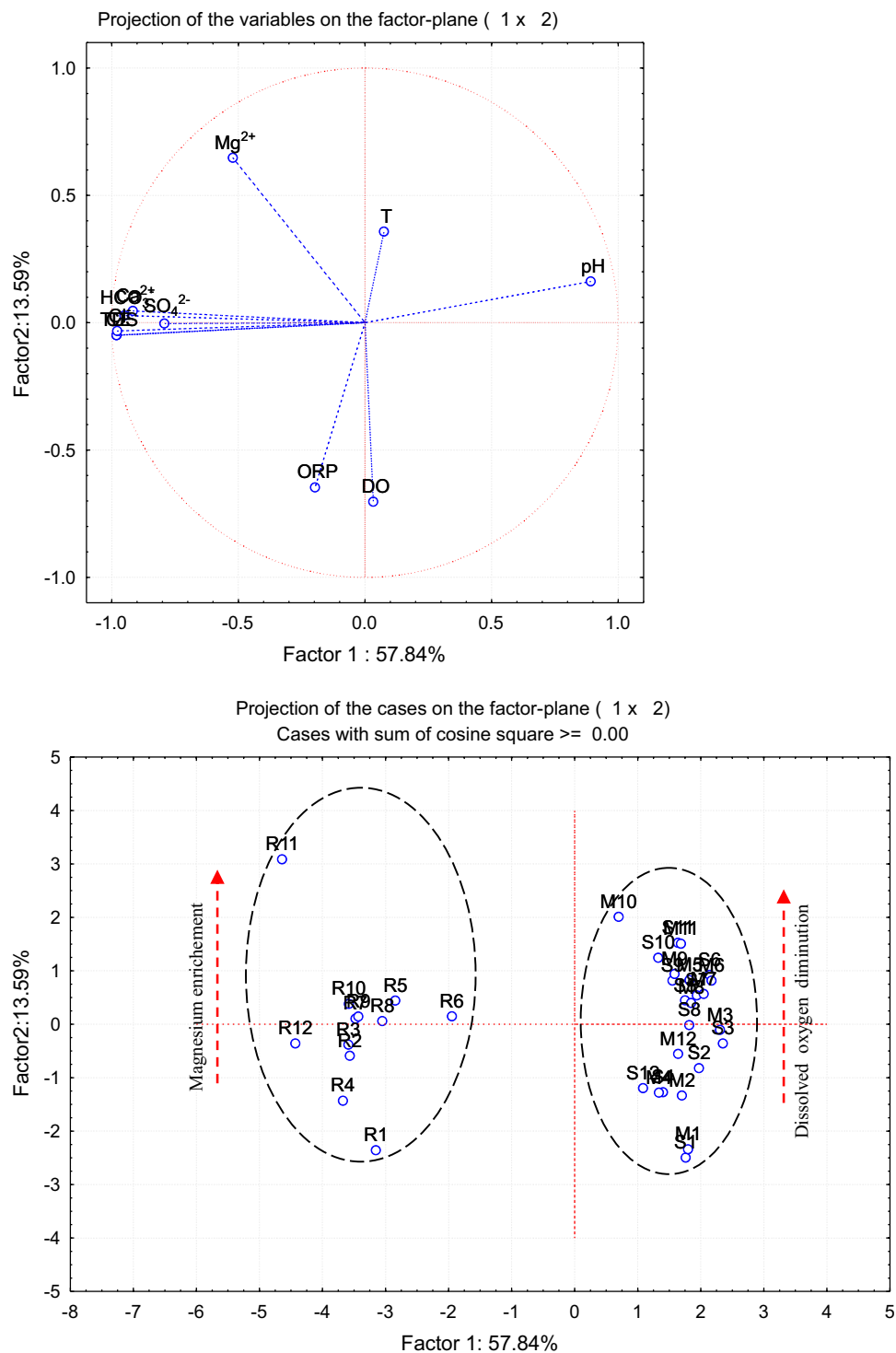


Fig. 2 (continued)

Table 3 Effect of water nature on measured parameters (means and homogeneous groups)

Water nature	T	pH	CE	DO	ORP	TDS	HCO ₃ ⁻	Ca ²⁺	Mg ²⁺	SO ₄ ²⁻	Cl ⁻
Tap water	19,33 A	7,14 C	2031,06 A	11,86 A	192,92 A	1015,37 A	127,81 A	102,86 A	55,13 A	138,59 A	269,72 A
Spring water	19,24 B	7,89 B	413, 42 B	11,35 A	178,65 B	206,69 B	50,83 B	36,07 B	31,58 B	50,15 B	28,89 B
Mineral water	19,41 A	8,02 A	423,39 B	11,77 A	178,93 B	210,78 B	26,05 B	28,37 B	38,67 B	36,91 B	26,11 B
LSD	0,083	0,05	13,86	0,699	2,92	7,06	5,37	9,35	7,42	33,74	16,52

Fig. 3 PCA projections of variables and observations



Global data correlations (Principal component analysis)

Explaining variations and correlations in global hydrochemical and water quality data using PCA projections is widely developed. The purpose of this analysis is to transform the data table into a new orthogonal and uncorrelated set of

factors called principal components (PC) and to extract significant information from the data. This new representation compresses the data by keeping only the most important information, simplifying the explanation, and exploring the structure and composition of the data (Abdi and Williams 2010). The proximity of lines for two variables signifies the

strength of their reciprocal association (Qu and Kelderman 2001).

In the present study, PCA was applied (using XLSTAT software) to physical and chemical parameters (variables) of the ninety-nine groundwater samples (observations) from three water types to explain similarities and variations during a period of time.

Factor F1 (Fig. 3) explains 57.84% of the variance and correlated with 70% of variables (pH, CE, TDS, HCO_3^- , Ca^{2+} , Cl^- and SO_4^{2-}). This factor represents highly mineralized waters (Tap water), in which water chemistry evolution is the best illustrated.

Factor F2 explains 13.59% of the variance. It has a negative correlation with dissolved oxygen and a positive correlation with ORP and Mg^{2+} . This factor represents water enrichment by Magnesium associated with groundwater indicating intensive photosynthetic algae activity and microbial oxygen consumption. This factor demonstrates that the biological activity mainly influences spring and bottled mineral water.

Conclusions

Multivariate statistics were applied to hydrochemical data of three water types belong 78 days. This study shows the usefulness of analysis of variances (ANOVA) to identify significant relationships between measured parameters levels evolution with time. It also allows the understanding of the specific behavior of each water type and the complexity of factors that control water chemistry.

Applied methods explain modalities of temporal variability of eleven parameters which can be divided into (1) parameters with non-significant variations such as electrical conductivity, total dissolved solids, sulfates and chlorides. It is important to mention that even their conservation protocols time is too long. (2) Parameters with significant variations such as calcium and (3) parameters with high significance such as dissolved oxygen, pH, bicarbonates, magnesium and ORP in which conservation delay do not exceed 24 h.

Filling and hermetic sealing of the bottle cannot be considered a means of long-term preservation, but it increases the storage time. To conclude, the correct execution of conservation protocols ensures the quality and reliability of the obtained results.

Further studies should incorporate the evolution of BOD_5 , COD and Organic matter for more parameters investigation.

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Declarations

Conflict of interest There is no conflict of interest.

Ethical approval This article does not contain any studies with human participants or animals performed by any of the authors.

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