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An introductory note on statistical analysis of physio-chemical characteristics of natural waters. Application to some Central Apennines spring waters

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Geologia. — *An introductory note on statistical analysis of physio-chemical characteristics of natural waters. Application to some Central Apennines spring waters.* Nota (*) di LAURA DEFFENU (**), SALVATORE LOMBARDI (***) e CARLO FEDERICI (****), presentata dal Corrisp. B. ACCORDI.

RIASSUNTO. — Scopo del presente lavoro è lo studio di un metodo statistico per la discriminazione delle caratteristiche chimico-fisiche delle acque.

Dopo aver ottenuto, con l'applicazione dei metodi convenzionali di classificazione delle acque (Chebotarev, 1955), i due «termini estremi», si ricavano una serie di indici che descrivono quantitativamente, in termini percentuali, il grado di similitudine delle acque, che hanno diverse caratteristiche chimiche, in funzione dei «termini estremi» e il loro grado di miscelamento.

Tale metodo è stato applicato ad alcune sorgenti che sgorgano lungo l'alta Valle del Velino, dove le condizioni strutturali, agli effetti idrogeologici, sono simili a quelle osservate ai piedi dei Monti Lepini, dove esistono sorgenti le cui acque sono state esaminate per provare la validità del nuovo metodo statistico.

I risultati ottenuti dalla elaborazione dei dati delle sorgenti della Valle del Velino, sembrano confermare il probabile miscelamento di due falde formate da acque il cui chimismo è in parte rappresentato da quello delle acque prese come «termini estremi».

INTRODUCTION

Various classifications applied to spring waters—based on the determination of their main chemical characteristics by means of graphs (histograms, triangular diagrams, Schoeller's and Chebotarev's diagrams)—provide immediate criteria for classification of a most wide range of natural waters. A remarkable attempt to identify the evolutionary process of the principal water types was made by Chebotarev (1955).

The purpose of this paper is to differentiate waters from a series of springs by determining a quantitative index. This index should be able to indicate readily their differences and to provide information to reconstruct their genesis based on all available parameters.

In order to determine the most suitable method, the following steps were taken:

a) On the basis of information obtained from an analysis of major constituents of most spring waters in the Central Apennines, a series of

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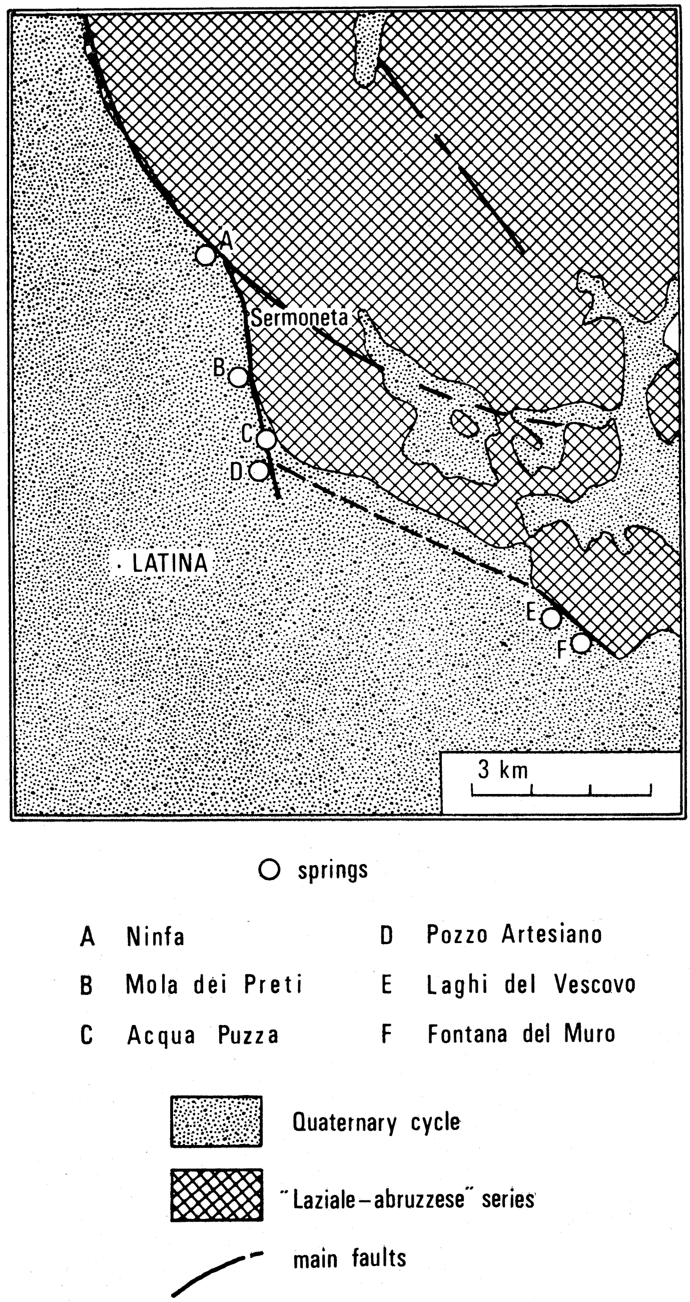

Fig. 1. – Location of the springs on the eastern side of the Pontina Plain, along the foothill of the Lepini Mountains. The springs are located along normal faults which cause the contact of two different stratigrafic successions, the Mesozoic carbonate rocks and the Plio-Pleistocene formations.

springs were selected and analyzed. They lie within a small area and the physico-chemical characteristics of their waters show wide variations. Due to their extremely variable chemical conditions, these waters appear to result from the combination of, at least, two " extreme terms ". The springs in question are located on the eastern side of the Pontina Plain (fig. 1), mainly along the foothills of the Lepini Mountains; in this zone the structural and hydrological conditions also indicate that there are probably aquifers with different subaqueous mixing rates.

b) By using physico-chemical data relevant to these waters, a method was devised capable of providing a most satisfactory procedure for differentiating them.

c) Such a method was applied in cases in which mixing of the theorical " extreme terms " occurs gradually and immediate assessment of the process by conventional methods is impossible. In detail the case was studied in which the relationship between chemism on one hand, and recharge and flow mechanisms on the other hand, has a particular geological meaning. In this respect, such a method was also applied to those springs which appear along the upper part of the Velino Valley (fig. 2), where we found hydrogeological conditions similar to those observed on the edge of the Lepini Mountains.

HYDROLOGIC FEATURES

The two groups of examined springs show similar structural and hydrological conditions. Both springs are located along deep faults that separate two different strathigraphic series:

– On the Pontina Plain we find an assemblage of Meso-Cenozoic shelf carbonate rocks (Latium-Abrutii succession) in tectonic contact with Plio-Peistocene clastic sediments (fig. 1).

– On the Velino Valley we find pelagic carbonate sediments to the West (Umbro–Marchigiana succession) and shelf carbonate rocks to the East (Latium-Abrutii succession). Both structures are closed from Neogene flyschioid cycle and Quaternary formation (fig. 2).

Both sediments of the carbonate shelf and of the basin are Mesozoic in age and heavily fractured and, consequently, permeable. They rest on a substratum of Triassic dolomite which has evaporite layers with gypsum and probably salt. Differential subsidence between the two Mesozoic successions outcropping along the Velino Valley was produced by faulting; the result being two different sedimentary enviroments. The faults remain active up to the last orogenesis. On the maps and on the schematic cross-sections (figs. 2 and 4) are illustrade hydrological an structural conditions which probably gave origin to the springs.

The general structural and hydrological conditions of the springs located at the eastern side of the Pontina Plain, at the foot of the Lepini Mountains,

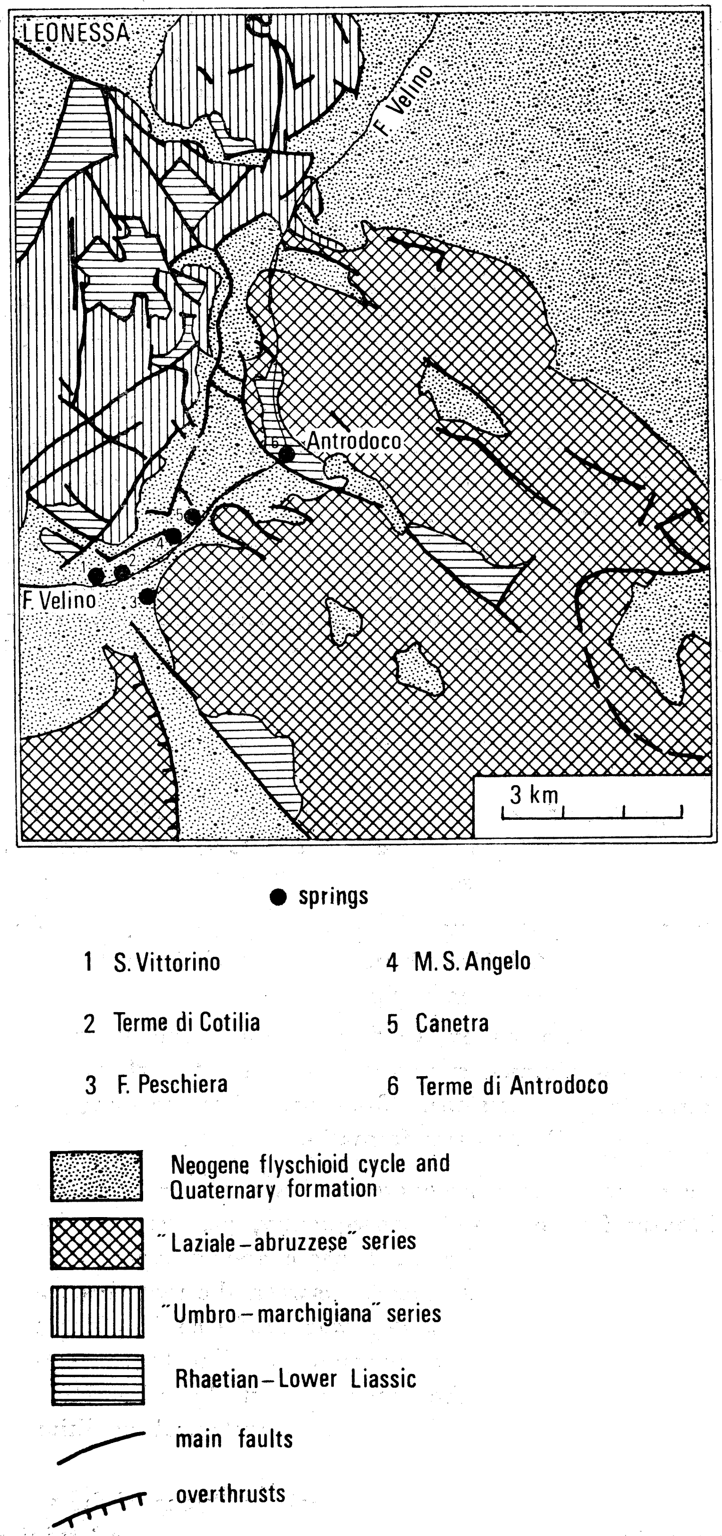

Fig. 2. – Location of the springs along the upper part of the Velino Valley and schematic map of the structural and geological conditions.

are more simple. As mentioned above, the thick carbonate sequence of the Latium-Abrutii shelf is affected by NNW-SSE trending normal faults which cause the contact of the Mesozoic limestones with the Plio-Pleistocene plastic sequence filling the plain.

From a hydrological point of view we observe that the springs are in a large part fed by bicarbonate cold water, for the remaining part, they are fed by hot water with sulphates, sulphides and carbon dioxide coming up along the fractures. In the upper Velino Valley the Karst aquifer feeds springs with huge discharges (Peschiera 15–20 m^3/sec). At the margin of the Lepini Mountains the Karst aquifer feeds the springs with a smaller amount of discharge (Ninfa 1,5–3 m^3/sec). The discharges of the hot springs with sulphates and sulphides are not more than some hundreds of l/sec.

The characteristics of the Karst aquifers are fairly known (Boni, 1973); on the contrary, the origin of the sulphate waters is not yet clear: bearing in mind the structural and hydrological situations, we can draw two hypotheses:

a) the waters which infiltrate through the carbonate outcrops descend deeply and dessolve the Triassic evaporitic salts (sulphate and probably sodium cloride). The sulphates are reduced to sulphides; the waters become more hot and less dense; enrich in gas (H_2S and CO_2), and rise along the fractures up to the surface where they mix at different rates with the waters of the Karst aquifer;

b) the waters of the Karst aquifer receive along large fractures a supply of liquid and/or gas coming from the deep; like the previous hypotesis, the waters dissolve the sulphates and rise to the surface. It is possible that both these processes overlap and contribute to water mineralization. Studies on the origin of the sulphate waters herein discussed at present carried on by many researchers; we hope that the use of isotope analysis may give an important contribution to the understanding of this hydrological problem.

PONTINA PLAIN SPRINGS

The Pontina Plain springs were used at first to test the effectiveness of the new differentiation method, in connection with both their wide chemical variations and structural similarities.

The waters from the Ninfa, Mola dei Preti, Acqua Puzza, Pozzo Artesiano, Laghi del Vescovo and Fontana del Muro springs were analyzed each month for a year according to the " Standard Methods for the Examination of Water and Wastewater ". The determination of the calcium, magnesium, sodium and potassium ions was done by flame spectrometry; the sulphates one by turbidimetry and the chlorine and bicarbonate ions ones by titrimetry. The data obtained, together with pH and conductivity values, are shown on Table I.

TABLE I. – *Chemical analysis of the Pontina Plain springs.*

Date	T°c	Ph	Conducib. a 18° μσ/cc	R.F. g/l	Hardness °F	Alcal. meq. HCO_3^-	Cl^- meq	SO_4^{--} meq	Ca^{++} meq	Mg^{++} meq	Na^+ meq	K^+ meq	$\frac{Ca}{Mg}$	$\frac{Cl}{Na}$	Σ^+	Σ^-
						Ninfa (A)										
29–I–72	13.2	7.6	340	0.255	24.3	4.30	0.43	0.23	3.70	1.12	0.176	0.018	—	—	4.96	5.01
29–II–72	13.3	7.9	348	0.261	24.9	4.37	0.44	0.24	3.78	1.13	0.180	0.018	—	—	5.11	5.04
29–III–72	13.7	7.9	359	0.269	25.7	4.57	0.45	0.24	3.90	1.16	0.186	0.018	—	—	5.26	5.20
7–V–72	13.8	7.7	362	0.271	25.9	4.65	0.45	0.25	3.93	1.18	0.187	0.019	—	—	5.32	5.35
7–VI–72	13.8	7.8	368	0.276	26.2	4.63	0.46	0.25	4.00	1.19	0.190	0.020	—	—	5.40	5.34
4–VII–72	14.1	7.7	374	0.277	26.1	4.65	0.46	0.24	4.05	1.20	0.180	0.022	—	—	5.45	5.35
						Mola dei Preti (B)										
29–I–72	14.3	7	633.88	0.475	42.48	7.90	0.33	1.06	6.13	2.36	0.41	0.15	2.6	0.8	9.06	9.29
29–II–72	14.5	7.09	619.57	0.465	40.98	7.45	0.33	1.08	6.25	1.94	0.42	0.12	3.22	0.79	8.77	8.87
29–III–72	14.2	7.2	625	0.469	38.28	7.10	0.42	1.08	5.67	1.98	0.68	0.14	2.86	0.62	8.47	8.53
7–V–72	14.9	7.3	624.33	0.468	38.98	7	0.30	0.92	5.74	2.05	0.46	0.04	2.8	0.65	8.29	8.22
7–VI–72	14.5	7.4	652.17	0.489	39.98	7.65	0.35	0.90	6.05	1.94	0.64	0.20	3.12	0.55	8.83	8.96
24–VII–72	15	7.01	644.4	0.4833	41.98	7.50	0.50	0.98	6.25	2.14	0.55	0.20	2.92	0.8	9.15	8.98
						Acqua Puzza (C)										
29–I–72	15.4	6.94	1808.50	1.356	51.98	9.1	4.73	1.45	7.92	2.87	3.89	0.28	2.75	1.24	14.88	15.20
29–II–72	15.6	7.21	1696.71	1.273	53.48	9	4.70	1.53	7.92	2.77	3.98	0.28	2.85	1.18	14.95	15.23
29–III–72	15.4	7.85	1812.37	1.359	52.98	9.1	4.70	1.53	7.58	3	4.08	0.28	2.53	1.15	14.95	15.33
7–V–72	15.7	8.33	1074.82	0.806	55.47	8.6	5.00	1.89	8.22	2.86	4.16	0.21	2.87	1.20	15.45	15.29
7–VI–72	15	6.9	1181.52	0.886	49.98	8.5	4.90	1.56	7.08	2.90	4.26	0.35	2.44	1.15	14.60	14.36
4–VII–72	15.8	7	1263.60	0.947	48.18	8.5	5.18	1.523	7.08	2.75	4.68	0.35	2.57	1.10	14.86	15.20

Continued: TABLE I.

Date	T°C	Ph	Conducib. a 18° μσ/cc	R.F. g/l	Hard-ness °F	Alcal. meq. HCO_3^-	Cl^- meq	SO_4^{--} meq	Ca^{++} meq	Mg^{++} meq	Na^+ meq	K^+ meq	$\frac{Ca}{Mg}$	$\frac{Cl}{Na}$	Σ^+	Σ^-
Pozzo Artesiano (D)																
29–I–72	15.8	7.25	910.05	0.682	35.99	7.0	3.72	0.88	5.69	1.50	3.54	0.68	3.79	1.05	11.41	11.6
29–II–72	15.2	7.21	864.17	0.648	35.99	6.8	4.1	1.14	5.69	1.50	4.06	0.61	3.79	1.01	11.86	12.04
29–III–72	15.8	7.3	896.62	0.672	35.88	6.72	4.14	1.15	3.58	1.59	4.04	0.64	3.51	1.02	11.85	12.01
7–V–72	15.8	8.02	1033.05	0.775	35.99	6.75	4.49	1.34	5.48	2.71	3.90	0.69	3.21	1.15	12.78	12.58
7–VI–72	16	7.28	995.81	0.747	32.99	6.75	4.1	1.17	5.12	1.47	4.02	1.25	3.48	1.02	11.86	12.02
4–VII–72	16	7.17	1027.04	0.770	33.99	6.70	4.1	1.12	5.29	1.50	4.02	0.96	3.52	1.02	11.77	11.92
Fontana Muro (F)																
29–I–72	15	7	805.58	0.604	34.99	6.1	3.46	0.61	4.79	2.02	3.14	0.18	2.17	1.10	10.13	10.17
29–II–72	15	7.37	805.58	0.604	32.99	6	3.36	0.83	4.35	2.24	5.20	0.14	1.94	1.05	9.93	10.19
29–III–72	14.9	7.85	839.61	0.630	34.89	5.85	3.62	0.85	4.96	2.01	3.37	0.16	2.47	1.07	10.50	10.32
7–V–72	15	8.52	751.87	0.564	34.49	5.85	3.5	0.65	4.56	2.35	2.87	0.12	1.96	1.22	9.88	10
7–VI–72	15	7.38	837.81	0.628	34.99	5.85	3.64	0.82	4.97	2.02	3.35	0.16	2.46	1.09	0.50	10.31
4–VII–72	15	7.14	859.20	0.644	33.99	5.8	3.88	0.75	4.55	2.24	3.52	0.15	2.03	1.10	10.46	10.43
Laghi del Vescovo (E)																
29–I–72	19.8	6.61	3671.50	2.7536	111.44	14.5	31.6	3.56	14.7	7.57	27.47	0.61	1.94	1.15	50.35	49.66
29–II–72	19.6	6.7	3961.35	2.971	119.45	14.2	34.4	4.92	15.87	8	28.9	0.61	1.98	1.19	53.38	53.52
29–III–72	23	7.1	3677.13	2.7578	120.95	13.9	34.53	3.19	15.04	9.12	27.47	0.63	1.65	1.25	52.26	51.62
7–V–72	21	7.27	3788.58	2.8414	115.45	13.85	32.5	5.00	15.05	8.018	27.08	0.59	1.87	1.20	50.74	51.35
7–VI–72	20	6.71	3632.90	2.7247	96.96	13.92	32.1	4.33	13.14	6.24	26.75	0.89	2.10	1.20	49.35	48.02
4–VII–72	19.5	6.59	3384.50	2.538	94.96	12.60	28.1	3.64	13	6.18	23.42	0.83	2.10	1.19	43.42	44.33

From these data and particulary from a Chebotarev graph (fig. 3) it was possible to determine the waters constituting the "extreme terms" of the group (Ninfa and Laghi del Vescovo). The waters coming from the other springs can be considered as formed by their combination. The points which represent the chemism of the Mola dei Preti, Acqua Puzza, Pozzo Artesiano and Fontana del Muro springs on a Chebotarev graph lie on the curve whose extreme values are represented by the Ninfa and Laghi del Vescovo waters.

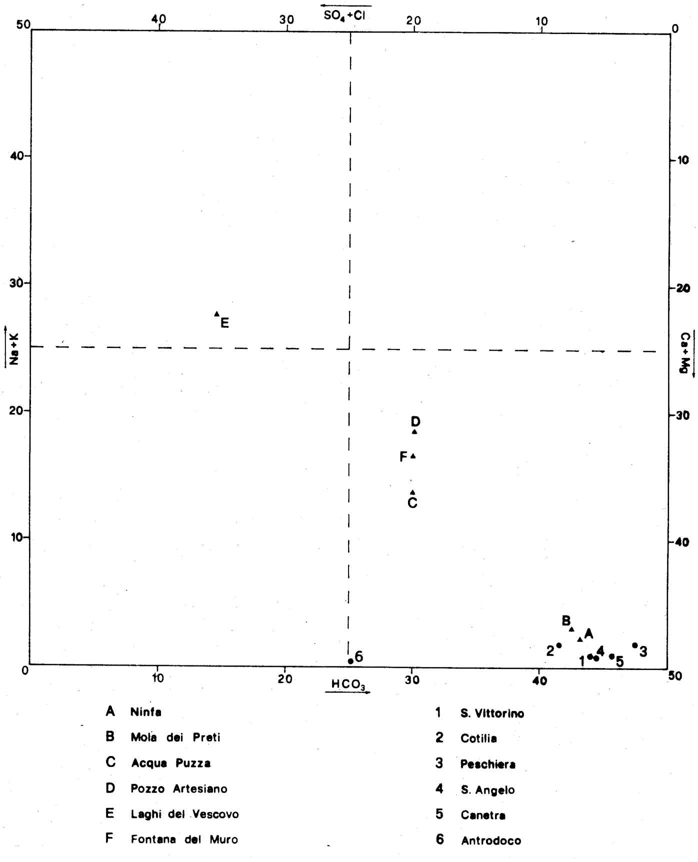

Fig. 3. – Chebotarev graph. It is possible to determine the waters representing the "extreme terms" (Ninfa and Laghi del Vescovo), choosen by the writers for the statistical analysis. The points, representing the chimism of the Mola dei Preti, Acqua Puzza, Pozzo Artesiano and Fontana del Muro, lie, in fact, on a curve whose extreme values represent the Ninfa and Laghi del Vescovo springs. Similar disposition may be noted about the upper Velino Valley springs.

Method for the Classification of Springs

In the previous section, the chemical characteristics of the Ninfa and Laghi del Vescovo springs were defined. It can be assumed in theory that the waters of the other springs of the group result from various combinations of them. According to this idea, it was planned for future studies to determine the extreme terms using a computer rather than conventional methods.

The method adopted and the computer calculations done to express the degree of mixing observed at the Acqua Puzza, Mola dei Preti and Pozzo Artesiano springs as a percentage of the two extreme terms follow below.

First, monthly averages of the physio-chemical data obtained for the spring waters over the whole observation period were calculated according to the following formula:

$$\frac{\sum_1^{\text{N months}} x_i}{\text{N months}} = \bar{x}$$

where $\bar{x}$ is the average concentration for each component and N the number of months during which sampling was carried out.

An expression for the composition of any term *i* of an intermediate spring C obtained by mixing the extreme terms A and B can be written:

$$a_i \mathrm{A} + b_i \mathrm{B} = \mathrm{C}_i$$

bearing in mind that:

$$a + b = 1\,.$$

In practice, by feeding into the computer each time the data pertaining to a chemical component, it is possible to calculate the amount of a component A contained in a given spring. Once the *a* coefficient has been obtained, the value of the other components's concentrations can be readily calculated.

Then, the difference between the values calculated by using the a_i coefficient and those obtained by the chemical analysis is calculated (*i* varies between 1 and the total number of components present). The sum of the square of the deviations for each component is then divided by the number of components. This procedure is repeated for each component. The *a* coefficient value showing the least variation from the data obtained by chemical analysis is selected on the basis of the least mean square deviation.

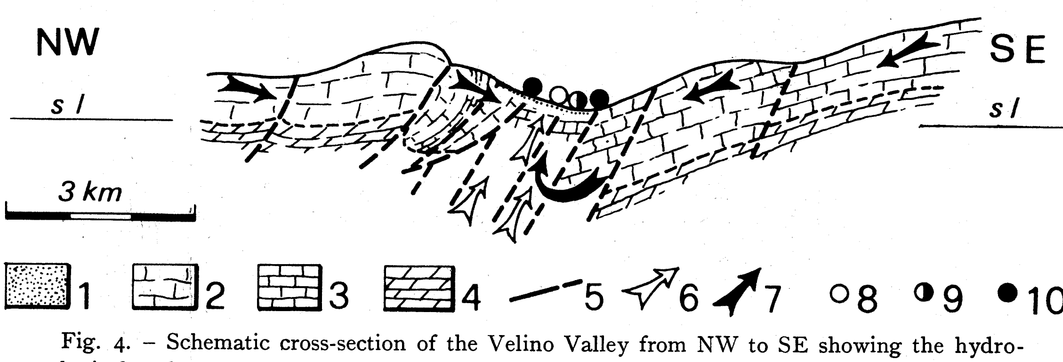

Fig. 4. – Schematic cross-section of the Velino Valley from NW to SE showing the hydrological and structural conditions which probably originated the springs. LEGEND: 1) Quaternary detritus and alluvium. 2) Basin carbonate succession series (Umbro-Marchigiana). Lias to Miocene. 3) Carbonatic shelf successions (Laziale-Abruzzese). Lias to Miocene. 4) Evaporites and dolomites. Trias. 5) Faults. 6) Cold bicarbonate-calcic waters. 7) Warm sulphureous waters. 8) Springs of warm sulphureous. 9) Springs of mixed waters. 10) Springs of cold calcium bicarbonate.

TABLE II. – *Chemical analysis of the Velino Valley springs.*

Date	T°c	Ph	Conducib. a 18° μσ/cm	R.F. g/l	Hardness °F	Alcal. meq. HCO_3^-	Cl^- meq	SO_4^{--} meq	Ca^{++} meq	Mg^{++} meq	K^+ meq	Na^+ meq	Ca/Mg	Cl/Na	Σ^+	Σ^-
						Peschiera (3)										
13–X–71	10.2	6.70	487	0.365	34.75	6.15	0.16	0.16	4.84	1.62	0.02	0.11	2.98	1.40	6.59	6.47
11–XII–71	10.2	6.87	487	0.365	33.23	6.25	0.16	0.17	4.92	1.62	0.02	0.11	3.03	1.46	6.67	6.58
26–I–72	10.0	7.21	478	0.358	32.58	6.15	0.15	0.17	4.74	1.57	0.03	0.11	2.99	1.40	6.45	6.47
28–II–72	10.0	6.25	490	0.367	33.41	6.35	0.16	0.17	5.01	1.67	0.02	0.11	2.99	1.45	6.81	6.68
30–III–72	10.2	7.74	518	0.388	34.59	6.55	0.17	0.18	5.16	1.75	0.02	0.12	2.94	1.45	7.05	6.90
30–IV–72	10.4	7.58	509	0.381	34.29	6.55	0.16	0.18	5.10	1.75	0.02	0.11	2.92	1.40	6.98	6.89
31–V–72	10.6	7.64	488	0.361	32.49	6.45	0.15	0.17	4.85	1.64	0.02	0.12	2.95	1.39	6.63	6.76
30–VI–72	11.3	7.24	508	0.381	34.65	6.55	0.16	0.18	5.11	1.67	0.02	0.11	2.91	1.40	6.91	6.89
27–VII–72	11.5	7.38	500	0.375	34.08	6.45	0.16	0.18	5.12	1.63	0.02	0.11	2.90	1.43	6.88	6.79
						Canetra (5)										
21–X–71	12.0	6.90	650	0.487	43.90	8.70	0.25	0.56	7.06	2.10	0.02	0.14	3.38	1.78	9.32	9.51
11–XII–71	10.6	6.85	675	0.506	45.64	8.40	0.26	0.63	7.02	2.05	0.03	0.16	3.46	1.64	9.26	9.29
26–I–72	10.6	7.02	638	0.479	43.53	8.00	0.25	0.59	6.56	1.92	0.03	0.15	3.44	1.69	8.66	8.85
28–II–72	10.6	7.05	639	0.479	43.76	8.30	0.23	0.60	6.98	1.63	0.03	0.14	3.67	1.65	8.78	8.83
30–III–72	10.6	7.28	651	0.488	44.06	8.30	0.23	0.61	7.04	1.75	0.03	0.14	3.58	1.61	8.97	9.15
30–IV–72	10.7	7.26	661	0.496	44.83	8.25	0.23	0.62	7.08	1.87	0.03	0.13	3.45	1.68	9.11	9.10
31–V–72	10.5	7.19	665	0.489	44.11	8.25	0.22	0.61	7.04	1.77	0.03	0.12	3.51	1.73	8.96	8.81
30–VI–72	11.0	7.04	667	0.501	45.62	8.20	0.22	0.63	7.06	1.95	0.03	0.13	3.64	1.64	9.17	9.05
27–VII–72	11.0	6.98	667	0.501	45.14	8.20	0.17	0.64	7.27	2.01	0.03	0.11	3.63	1.58	9.41	9.01
						Monte S. Angelo (4)										
13–X–71	14.0	7.70	1927	1.445	147.75	27.65	0.51	2.98	24.92	5.01	0.10	0.43	4.98	1.18	30.46	31.14
11–XII–71	12.6	7.55	1941	1.455	148.87	27.80	0.51	2.53	24.71	5.03	0.10	0.44	4.90	1.14	30.36	30.89
21–I–72	12.6	7.30	1831	1.373	140.99	26.75	0.48	2.49	23.19	4.75	0.11	0.42	4.88	1.15	29.72	28.48
28–II–72	12.4	7.23	1894	1.421	145.29	27.20	0.50	2.68	24.11	4.92	0.11	0.44	4.90	1.13	29.71	30.38
30–III–72	12.5	6.46	2003	1.503	153.66	28.70	0.53	2.83	25.50	5.20	0.11	0.46	4.90	1.14	31.29	32.06
30–IV–72	12.6	6.34	1998	1.499	153.25	28.65	0.53	2.83	25.44	5.19	0.10	0.44	4.90	1.19	31.17	32.01
31–V–72	13.0	6.44	1921	1.441	147.32	27.55	0.51	2.72	24.43	5.01	0.11	0.44	4.88	1.15	29.99	30.78
30–VI–72	13.0	6.26	2034	1.525	155.90	29.15	0.54	2.89	25.93	5.22	0.12	0.46	4.96	1.17	31.73	32.58
27–VII–72	13.4	6.26	2012	1.510	154.29	28.85	0.53	2.85	25.62	5.21	0.11	0.46	4.91	1.14	31.41	32.23

Continued: TABLE II.

Date	T°C	Ph	Conducib. a 18° μσ/cm	R.F. g/l	Hardness °F	Alcal. meq. HCO_3^-	Cl^- meq	SO_4^{--} meq	Ca^{++} meq	Mg^{++} meq	K^+ meq	Na^+ meq	Ca/Mg	Cl/Na	Σ^+	Σ^-
						S. Vittorino (1)										
13–X–71	12.5	6.91	612	0.459	47.81	8.20	0.25	0.85	7.37	2.03	0.02	0.17	3.63	1.46	9.59	9.30
11–XII–71	10.2	6.95	658	0.494	48.48	8.57	0.28	0.84	7.37	2.08	0.03	0.17	3.54	1.64	9.65	9.69
26–I–72	10.2	6.84	633	0.475	46.48	8.20	0.25	0.79	7.24	2.04	0.03	0.18	3.54	1.77	9.49	9.24
28–II–72	10.0	6.89	662	0.496	46.48	8.20	0.25	0.84	7.18	2.11	0.03	0.18	3.40	1.44	9.49	9.27
30–III–72	10.0	7.21	686	0.514	48.72	8.35	0.30	0.87	7.21	2.12	0.03	0.19	3.40	1.58	9.55	9.52
30–IV–72	12.0	7.42	661	0.495	46.98	8.37	0.30	0.81	7.38	2.01	0.03	0.18	3.67	1.66	9.60	9.48
31–V–72	9.8	7.30	694	0.520	47.28	8.35	0.30	0.88	7.30	2.15	0.03	0.19	3.40	1.58	9.67	9.53
30–VI–72	10.4	6.93	735	0.551	47.98	8.39	0.30	0.95	7.53	2.06	0.03	0.19	3.65	1.54	9.81	9.64
27–VII–72	10.5	7.55	723	0.542	47.62	8.36	0.26	0.92	7.49	2.03	0.03	0.16	3.69	1.58	9.55	9.71
						Cotilia (2)										
13–VII–71	15.5	7.70	2228	1.671	182.36	32.50	1.19	4.77	29.90	6.47	0.18	1.34	4.58	0.80	37.93	38.46
13–X–71	15.5	7.70	2419	1.814	200.00	33.33	1.22	5.59	31.94	7.02	0.14	1.35	4.55	0.90	40.45	40.14
11–XII–71	14.2	6.71	2441	1.808	195.92	34.00	1.28	5.62	32.07	7.08	0.18	1.44	4.53	0.89	40.77	40.89
26–I–72	14.4	6.64	2290	1.718	187.44	31.70	1.22	5.34	30.41	7.04	0.16	1.36	4.58	0.89	38.57	38.26
28–II–72	14.3	6.39	2380	1.785	194.86	32.65	1.20	5.56	31.25	6.89	0.15	1.36	4.54	0.88	39.65	39.41
30–III–72	14.5	6.31	2284	1.713	187.94	32.85	1.16	5.32	31.34	6.92	0.16	1.29	4.53	0.90	39.61	39.33
30–IV–72	14.6	6.44	2400	1.800	196.46	32.97	1.16	5.54	31.69	6.97	0.27	1.33	4.55	0.87	40.26	39.67
31–V–72	14.8	6.41	2322	1.741	190.06	32.05	1.15	5.43	30.54	6.77	0.15	1.29	4.51	0.91	38.72	38.63
30–VI–72	15.0	6.35	2309	1.732	188.99	32.00	1.15	5.36	30.59	6.78	0.15	1.29	4.52	0.89	38.81	38.51
27–VII–72	15.1	6.32	2410	1.807	197.26	32.95	1.20	5.66	31.40	7.02	0.15	1.36	4.47	0.88	39.93	39.80
						Antrodoco (6)										
13–X–71	18.5	7.70	1838	1.379	153.51	15.62	0.24	15.08	25.49	5.36	0.08	0.26	4.75	0.92	31.16	31.12
11–XII–71	18.0	7.20	1800	1.350	150.93	15.55	0.22	15.21	24.91	5.25	0.09	0.23	4.74	0.92	30.48	30.98
26–I–72	18.0	7.05	1800	1.350	149.95	14.80	0.24	15.54	24.84	5.12	0.07	0.26	4.85	0.93	30.30	30.60
28–II–72	18.0	6.57	1800	1.350	151.45	15.05	0.24	15.63	24.80	5.46	0.07	0.25	4.55	0.94	30.58	30.92
30–III–72	18.0	6.65	1800	1.350	134.96	15.45	0.24	12.24	22.34	4.63	0.07	0.26	4.82	0.93	27.30	27.93
30–IV–72	18.0	6.76	1800	1.350	151.45	15.35	0.24	15.03	25.04	5.17	0.07	0.25	4.85	0.93	30.55	30.62
31–V–72	18.0	6.77	1800	1.350	152.45	15.35	0.24	15.09	25.14	5.32	0.06	0.25	4.72	0.95	30.64	30.68
30–VI–72	18.5	6.63	1780	1.335	146.95	15.15	0.22	15.13	24.30	5.06	0.08	0.23	4.80	0.93	29.68	30.50
27–VII–72	18.5	6.52	1880	1.410	147.45	15.30	0.26	15.06	24.28	5.18	0.06	0.27	4.69	0.93	29.81	30.62

The results obtained by processing the chemical data for the Pontina Valley springs confirm the validity of the hypotheses made and of the method employed. The per cent values obtained are shown on Table III.

TABLE III.

Theoretical mixing per cent calculated by computer for the Pontina Plain springs.

SPRINGS	% Ninfa spring
Mola dei Preti	98.8
Acqua Puzza	87.0
Pozzo Artesiano	87.5
Fontana del Muro . . .	87.0

TESTING ON THE VELINO VALLEY SPRINGS

The same statistical method was applied to a series of springs waters coming out in the upper Velino Valley. On the eastern side of the Velino Valley lie the Peschiera springs, supplied by the Karst aquifer of the carbonate shelf sediments. On the other side there are the Terme di Antrodoco spring, fed mainly by waters rising along deep fractures. Down in the valley, along the high-throw fault zone, outlining the border line between the two series, a large number of the other springs gush out (S. Vittorino, Terme di Cotilia, Canetra, M. S. Angelo) (fig. 2).

The springs chosen as " extreme terms ", on the basis of the chemical data are Peschiera and Terme di Antrodoco.

The results obtained by processing the data supplied by the physico-chemical analyses of samples collected monthly for a year (Table II) are in agreement with the hypotheses.

The results obtained using as extreme terms the data pertaining to springs other than Peschiera and Terme di Antrodoco, were unreliable and the mean square deviation greater then before. The percentage values obtained using as extreme terms Peschiera and Terme di Antrodoco are shown on Table IV.

From the previous Table it can be observed that some springs (San Vittorino, Canetra) show chemical characteristics very similar to those of the Peschiera River. So, it can be assumed that, as far as indicated by their per cent values, they originate from waters whose chemical characters are similar to the Peschiera ones. The other springs (Terme di Cotilia, Monte Sant'Angelo) on the contrary, appear to be constituted by more than 50 % of waters similar to the Terme di Antrodoco ones. Although they contain mostly alkaline bicarbonates, their sulphate content is also considerable. In particular, for Monte Sant'Angelo it was possible to determine by computer the presence of a very high percentage of waters of the Terme di Antrodoco type. This proves mathematically, as had been expected intuitively, that a mixture between the waters of the two springs actually supplying the two " extreme " springs occurs.

TABLE IV.

Theoretical per cent of mixing obtained by computer for the springs of the Upper Velino River Valley.

SPRINGS	% Peschiera spring
S. Vittorino	87.6
Terme di Cotilia	34.1
Canetra	89.5
Monte S. Angelo	1.5

CONCLUSIVE CONSIDERATIONS

A statistic method to differentiate the chemical characters of spring waters was developed. Such a method defines a coefficient which can describe quantitatively, in per cent, the theoretical degree of mixing of waters showing different chemical characters. Two " extreme terms " are obtained through the application of conventional water classification method (Chebotarev, 1955).

This method was applied to two groups of springs which gush out the first along the foothill of the Lepini Mountains and the second along the upper part of the Velino Valley. The result obtained by the calculations of physico-chemical data, confirm the working hypothesis, which, based on the hydrogeological and chemical data, indicates a probable mixing of aquifers characterized by different waters.

The utility of the statistic method is useful to readily compute a high number of data and, over all, to obtain a quantitative index showing the variation between the different springs, and possibly to give information for their genetic origin.

This index is deduced as follows:

a) the two springs showing the most different chemical characteristics among the sampled ones are chosen as the " extreme springs ".

b) for each spring the percentage of one mixing term (α) and of the other one ($1 - \alpha$) is chosen on the ground of the chemical parameter which makes the smallest the mean square deviation among the values measured and elaborated by the analysis of major constituents.

The validity limits of the method are represented by the circumstance that the extreme terms have been " chosen " and not identified on statistical bases. There exist indeed statistical methods (Q-mode analysis) able to identify the extreme " springs " of a given whole under the hypothesis that each component of the considered " universe " may be contemplated as a linear combination of the " springs " themselves.

It has not been possible to utilize this method because of the scarcity of available data. We intend to enlarge this analysis as soon as more data will be available.

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