

# Hydrochemical applications of the analysis of repeated measurements

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## Abstract

A modified method for multivariate statistical analysis of repeated samples, including coincidence and proportionality tests, has been programmed and applied to mineral and normal waters from the Basque Country (NE of Spain). The application includes the comparison of selected samples that are both replicated and geographically associated.

Springs are characterised by water and air temperatures, flows (not used for comparison) and thirty parameters, including major and minor constituents, dissolved gases, pH, electrical conductivity and residues (at 110°C and 600°C).

Results corresponding to coincidence and proportionality (by dilution or different contact time with rocks) and not by proportionality of samples, based on determined parameters, are presented. Further applications of the method to the last samples, excluding some parameters to get proportional contents for the rest of the constituents, are included for cases where the lack of proportionality is attributed to the contact with more than one type of rock or to the occurrence of a cationic exchange process.

Future applications for the proposed method, mainly in the area of environmental chemistry, are suggested.

## Introduction

The past decade has seen a remarkable advance in the application of some statistical multivariate techniques for the explanation of hydrochemical problems, mainly factor (Bronchi *et al.*, 1983; Gomez, 1984; Van Tonder and Hodgson, 1986) or cluster analyses (Van Tonder and Hodgson, 1986) and multiple linear regression (Gomez, 1984) with the purpose of finding relations between many samples, characterised by a great number of parameters.

Nevertheless, no attention seems to have been devoted to the use of statistical methods for the comparison of two samples, equally characterised by a great number of parameters.

Such a comparison, which may provide an important tool for interpreting many natural or man-promoted phenomena, has been previously established in a general sense (Morrison, 1976) and used for the study of biological experiments.

The aim of this paper is to describe modifications of the multivariate repeated measurements technique and to consider their applications in hydrochemistry by means of a number of selected examples.

Additional features of the same research (Villagra, 1987), including factor and cluster analyses and multiple linear regression, as well as applications of the described multivariate method to different systems, mainly in the area of the environmental chemistry, will be included in the objectives of future papers.

## Methods

### Sampling and chemical analysis

The total study embraced 60 individual (and 24 replicated) samples. The sampling points are shown in Fig. 1. For the studied zone, the samples included all the thermal (25) and saline (4) waters and a selection of sulphur (13) and iron containing waters (4). For comparison, some "normal" springs (14) were also sampled. This paper, however, is only based on some of the former waters.

Sampling techniques and chemical analyses were adjusted and carried out according to known methods (APHA, 1980; Rodier, 1981; Grasshoff *et al.*, 1983). Water and air temperatures and flow were also measured. Chemical parameters included pH, electrical conductivity, 110°C and 600°C residues, dissolved oxygen, carbon dioxide, sulphide, organic matter, silica, ammonia, nitrite, nitrate, bicarbonate, sulphate, chloride, boron, fluoride and metals (Li, Na, K, Mg, Ca, Fe, Mn, Al, Zn, Cu, Co, Ni and Cd).

### Data treatment

For comparison of two (replicated or associated) samples, a procedure based on a known multivariate method of analysis of repeated measurements (Morrison, 1976) was developed, programmed (IBM Personal Computer AT) and applied to selected samples, for the 0,95 confidence level.

The original method was applied to two samples, characterised by  $N$  parameters. The first step was the calculation of the differences between the values of each parameter for both samples,  $d_i = X_{1i} - X_{2i}$ , with  $i = 1, 2, \dots, N$ . If  $d$  and  $sd$  are respectively the mean and standard deviation of the  $d_i$  differences, the statistical test is  $T = [d\sqrt{N}]/sd$ . If the null hypothesis is true,  $T$  has the Student-Fisher  $t$  distribution with  $N-1$  degrees of freedom, for the desired significance level.

The adopted modifications of the method (see flow diagram in Fig. 2) included:

- The selection of parameters to be used for comparison between samples.
- Normalisation of samples to get the same weighing for parameters. For normalisation it was necessary to exclude those parameters with measured values for the second sample and below detection limits for the first one. When the values for both samples were below detection limits, their quotient was supposed to be unity and the parameter was accepted. In consequence the number of parameters finally used for calculating differences,  $N^*$ , may be lower than  $N$ .
- Coincidence test, with calculations of the differences of values of the used parameters, previously normalised with respect to the first sample, namely  $d_{ci} = 1 - (X_{2i}/X_{1i})$ . Coincident samples must be proportional with values of  $f$  in the range 0,95 to 1,05.

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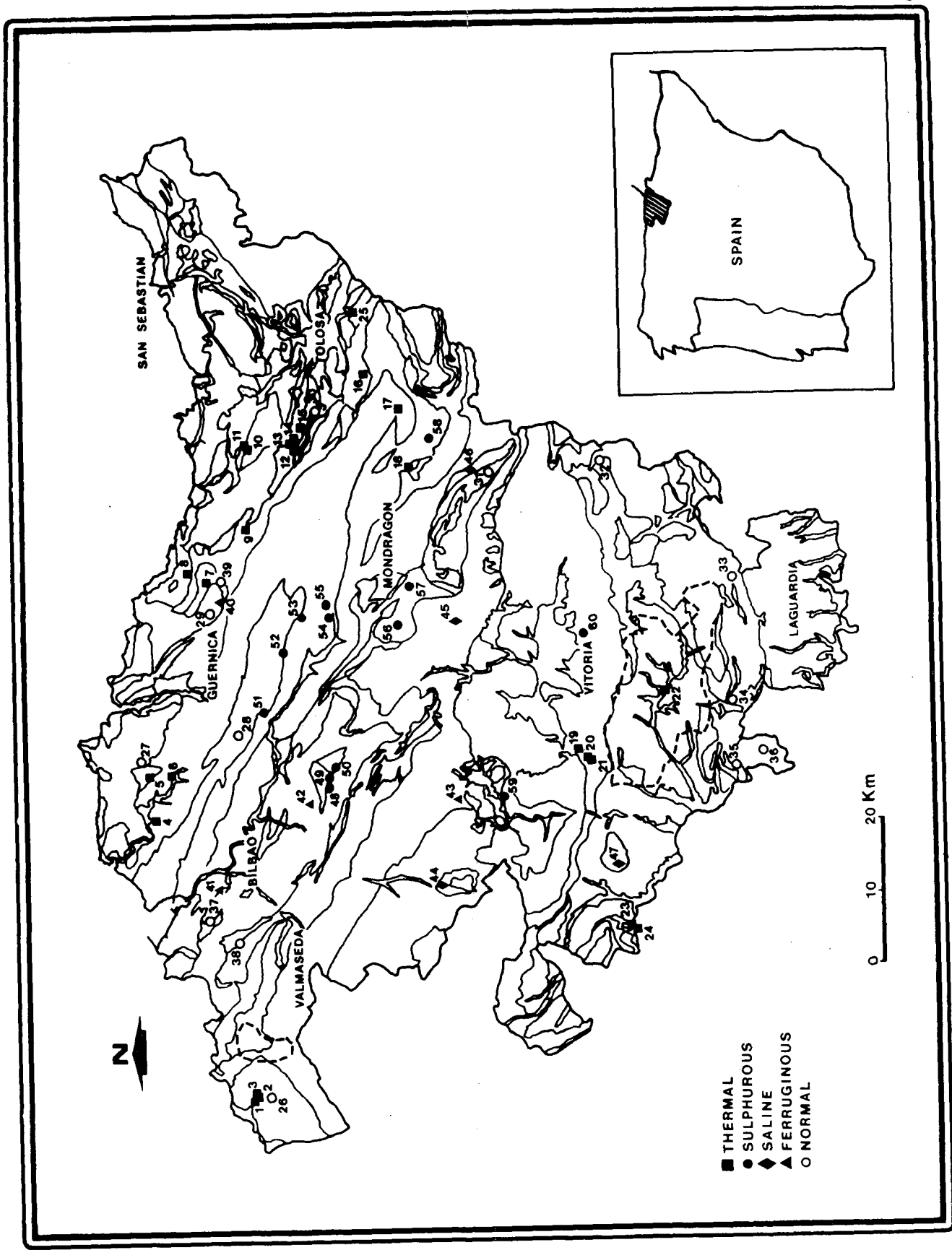


Figure 1  
Geographical position of sampling points.

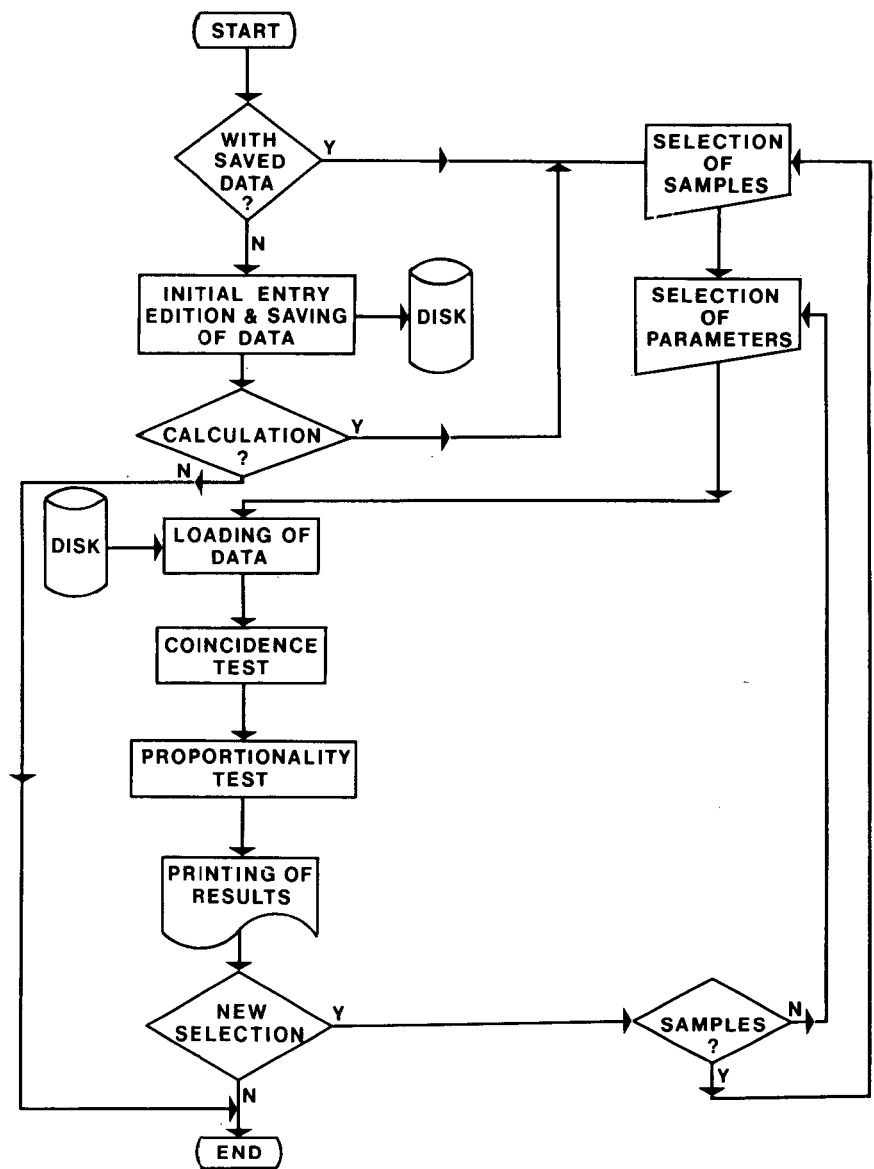


Figure 2  
Computer flowsheet of proposed method.

- Proportionality test where the normalised differences correspond to the proportionality factor for each parameter divided by the average factor. The algorithm used was  $d_{pi} = 1 - [(X_{2i}/X_{1i})/f]$ , with  $f = [\Sigma(X_{2i}/X_{1i})]/N^*$ . Proportionality, without coincidence, is equivalent to having a sample more concentrated (or diluted) in all accepted parameters.

The mean values and standard deviations of the former differences,  $d_c$  and  $sd_c$  (or  $d_p$  and  $sd_p$ ), were used for the calculation of  $T_c$  (or  $T_p$ ) to be compared with the Student-Fisher  $t$  distribution for  $N^* - 1$  degrees of freedom for the 0,95 confidence level.

## Results

### Selection of samples

From the global study (Villagra, 1987) a selection of pairs of samples was made to provide examples of the application of the proposed method to the three following situations for the two compared samples:

- Coincident compositions.

- Proportional compositions, where dilution phenomena or less contact with rocks may be inferred.
- No proportional compositions for all parameters, indicating more complex processes. For these cases a previous selection of parameters for the comparison may give rise to coincidence or proportionality and provide a reasonable explanation of processes determining chemical composition.

Analytical data for selected samples are included in Table 1. Most of the selected springs are thermal (6, 19, 10, 11, 7 and 9), with measured temperatures greater than 18°C (average temperature for the area is 12,9°C) though some sulphurous waters (60, 49 and 48) were also chosen. In three cases, replicated samplings (R) were chosen to study seasonal influences (differences from winter to summer). The other three pairs of samples were selected because of geographical proximity (less than 5 km between springs) to search for associations among components.

Analytical results for the rest of the samples shown in Fig. 1 are omitted for the sake of brevity. Some consequences obtained by the application of the proposed data treatment method are, however, presented.

**TABLE 1**  
**ANALYTICAL RESULTS FOR SELECTED SAMPLES**

Sample	6	6R	19	19R	60	60R	7	9	11	10	49	48
Water temperature (°C)	18,0	18,5	20,8	21,3	10,5	12,5	27,0	30,0	31,5	25,0	14,0	13,0
Air temperature (°C)	14,0	23,0	14,0	16,0	6,0	18,0	26,0	15,0	22,0	21,0	7,0	7,5
Flow (ℓ/s)	2	2	6	3	0,035	0,040	9,0	2,5	1,0	0,8	0,2	0,065
Bicarbonate (mg/ℓ)	180	180	205	270	1050	910	195	180	125	140	305	295
Sulphate (mg/ℓ)	375	381	30	100	30	15	20	15	1988	751	809	222
Chloride (mg/ℓ)	27	29	14	32	305	256	57	64	3220	1190	15	12
Na (mg/ℓ)	17	18	11	26	590	450	36	43	2000	760	16	17
K (mg/ℓ)	1,2	1,4	0,8	3,3	3,7	5,0	1,4	1,1	25	11	1,4	0,8
Ca (mg/ℓ)	170	180	50	79	6,4	26	48	59	741	310	360	120
Mg (mg/ℓ)	27	34	15	16	5,2	8,8	5,6	5,5	90	35	47	41
Li (mg/ℓ)	0,012	0,012	0,010	0,021	0,12	0,11	0,034	0,046	0,39	0,16	0,034	0,014
B (mg/ℓ)	*	*	0,03	0,09	1,6	1,9	0,03	0,03	0,12	0,05	0,04	0,03
F (mg/ℓ)	0,14	0,15	0,18	0,98	9,4	8,2	0,08	0,16	1,1	0,48	0,24	0,21
Fe (mg/ℓ)	0,01	0,02	*	*	0,01	0,02	0,05	*	0,88	0,05	0,07	0,12
Mn (mg/ℓ)	*	*	*	*	0,06	*	*	*	*	*	0,06	0,06
Al (mg/ℓ)	0,16	*	0,04	0,05	0,5	0,9	0,04	0,06	*	0,04	0,08	0,08
Zn (mg/ℓ)	0,03	0,026	*	0,012	0,005	0,005	0,022	0,005	0,017	0,019	0,008	0,003
Ni (mg/ℓ)	*	*	*	0,005	*	*	*	*	*	*	*	*
Cd (mg/ℓ)	*	*	*	*	*	*	*	*	*	*	0,005	*
pH	7,5	7,4	7,5	7,5	8,1	8,0	7,6	8,0	7,5	7,7	6,9	7,2
Conductivity μS/cm	883	891	466	603	2100	1900	451	445	9630	4112	1432	711
110 °C residue (mg/ℓ)	751	738	256	379	1705	1232	276	290	8290	3218	1462	609
600 °C residue (mg/ℓ)	622	638	168	271	1638	1172	207	220	7760	3038	1284	473
Dissolved oxygen (mg/ℓ)	2,2	2,1	1,4	*	2,2	1,6	1,8	3,8	4,4	4,2	2,0	1,3
Carbon dioxide (mg/ℓ)	21	14	14	16	12	15	13	4	8	4	17	32
Sulphide (mg/ℓ)	*	*	*	*	9,9	6,2	*	*	*	*	12	3,9
COD (mg O <sub>2</sub> /ℓ)	*	0,2	0,9	0,5	8,2	7,4	0,7	*	20,2	8,5	2,9	*
Silica (mg/ℓ)	18	17	7,4	9,8	20	15	11	13	31	16	18	27
Ammonia (mg N/ℓ)	0,48	*	0,16	2,0	0,28	0,99	0,72	*	0,13	*	0,13	*
Nitrate (mg N/ℓ)	0,59	0,54	1,5	0,023	*	0,47	0,079	0,32	0,15	1,3	*	0,045

\* Below detection limits. The contents of Cu, Co and nitrite were also below detection limits for all these samples.

### Coincidence and proportionality tests

Table 2 is a summary of computer calculation. Treated samples have been classified as repeated or associated. Comparisons were performed, as shown in the first column, in the order **2nd vs. 1st**. Three parameters (water and air temperatures and flow) were not considered for calculations because of their presumably random character. Parameters below detection limits, automatically excluded by the computer program, are shown in the last column.

The values obtained for  $T_c$ ,  $T_p$  and  $f$ , as well as maxima of Student-Fischer  $t$  for acceptance, are included. From these data, coincidence and/or proportionality for two samples were accepted (**A**) or rejected (**R**). For samples rejected as proportional, a third block of comparisons with selection of parameters was performed. Additional exclusions are shown in the last column.

### Discussion

**Coincident compositions** were found for two of the selected pairs of samples.

- The first one corresponds to replication of sample 6, with a hypothermal character. Coincidence must be ascribed to the chemical and isotopic stability of this type of waters (Albert, 1979), when dilution or mixing phenomena are absent. Most of the thermal springs in the global study were coincident.
- Samples 7 and 9, associated by geographical reasons, have coincident compositions, though their temperatures differ somewhat. A common origin and two different ways to the surface, without dilution or mixing, must be invoked to explain the situation of these thermal springs. In the global study, samples 12 and 14 had the same behaviour.

**Proportional compositions**, suggesting dilution phenomena or different contact with the same type of rocks, occurred in two of the selected pairs.

- The first case corresponds to repeated samplings of a thermal spring (19R vs. 19), with different flows and water temperatures. The greater flow is accompanied by smaller

temperature and increased content in dissolved oxygen. The average proportionality factor was  $f = 0,725$ , indicating an intense dilution for sample 19. Meteorological data for the zone showed that, in the month previous to sampling, the rainfall was 223 (19) versus 63  $\text{mm}^2$  (19R), according to compositions. In the global study, some other repeated samples, with thermal (4, 15, 20), sulphurous (50, 56), saline (46) or normal (26, 27) character showed this dilution phenomenon with proportionality factors close to unity and a greater dissolved oxygen content for the diluted sample. A pair of saline springs, with the same features, had a factor  $f = 0,754$ .

- The second one is an example of geographically associated samples where the dilution phenomenon is most probably absent. Both thermal springs (10 vs. 11, with  $f = 0,403$ ) were sampled on the same day and showed the same content in dissolved oxygen. The more concentrated one (11) was even repeated with coincident composition. These facts and the higher measured temperature for sample 11 suggest a longer contact with the same type of rocks.

In the global study, many cases of proportionality in all parameters were found between two geographically associated samples both for the same type or for comparing a normal with a mineral water (thermal, sulphurous, saline, Fe-containing). Normal waters were generally more diluted than the mineral ones. The discussion of these data will be the object of future papers on different types of springs.

**The selection of a group of parameters** can be used for additional comparisons of no proportional compositions. Two possibilities are discussed in this paper:

- Lack of proportionality due to more than one type of rock in contact with geographically associated waters, leading to proportional relations for one or more of the selected groups of parameters.

As an example, the comparison between two sulphurous waters (sample 48 vs. 49) was selected for this paper. A factor  $f_1 = 0,969$  was found with the exclusion of a group of constituents (sulphate, K, Ca, Li, Zn, sulphide, electrical conductivity, and residues at 110°C and 600°C). The calculation of proportionality with these constituents with exclusion of the others, led to a factor  $f_2 = 0,414$ .

Enrichment or decrease in some constituents, with respect to geographically associated normal springs, was appreciated for the studied zone in all types of mineral waters. In the case of thermal waters, for instance, some components were preferentially concentrated (e.g. silica, Li, fluoride, carbon dioxide and sometimes major constituents, namely chloride-Na-K or sulphate-Ca-Mg) and some others were diluted (e.g. bicarbonate, nitrate, dissolved oxygen). An analysis of these phenomena for each type of spring will be included in future papers.

- Lack of proportionality due to chemical reactions of some constituents. The comparison of sample 60R vs. 60 led to a factor  $f = 0,813$  when the cations Na, K, Ca, Mg, Li, Al and ammonia were excluded. Ionic balances were as follows:

Sample	$\Sigma$ Anions (meq/l)	$\Sigma$ Cations (meq/l)
60	26,4	26,5
60R	22,4	21,7

With independence of the more diluted composition of repeated samples (lower anion and cation concentration), a cationic exchange phenomenon, with substitution of ammonia-K-Ca-Mg-Al (greater in sample 60R) for Na (greater in sample 60) with proportional contents in the main anions (bicarbonate, sulphate and chloride) could be easily inferred from analytical data (Table 1).

**TABLE 2**  
**APPLICATION OF PROPOSED METHOD TO REPLICATED AND ASSOCIATED SAMPLES. SELECTION OF PARAMETERS FOR DISCUSSION OF NO PROPORTIONAL CONTENTS**

Samples	Max. t	$T_c$	Coincidence	$T_p$	Proportionality	f	Excluded parameters
<b>Repeated</b>							
6R vs. 6	2,048	0,882	A	0,861	A	1,006	COD
19 vs. 19R	2,048	0,872	R	0,998	A	0,725	Diss.oxygen
60R vs. 60	2,048	1,138	R	2,420	R	—	Nitrate
<b>Associated</b>							
9 vs. 7	2,045	0,466	A	0,427	A	1,005	None
10 vs. 11	2,048	0,464	R	1,663	A	0,403	Al
48 vs. 49	2,048	2,913	R	3,770	R	—	Nitrate
<b>Selection of parameters</b>							
60R vs. 60	2,074	1,400	R	1,237	A	0,813	Na,K,Ca, Mg,Li,Al, Ammonia
48 vs. 49	2,093	0,875	A	0,591	A	0,969	Sulphate,K,Ca, Li,Zn,Sulphide, Conductivity, Residues
48 vs. 49	2,306	21,048	R	0,583	A	0,414	The others

## Final remarks

The analysis of repeated measurements, modified to perform coincidence and proportionality tests, is a good complement for the interpretation of chemical analyses of water samples by trilinear diagrams and other multivariate statistical methods, e.g. factor and cluster analyses, and multiple linear regression. A procedure is provided for direct comparison of repeated or associated samples, where the analogies and differences between parameters may be enhanced, with the added advantage of not being dependent only on the major ion composition. Other ions and non-chemical data could also be included for comparison.

The proposed methods seem to be a general tool for discussing not only hydrochemical problems, but also natural or man-promoted phenomena depending in several ways on a great number of variables. At the moment, environmental studies, such as air or water pollutant dispersion from sources, are *inter alia* being treated partially by us according to described procedures.

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