Atti e Memorie della Commissione Grotte "E. Boegan"	Vol. 34 (1996)	pp. 71-80	Trieste 1997

GIANPIERO ADAMI, PIERLUIGI BARBIERI, BARBARA CAMPISI,
EDOARDO REISENHOFER (*)

CHEMOMETRIC CHARACTERIZATION OF SOME KARSTIC FRESHWATERS

(Fonte Oppia and Torrente Rosandra, near Trieste, Italy)

SUMMARY

A method for characterizing karstic freshwaters was tested, starting from monitoring of a few selected chemical-physical parameters, used as 'natural indicators'. Sodium, potassium, calcium, magnesium, chlorides, nitrates, sulphates, conductivity, temperature and pH were determined in Fonte Oppia and Torrente Rosandra, at two very close sampling sites, both in autumnal and spring periods, for verifying seasonal effects. The principal component analysis performed on the experimental data gives a synthetic description of the examined waters in terms of 3 principal components (PCs). The scores relative to the extracted PCs allow us to discriminate between the examined freshwaters. The scores versus time plottings confirm that Fonte Oppia, a typically karstic spring, has lower seasonal variability of composition with respect to the epigeous Torrente Rosandra. The complex equilibria between the dissolved carbon dioxide, regulating the pH, and the major ions, Ca and Mg, typical of this calcareous area, constitute a relevant factor for characterizing and discriminating the karstic freshwaters.

RIASSUNTO

CARATTERIZZAZIONE CHEMIOMETRICA DI ALCUNE ACQUE CARSICHE (FONTE OPPIA E TORRENTE ROSANDRA, TRIESTE, ITALIA)

Si è verificato un metodo per la caratterizzazione di acque carsiche, impostato sul monitoraggio di pochi parametri chimico-fisici, opportunamente scelti quali 'indicatori naturali'. Sodio, potassio, calcio, magnesio, cloruri, nitrati, solfati, conduttività, temperatura e pH sono stati determinati nelle acque di due siti praticamente contigui, Fonte Oppia e Torrente Rosandra, durante il periodo autunnale e la successiva primavera, per verificare possibili effetti stagionali. L'analisi delle componenti principali sui dati sperimentali ha fornito una descrizione sintetica di queste acque in termini di 3 componenti principali. I punteggi relativi a queste componenti hanno permesso una discriminazione netta tra le acque dei due siti, pur così vicini. Le variazioni dei punteggi nel tempo fanno rilevare che le acque della Fonte Oppia, risorgiva tipicamente carsica, presentano una variabilità stagionale nettamente inferiore rispetto alle acque epigee del Torrente Rosandra. I complessi equilibri che implicano l'anidride carbonica disciolta e gli ioni maggiori, calcio e magnesio, tipici di quest'area calcarea, costituiscono un fattore rilevante ai fini della caratterizzazione e discriminazione delle diverse acque carsiche.

(*) Department of Chemical Sciences, University of Trieste, Via Giorgieri 1, 34127 Trieste, Italy

ZUSAMMENFASSUNG

CHEMOMETRISCHE CHARAKTERISIERUNG EINIGER KARSTGEWÄSSER (FONTE OPPIA UND TORRENTE ROSANDRA BEI TRIEST, ITALIEN)

Eine Methode zur Charakterisierung von Karstgewässer wurde überprüft, indem bestimmte chemisch-physikalische Parameter als 'natürliche Indikatoren' gewählt wurden. Um etwaige saisonbedingte Einflüsse festzustellen, wurden bei zwei in unmittelbarer Nähe voneinander liegenden Gewässern - der Fonte Oppia und dem Wildbach Rosandra - im Herbst und dem darauffolgenden Frühjahr der jeweilige Gehalt an Natrium, Kalium, Kalzium, Magnesium, Chloriden, Nitraten, Sulphaten sowie die Leitfähigkeit, die Temperatur und der pH-Wert des Wassers gemessen. Die Hauptkomponentenanalyse der experimentellen Daten lieferte eine zusammenfassende Beschreibung dieser Gewässer, wobei drei Hauptkomponenten identifiziert wurden, welche trotz der großen Nähe eine klare Unterscheidung der beiden Gewässer zuläßt. Die über den besagten Zeitraum gemessenen Werte zeigen, daß das Wasser der Fonte Oppia, einer typischen Karstquelle, eine einwandfrei niedrigere jahreszeitliche Variabilität aufweist als das Oberflächenwasser des Rosandra-Baches. Die komplexen Gleichgewichte zwischen dem aufgelösten Kohlendioxid und den Kalzium- und Magnesium-Ionen, die für dieses Kalksteingebiet charakteristisch sind, stellen im Hinblick auf die Charakterisierung und die Unterscheidung verschiedener Karstgewässer einen wesentlichen Faktor dar.

POVZETEK

KEMO-METRIČNA KARAKTERIZACIJA NEKATERIH KRAŠKIH VODA (IZVIR KLINČICA IN HUDOURNIK GLINŠČICA, TRST, ITALIJA)

Avtorji so preverili metodo za karakterizacijo kraških voda, ki sloni na pregledu maloštevilnih fizikalno-kemičnih parametrov, ki so jih zbrali kot "naravne indikatorje". Pri dveh vodah, to je v izviru Klinčica in v hudourniku Glinščica, ki se praktično dotikata, so merili jeseni in naslednjo pomlad natrij, kalij, magnezij, kloride, nitrate, sulfate, električno prevodnost, temperaturo in pH z namenom, da bi preverili morebitne sezonske spremembe. Analiza glavnih sestavin in eksperimentalnih podatkov je pokazala, da vsako izmed teh dveh voda lahko opišemo potom treh glavnih sestavin. Količina teh treh sestavin omogoča jasno ločitev med tema dvema vodama, čeprav se nahajata druga ob drugi. Spremembe v količini teh treh sestavin pa so pokazale, da izvir Klinčica, tipičen kraški izvir, kaže odločno manjše spremembe kot površinski tok hudournika Glinščica. Zapletena ravnovesja, ki zadevajo ogljikov diosid, ki je raztopljen v vodi ter jone kalcija in magnezija, ki sta tipična za to kraško področje, predstavljajo odločilen faktor za karakterizacijo in ločitev različnih kraških voda.

Introduction

We have started in 1992/93 to study freshwaters - springs, ponds - referable to Timavo river, on the purpose to descript the characteristics of this interesting hydrographic system in terms of chemical-physical parameters [Reisenhofer E., Adami G. and Barbieri P., 1996]. As a first approach, we have determined some trace heavy metals - intended as 'natural markers' - in water sampled with monthly frequency at the 3 springs flowing near S. Giovanni di Duino. The univariate analysis of the trace metal contents pointed out the different quality of these waters, notwithstanding they are situated practically contiguous, in a very narrow area. Moreover, the results of the data analysis suggested possible seasonal effect on the composition of these waters.

These preliminary results leaded us to focus our attention on samples taken in well characterized seasonal periods, as, for instance, during the intense rainfalls following the dry summer season, typical in this mediterranean area. At the same time, we have planned a higher number of sampling sites, going from the southern Val Rosandra to the northern Isonzo river.

A geochemical-isotopic study of this hydrological system, covering a space time from November 1984 to July 1988, was made by Longinelli [1988]: the method used in his study was based on the determination of $^{18}O/^{16}O$ isotopical ratios. This methodology seems very suitable to attest the source of waters, provided that mixing effects don't occur between waters of different, contiguous basins: on the other hand, these mixing-situations between different waters are not improbable in these karstic aquifers.

In the present work, we consider the waters of the 'Fonte Oppia', that present the typical features of a karstic, subterranean spring, and those of Torrente Rosandra, an epigeous stream, sampled very close to Fonte Oppia. Notwithstanding the respective waters were sampled at two very close sites, only few meters apart (see Fig.1), it is likely that their characteristics are very different. Main purpose of the present study is to verify the suitability of an alternative method for characterize freshwaters, and, at the same time, to foresee their time variation: this approach is based on the analytical determination of few selected chemical-physical parameters, used as 'natural indicators', followed by a chemometric evaluation of the experimental data, by applying the methods of the multivariate statistical analysis. This chemometric approach can constitute a fit alternative for methods which use active tracers. In fact, many authors have attempted to characterize this fluvial system by means of both artificial markers [Flora O., Galli G., Negrini L. and Longinelli A., 1990; Timeus G., 1911; Boegan E., 1938; Eriksson E., Mosetti F., Hodoscek K., Ostanek L., 1963; Gemiti F., 1982] and natural ones [Gemiti F. e Licciardello M., 1977; Mosetti F. e Pomodoro P., 1967; Cancian G., 1987]. The determined parameters were: sodium, potassium, calcium, magnesium, chlorides, nitrates, sulphates, conductivity, temperature and pH. The choice of the parameters to determine was conditioned by the necessity to obtain accurate measurements, *in situ* or in the laboratory: in the latter case, the analysis must be performed within few hours from the sampling operations. Precision and accuracy of the analytical data constitute essential conditions for the following statistical analysis of the experimental data leads to reliable results.

Experimental

Sampling

We have sampled the freshwaters of Fonte Oppia (FO), just at the exit of the spring, and those of Torrente Rosandra (RO) slighly upstream of FO (see Fig. 1). A first set of samples (6 cases) covers the rainy period following the dry summer season (from September 23 to October 29, 1994). A second set (5 cases) covers the spring period from April 4 to May 2, 1995. All samples were collected in poliethylene bottles, preconditioned with HCl for several days, then rinsed with Milli-Q water, and, finally, with the same sampled waters.

Analytical methods and instruments

Conductivity, temperature and pH were determined *in situ*. A portable conductometer (Metroohm Model 587), and pHmeter (Metrohm Model 588) were used. The temperature was measured by an Anritherm probe, with a precision of 0.1°C.

The chemical parameters were determined in laboratory, within few hours from the sample collection. Chloride, nitrate and sulphate contents were determined by high-performance ion-exchange chromatography (HPIEC), using a Thermo Separation Products Constametric 3200 isocratic pump, a Rheodyne 7125 injector, and a Conductomonitor detector. Sodium, potassium, calcium and magnesium were determined by atomic absorption spectrometry (AAS): a SpectraAA20 Varian Spectrometer was used. Reference solutions for calibration procedures were prepared by dilution of the respective standards with Milli-Q water. All reagents were of analytical grade.

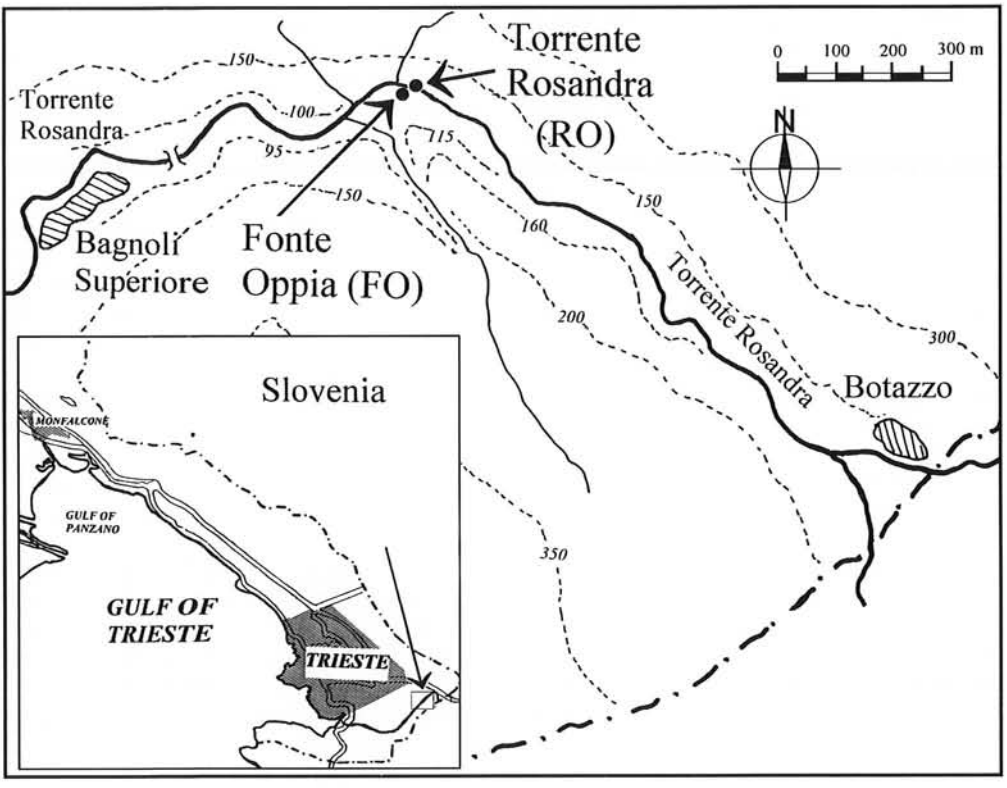

Fig. 1. Sampling sites: Fonte Oppia (FO) and Torrente Rosandra (RO).

	Fonte Oppia (FO)							*Torrente Rosandra (RO)*						
Variable	Mean	Min	Max	SD	Kurt	Skew	Cases	Mean	Min	Max	SD	Kurt	Skew	Cases
C	412	367	492	39.8	0.0	0.8	11	362	302	429	42.2	-1.4	0.2	11
pH	7.2	6.5	7.6	0.3	0.6	-1.1	11	8.3	7.4	8.7	0.4	2.3	-1.4	11
T	12.4	11.9	12.9	0.4	-1.7	0.0	11	11.3	8.9	15.6	2.1	0.6	0.9	11
Na	2.6	1.4	3.7	0.9	-1.9	-0.1	11	4.9	3.1	6.6	1.2	-1.3	-0.1	11
K	0.8	0.3	3.2	0.8	9.3	3.0	11	1.5	1.2	2.2	0.3	0.9	1.5	11
Ca	57.2	22.8	73.8	19.2	-0.4	-1.0	11	51.1	26	68.2	16	-1.8	0.2	11
Mg	3.7	3.1	4.5	0.6	-2.0	0.0	11	3.6	1.9	4.9	1.3	-1.8	-0.4	11
Cl	4	2.2	5.3	1.1	-1.0	-0.2	11	5.2	3.6	7.5	1	1.4	0.6	11
NO_3	3.4	1.9	5.1	1.1	-1.2	0.4	11	3.8	1	8.4	2.7	-1.2	0.5	11
SO_4	12.3	7	16.6	3	-0.9	0.3	11	28.6	17.7	38.2	6.1	-0.6	0.2	11

Table 1. Basic statistics of 10 chemical-physical variables, at 2 sampling sites (FO a RO)

Results and Discussion

We have collected experimental data, at 2 different sampling sites, during autumnal, rainy period (6 cases) and the following spring (5 cases), with the purpose to verify if the seasonal effects are conditioning the composition of these freshwaters. In each sample, we determined the following 10 chemical-physical parameters: conductivity (C), pH, temperature (T), sodium (Na), potassium (K) calcium (Ca), magnesium (Mg), chlorides (Cl), nitrates (NO_3) and sulphates (SO_4). On the whole, we have at disposal a starting data matrix containing 10 variables, as determined at 2 different sites, for 11 cases (sampling days). The basic statistics for this data populations are reported in Table 1.

The correlation matrix obtained from a 10x22 normalized data matrix is reported in Table 2. We have then performed a principal component analysis (PCA) [MALINOWSKI E. R., 1991]. The PCA results, reported in Table 3, allow the extraction of 3 eigenvalues, that explicate 80.9% of the variance. We can therefore interpret the system constituted by the here considered freshwaters in terms of 3 principal components (PCs).

The eigenanalysis shows that the first component (PC1, with 43.8 pct of explained variance), has the highest loadings on conductivity, chlorides, nitrates, sulphates, sodium, potassium, calcium and magnesium: *i.e.*, PC1 is strongly correlated with the ionic solutes of the waters. The second component (PC2, with 25.3 pct of explained variance) has high loadings on hand on pH and, on the other hand, on calcium and magnesium, but with opposite signs. We can interprete PC2 in terms of the complex chemical equilibria between the dissolved carbon dioxide (regulating the pH) and calcium and magnesium ions, typical of the karstic freshwaters, whose hardness depends on the shifting of the above-mentioned equilibria in different environmental or seasonal conditions. The third, less important component (PC3, with 11.8 pct of explained variance) is correlated to temperature. The unrotated loadings of the chemical-physical variables on the axes of the 3 extracted PCs are plotted in Fig. 2.

The plotting of the factor scores of the 2 sampling sites on the axis of PC1 (correlated with water salinity) points out a clear separation between waters of the 2 sites (see Fig.3): Fonte Oppia presents always lower values, both in autumn and in spring, with respect to Rosandra waters. At the same time, we observe a seasonal effect: the values of both freshwaters are lower in autumnal period (cases 1-6) than in spring (cases 7-11). We interpret this fact in term of dilution of the waters, that decrease their salinity, owing to the rainfalls, typical of the autumnal period.

The factor scores relative to PC2 (correlated to equilibria implicating dissolved carbon dioxide, calcium and magnesium ions) shows that the second principal component allows to discriminate the 2 sampling sites, FO and RO, in autumn (see Fig.4). The spring period presents an overlapping of the factor score values, that don't allows to differentiate the composition of the 2 sites. It is meaningful that the scores of Fonte Oppia are rather constant througout the different seasons: this characteristic is typical for hypogeous freshwaters, whose compositions are scarcely influenced by external conditions.

A more comprehensive insight of overall information given by our data matrix, constituted by the chemical-physical parameters determined in the 2 here considered sampling sites, during 2 different seasonal periods, early autumn and the following spring, can be obtained from a three-dimensional plot of the principal component scores relative to FO and RO sampled freshwaters: in Fig.5, the 3 axes are PC1, PC2 and PC3 respectively.

This three-plot shows a sharp separation of the Fonte Oppia spring-waters (black points)

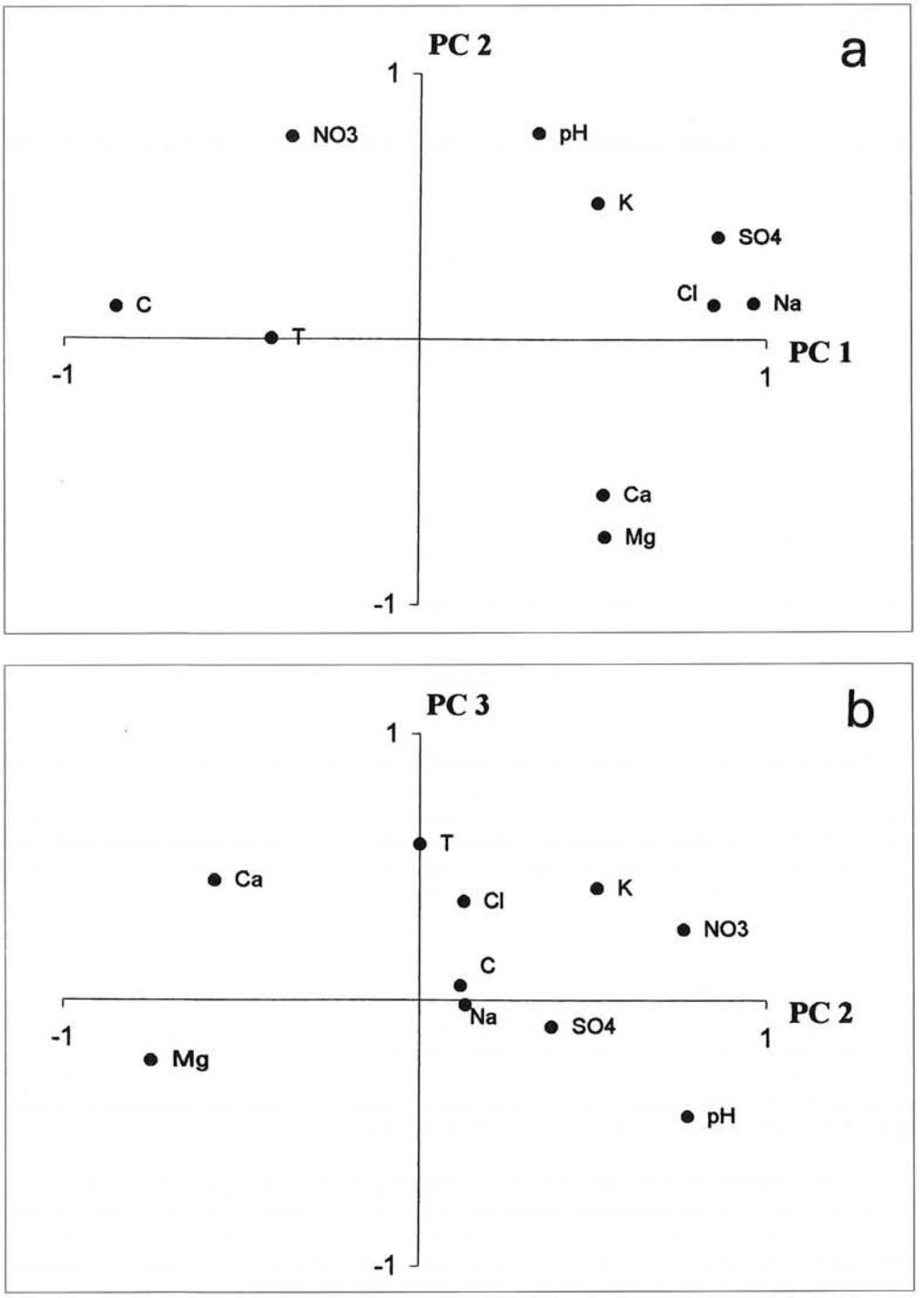

Fig. 2. Plottings of unrotated factor loadings of the 10 chemical-physical variables on the PC1-PC2 axes (a) and PC2-PC3 axes (b).

	C	pH	T	Na	K	Ca	Mg	Cl	NO_3	SO_4
C	1.000									
pH	-0.221	1.000								
T	0.285	-0.257	1.000							
Na	-0.769	0.462	-0.350	1.000						
K	-0.387	0.305	-0.092	0.502	1.000					
Ca	-0.416	-0.448	-0,114	0.421	0.081	1.000				
Mg	-0.516	-0.280	-0.327	0.424	-0.182	0.581	1.000			
Cl	-0.608	0.225	-0.205	0.829	0.558	0.562	0.293	1.000		
NO_3	0.463	0.319	0.123	-0.273	0.226	-0.409	-0.790	-0.043	1.000	
SO_4	-0.642	0.666	-0.305	0.909	0.512	0.191	0.195	0.732	-0.095	1.000

Table 2. Correlation matrix.

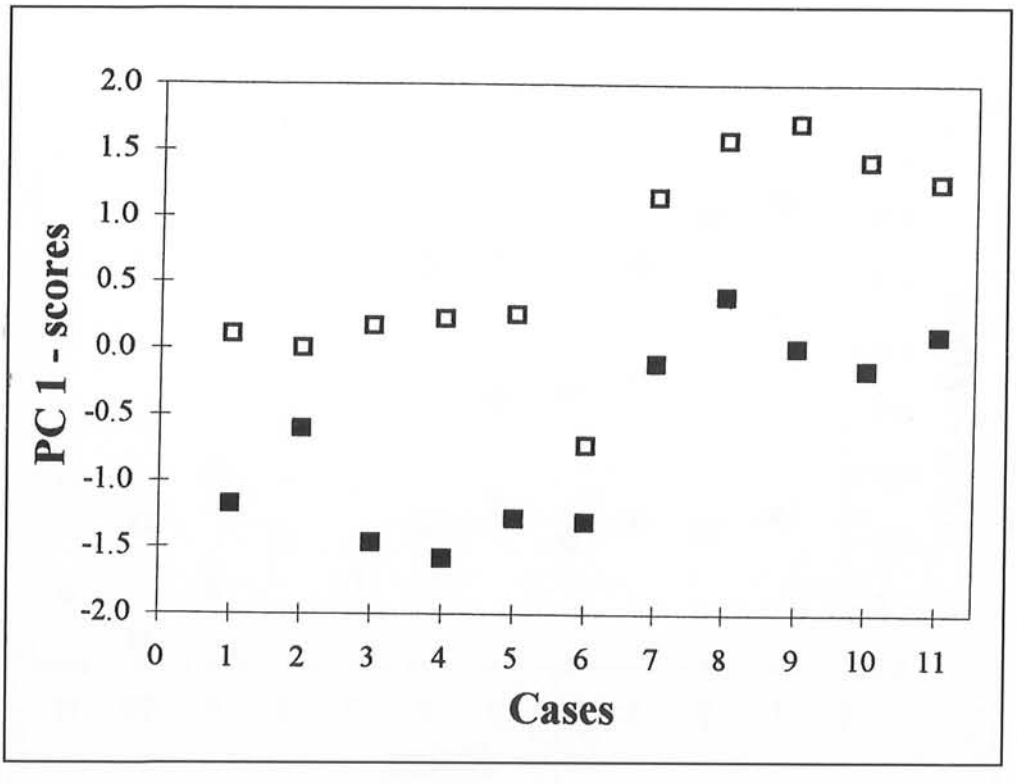

Fig. 3. Factor scores relative to PC1 of the samples collected in FO (■) and in RO (□), in autumn (cases 1-6) and spring (cases 7-11).

Final Statistic

Variable	Communality	Factor	Eigenvalue	Pct of Var	Cum Pct
C	0.740	1	4.381	43.8	43.8
pH	0.907	2	2.531	25.3	69.1
T	0.523	3	1.181	11.8	80.9
Na	0.947				
K	0.700				
Ca	0.826				
Mg	0.896				
Cl	0.874				
NO_3	0.785				
SO_4	0.895				

Table 3. Principal component analysis.

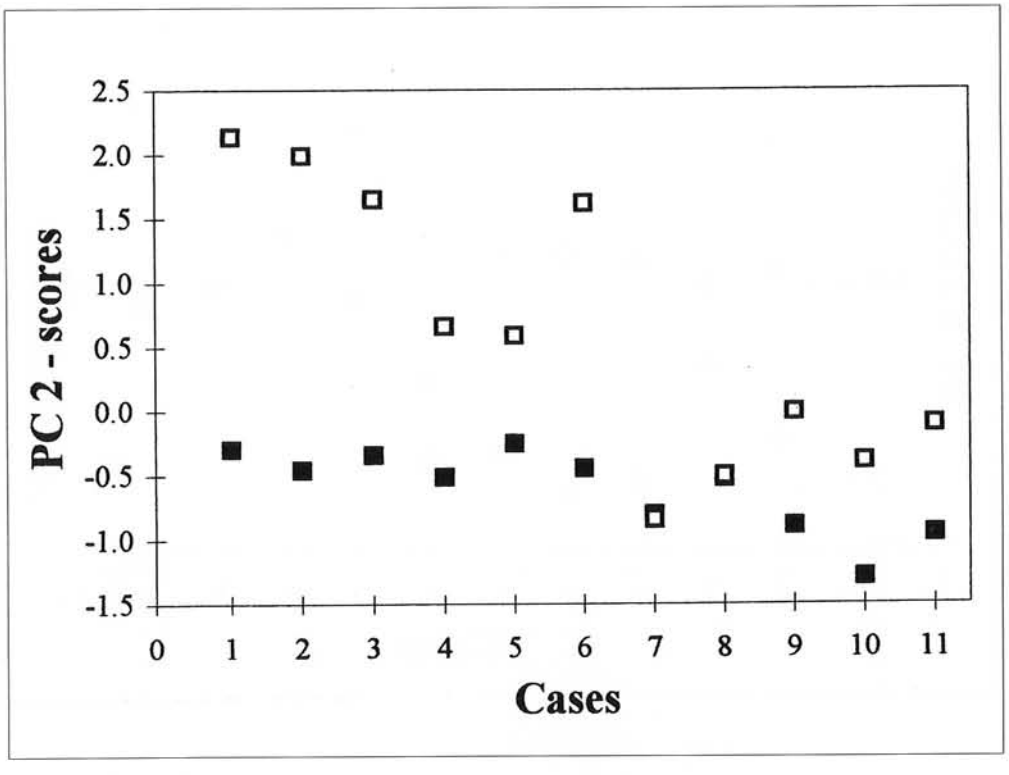

Fig. 4. Factor scores relative to PC2 of the samples collected in FO (■) and in RO (□), in autumn (cases 1-6) and spring (cases 7-11).

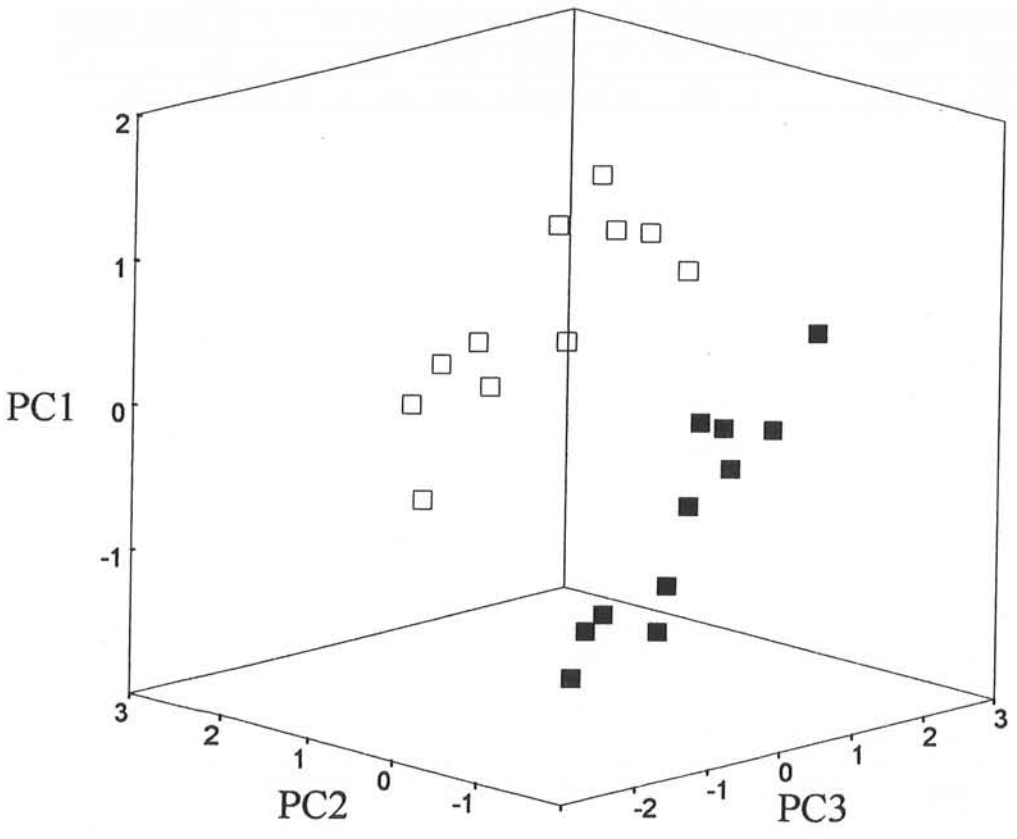

Fig. 5. Three-plot of the principal component scores on the PC1-PC2 and PC3 axes, corresponding to 11 cases, and 2 sites (FO: ■, and RO: □).

from the Rosandra freshwaters (clear points). This plot shows also that the scores have a remarkable dispersion along the PC1 axis: the first principal component is very effective for displaying the seasonal variations of the sampled freshwaters. The FO and RO score points lie distinctly apart also with respect to the PC2 axis: *i.e.*, the second principal allows the discrimination between FO and RO freshwaters.

In conclusion, the analytical determination of few, properly selected chemical-physical parameters, allows us an easy characterization of freshwaters. Most analytical operations can be performed *in situ*, making this approach simple and unexpensive. Moreover, a multivariate statistical analysis of the data matrix, using routine methods as, for instance, the eigenanalysis of the correlation matrix, gives useful information about the typologies of the examined freshwaters, and allows us to discriminate waters which - under a superficial examination - appear to be very similar. In the same time, this statistical evaluation of the data makes evident the seasonal effects on the composition of the waters: the typically karstic freshwaters, as, for instance, those flowing from a spring, exhibit, however, a very low seasonal variability. The parameters that better reflect their composition are those correlated to PC2, *i.e.*, pH, calcium

and magnesium ions: the planning of an extensive monitoring of karstic freshwaters can not renounce to these 3 variables. In fact, the complex equilibria between the dissolved carbon dioxide (which rules the pH) and the major dissolved ions, typical of this calcareous area, constitute a relevant factor for characterizing and discriminating the karstic freshwaters.

REFERENCES

BOEGAN E., 1938 - *Il Timavo Studio sull'idrografia carsica subaerea e sotterranea* - Mem. Ist. Ital. Speleol., Serie Geol. e Geof., Trieste, 3, 1.

CANCIAN G., 1987 - *L'idrologia del Carso goriziano-triestino tra l'Isonzo e le risorgive del Timavo* - Acta Geologica, 64: 77-98.

ERIKSSON E., MOSETTI F., HODOSCEK K., OSTANEK L., 1963 - *Some results on the carstic hydrology with the employ of tritiated water as tracer* - Boll. Geol. Teor. Appl., VII: 19-32.

FLORA O., GALLI G., NEGRINI L. and LONGINELLI A., 1990 - *Studio geochimico isotopico di alcune sorgenti carsiche: un nuovo modello idrologico* - Atti e Memorie Comm. 'E. Boegan', Trieste, XXIX: 83-102.

GEMITI F., 1982 - *Nuova ed originale prova di marcatura delle acque del Timavo* - Ann. Gr. Grotte Assoc. XXX Ott., Trieste, 6: 43-63.

GEMITI F. e LICCIARDELLO M., 1977 - *Indagine sui rapporti di alimentazione delle acque del Carso triestino e goriziano mediante l'utilizzo di alcuni traccianti naturali* - Ann. Gr. Grotte Assoc. XXX Ott., Trieste, 6: 43-61.

LONGINELLI A., 1988 - *Stable isotope hydrology of the classical Karst area, Trieste, Italy*, Rendiconti Soc. Ital. Mineral. Petrol., Vol. 43: 1175-1183.

MALINOWSKI E. R., 1991 - *Factor analysis in chemistry'*, 2nd ed., John Wiley & Sons, Inc., New York.

MOSETTI F. e POMODORO P., 1967 - *Nuove indagini con traccianti naturali sulla provenienza delle acque carsiche del sistema del Timavo* - L'acqua, 14: 3-9.

REISENHOFER E., ADAMI G. and BARBIERI P., 1996 - *Trace metals used as natural markers for discriminating some karstic freshwaters near Trieste (Italy)*, Toxicological and Environmental Chemistry, Vol. 54: 233-241.

TIMEUS G., 1911 - Atti Soc. Ital. Progr. Sc., 116: 751-771.