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HYDROGEOLOGY: A PRIVILEGED FIELD FOR ENVIRONMENTAL STABLE ISOTOPES APPLICATIONS SOME ITALIAN EXAMPLES

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RIASSUNTO. — Vengono presentati alcuni esempi di utilizzazione degli isotopi stabili (^{18}O, ^{2}H, ^{34}S) nello studio di tre parametri fondamentali del bilancio idrologico: precipitazioni, deflusso superficiale e circolazione sotterranea (= infiltrazione).

Per le precipitazioni sono state definite origine e circolazione delle masse d'aria umida nelle Alpi Occidentali, Prealpi Venete ed Appennino Centrale.

È stato studiato il comportamento isotopico dei principali corsi d'acqua della Pianura Padana e dell'Italia Centrale.

Gli esempi di utilizzazione delle tecniche isotopiche allo studio della circolazione sotterranea riguardano i mezzi permeabili per porosità primaria (settore piemontese e veneto della Padania), per fessurazione nei massicci cristallini (Alpi Occidentali) e per carsismo (Alpi Marittime ed Appennino Centrale).

ABSTRACT. — Some examples of environmental isotopes application to three parameters of hydrological budget (precipitation, runoff and underground flow) are presented.

Origines and circulations of wet air masses on the Western Alps, Venetian Prealps and Central Apennines are defined.

Cyclic fluctuation of river waters isotopic composition has been investigated in the Po Valley and in Central Italy.

Underground circulation in porous media (Piedmontese and Venetian areas on the Po Valley), in crystalline rocks (western Alps) and in Karst (Maritime Alps and Central Apennines) has been studied by means of stable isotopes.

1. Introduction

For more than 10 years some hydrogeologists of the Turin University are involved in the application of Nuclear Techniques to hydrogeological problems, covering several areas in and outside of Italy.

Some of the data, presented herewith, have been already published; however a major part of the data can be considered as « drawer data ». For years, the authors have committed a misdemeanour, for sloth or other reasons, delaying publications. We appreciate the opportunity of this meeting « to discharge », in part, the debt with the friends to whom we are obliged, at least, for the assistance in the analytical services.

Thus, the paper would be a kind of « summa » of many problems tackled and sometimes solved using Stable Isotopes.

These hydrogeological problems concern three Italian regions: Piedmont, Venity and Central Italy.

2. Precipitations

Due to its geographical position the Italian peninsula is submitted to meteorological events with different origins: cold and generally dry air masses coming from Eastern Europe, and warm and humid air masses coming from the west (Atlantic Ocean) and the south (western and central Mediterranean basin).

The influence of one on the other components originates a remarkable different situation with implication to the hydrogeological problems.

2.1. GRADIENTS

In the western Alps, mainly the Maritime ones, precipitations had normally originated from Atlantic air masses and secondary from Mediterranean ones. Therefore, the cross of the alpine system originate a significant isotopic fractionation with the altitude either if air masses are coming from the west or from the south. The gradient with the altitude (fig. 1) is 3.1 ‰ and 25 ‰ per thousand meters in oxygen-18 and deuterium respectively (BORTOLAMI et al., 1978). A similar relationship has been determined from sam-

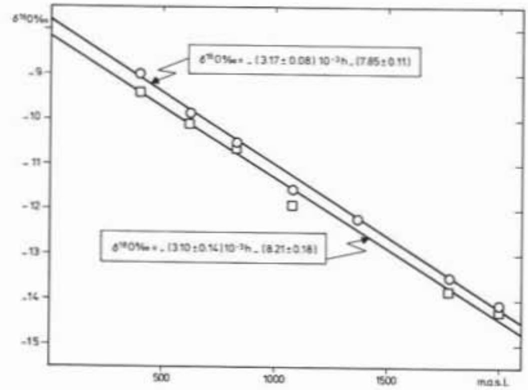

Fig. 1. — Oxygen—18-altitude gradient in Maritime Alps. The determination coefficients (r^2) for October 1974 and april 1976 are 0.98 and 0.99, respectively, whereas the standard errors are 0.13 (October) and 0.15 (April).
Squares indicate samples for October; circles for April. One can note that, generally, the mean temperatures for October and April are quite near the annual mean temperature. Therefore, the combination of these two equations closely describes the average annual isotopic gradient as a function of the altitude:

$$^{18}O = (3.12 \pm 0.10)\ 10^{-3}\ h - (8.03 \pm 0.13).$$

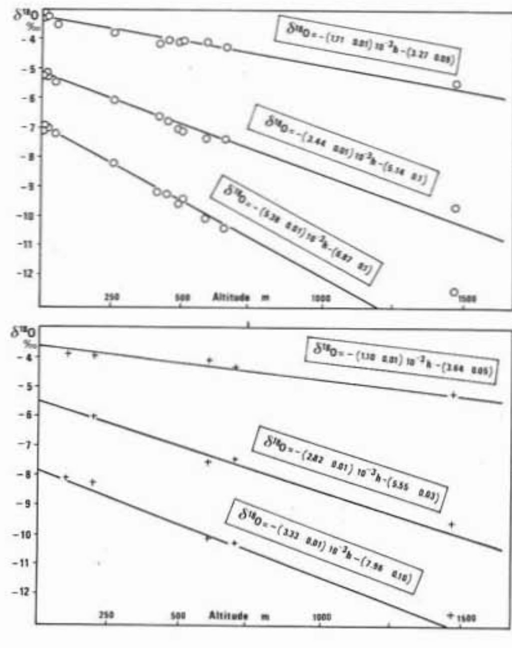

Fig. 2. — Isotopic gradient with altitude on the Tyrrhenian (*a*) and Adriatic (*b*) basins.
Upper curves: summer correlation; lower curves: winter correlation; mean curves: average annual correlation. To explain the difference in gradients between one side and the other one of Apennines system one can indeed account for the « mountain shadow effect ».

ples collected on French side of western Alps (Moser and Stichler, 1970), where a deuterium gradient equal to 40 per thousand meters was found; Jamier and Olive (1977) calculated a gradient in oxygen-18 of 3.5 ‰ per thousand meters on northern side of Mont Blanc.

In Central Italy, a cross section of the Apennines between Anzio and Ascoli P. (fig. 2) indicated that gradients on the Adriatic side are smoother than those in Tyrrhenian regions (Zuppi et al., 1974). Similarly the gradients in the Venetian Alps (fig. 3, tab. 1) give values smoother with respect to those found in Central Europe and more subjected to oceanic influence (Dinger et al., 1970). The case of 1972 is very significant: practically, during the period April-November no differences appear in the heavy isotopes content of precipitations.

Generally the removal of precipitation from the vapour reservoirs was modelled as a simple Rayleigh process (Dansgaard, 1964), whereby the condensed phase is formed in equilibrium with the vapour and then removed from the atmosphere as soon as it is formed. This model can explain the differences in isotopic composition of precipitations either from the ocean to the interior of continents (horizontal gradient) or on mountain side (vertical gradient). However in our cases, one deals with the « mountain shadow effect » (Yurtsever and Gat, 1981). This is the appearance of precipitations on the side of mountains closer to the vapour source more enriched in heavy isotopes, at lower altitudes and more depleted at higher altitudes than rain in the regions lee side. According to this point of view, the gradient in altitude is considered to be a consequence of the moisture loss from an air mass by cooling, regulated at the same time by the distance from the ocean and by the geographical patterns of the mountains.

2.2. Deuterium excess

The « *d* » quantity referred to « deuterium excess » is usualli close to +10‰ at oceanic stations (Craig, 1961). However if a significant part of the vapour mass has originated in a closed basin, the « *d* » parameter changes. In the eastern Mediterranean basin, the isotopic composition of the precipitations obeys the relationship:

$$^{2}H = 8\ ^{18}O + 22$$

(NIR, 1967; GAT and CARMI, 1970).

In this context, because of the peculiarity of Italy's position the « *d* » parameter, as well the chemical load of precipitations, changes with the season as a result of different wind patterns.

characterizes the maximum oceanic component in the rainfall (summer and fall), whereas the increasing chloride paralleled by increases in deuterium excess affirme that air masses from western Mediterranean arrive during winter and spring (fig. 4).

A seasonal variation in deuterium excess has been found in the Latium Apennines with a range of «*d*» values between +11.1‰ in winter and +16 ‰ in summer and in the Eastern Alps where the range is +10.2 ‰ and +14.0 ‰, respectively in

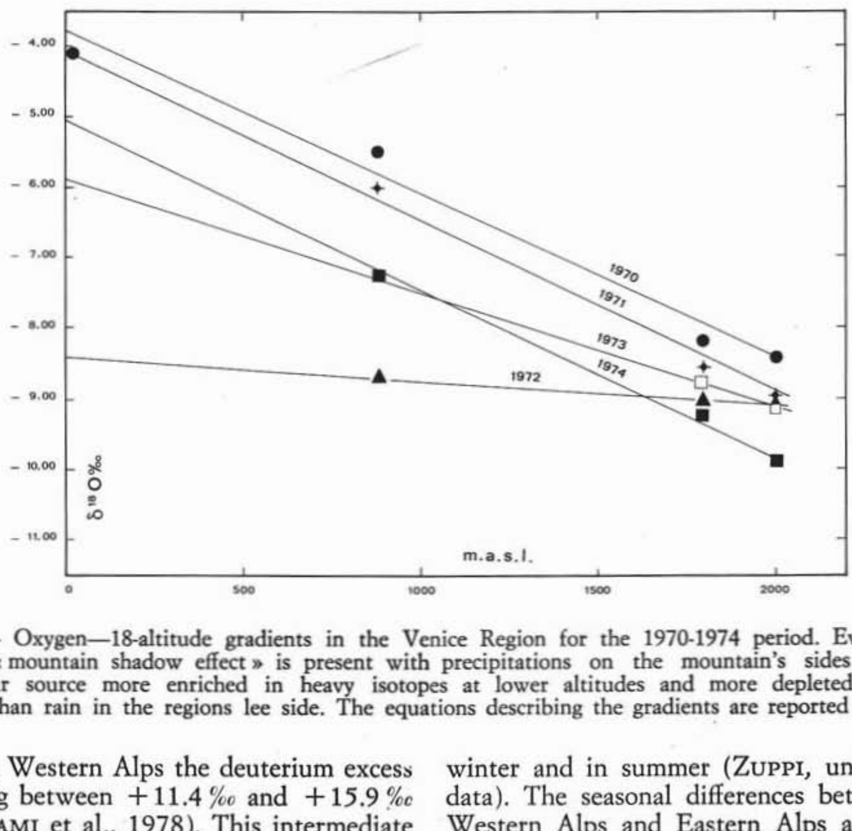

Fig. 3. — Oxygen—18-altitude gradients in the Venice Region for the 1970-1974 period. Even in this case the « mountain shadow effect » is present with precipitations on the mountain's sides closer to the vapour source more enriched in heavy isotopes at lower altitudes and more depleted at higher altitudes than rain in the regions lee side. The equations describing the gradients are reported in table 1.

In the Western Alps the deuterium excess is varying between +11.4 ‰ and +15.9 ‰ (BORTOLAMI et al., 1978). This intermediate position is due to the meteoric contributions which can be defined as « mixed ». Plotting the deuterium excess versus chloride activity (fig. 4) the points representing the fall season are closely grouped at the lower end of the line, whereas the points of spring show a larger spread at the upper part of the line.

It is known that the chloride contents at a certain distance from the coast become rather low and constant (JUNGE, 1963); the constant deuterium excess value (+11.2 ‰)

winter and in summer (ZUPPI, unpublished data). The seasonal differences between the Western Alps and Eastern Alps and Apennines are explained by the atmospheric circulation: the presence, in the winter, of a high pressure regime over the north Tyrrhenian Sea.

Therefore, the major contribution of Atlantic humid air masses occurs during summer in the Western Alps and during winter in the Eastern Alps and in Central Italy.

2.3. SULPHUR-34

The sulphur isotopic composition of dis-

TABLE 1

Annual and seasonal averages for oxygen-18 in Venice region weighted by the amount of precipitation

		1970		1971		1972		1973		1974	
		year	except winter	year	except winter	year	except winter	year	except winter	year	except winter
PASSO ROLLE 2000 m	δ	-8.45	-8.39	-9.05	-8.96	-9.10	-9.03	-9.16	-9.10	-9.89	-9.82
	mm	931	559	675	398	899	626	722	509	745	527
		27%	45 %	36 %	61 %	38 %	100 %	65 %	92 %	75 %	75 %
MONTE GRAPPA 1690 m	δ	-8.28	-8.18	-9.16	-8.53	-9.15	-9.02	-8.03	-8.80	-8.75	-9.26
	mm	1806	722	1657	714	2498	1019	1655	972	1382	781
		36 %	89 %	56 %	87 %	96 %	90 %	86 %	100 %	94 %	90 %
PONTE PIEVE TESINO 775 m	δ		-5.51		-5.96	-9.77	-8.71	-7.30	-7.31	-8.65	-7.27
	mm	1061	575	1130	540	1223	662	935	609	893	497
			47 %		27 %	72 %	90 %	50 %	85 %	67 %	88 %
VENICZ LIDO SAN NICOLO' 2 m	δ	-7.14	-4.09	-9.37	-8.36						
	mm	620	246	621	272						
		82 %	71 %	50 %	67 %						

GRADIENTS

1970 : $\delta^{18}O = -(2.27 \mp 0.10)\ 10^{-3}h - (3.98 \mp 0.28)$

1971 : $\delta^{18}O = -(2.53 \mp 0.10)\ 10^{-3}h - (4.05 \mp 0.45)$

1972 : $\delta^{18}O = -(0.34 \mp 0.04)\ 10^{-3}h - (8.40 \mp 0.06)$

1973 : $\delta^{18}O = -(1.66 \mp 0.09)\ 10^{-3}h - (5.90 \mp 0.12)$

1974 : $\delta^{18}O = -(2.38 \mp 0.10)\ 10^{-3}h - (5.10 \mp 0.19)$

The third value represents the percentage of the total annual or seasonal precipitation for which isotope data are available to calculate the weighted means. The seasons are spring, summer and fall. Winter precipitations, normally snow, are in general lightly evaporated.

solved sulphates in precipitations was investigated in Italy by CORTECCI and LONGINELLI (1970); the authors concluded that the main source of sulphates in rain waters was probably atmospheric oxidation of SO_2 from industrial activity.

In our case we analysed the sulphur-34 in precipitations to complete the study on the origin and movement of air masses over Central Italy. The samples are quarterly weighted. As indicated by previous authors, even in our case, the main source of sulphates is provided by the oxidation in the atmosphere of SO_2 from industrial activity. The relationship between sulphur-34 and the percentage of marine sulphate, as defined by MIZUTANI and RAFTER (1969), is quite similar to that evaluated by CORTECCI and LONGINELLI (1970):

$$\delta^{34}S = (0.22 \pm 0.09)\ \%\ SO^{--}_{4\ mar.} - (1.7 \pm 0.5).$$

Fig. 5 shows that summer samples are, generally, more enriched in marine sulphate than those from winter season. Thus, in the annual cycle of the geochemical evolution of these precipitations, the presence of a transition zone over Central Italy is observed.

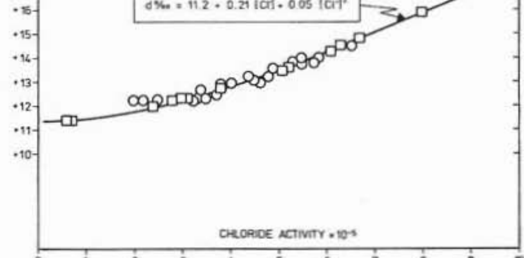

Fig. 4. — Deuterium excess plotted versus chloride activity in Maritime Alps.
Squares indicate the precipitation samples; circles the spring samples in crystalline rocks (see chapt. 4.3.2.). The points representing summer and autumn are closely grouped at the lower end of the line, whereas the points of winter and spring are more spread aut at the upper part of the line.

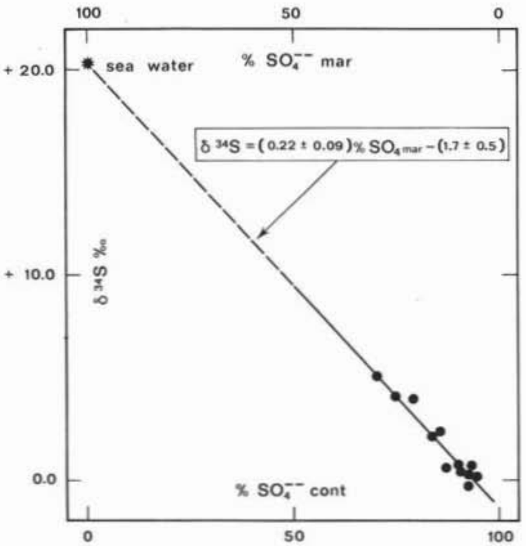

Fig. 5. — $\delta^{34}S$ plotted versus percentage of marine sulphate in Central Italy. It shows summer samples to be, generally, more enriched in marine sulphate than those from winter season. The coefficient of determination is 0.96 and the estimated standard error is 0.29.

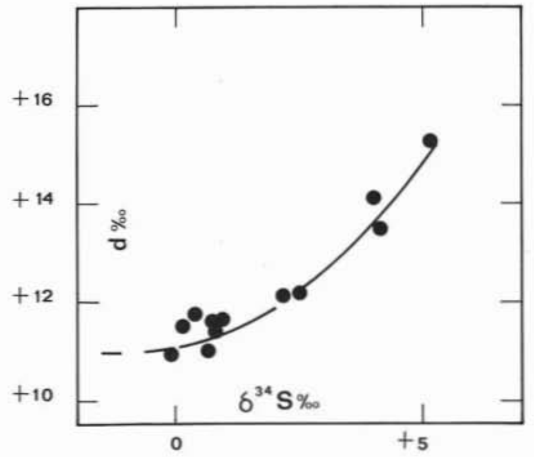

Fig. 6. — Deuterium excess and sulphur - 34 variation in precipitations on Central Italy. The diagram show as during winter the air masses arrive on the peninsula after a long circulation on the Europe and discharge precipitations affected by continental contributions.

Vapour from oceanic origin passes over the continent in winter and is substituted by marine vapour from Tyrrhenian Sea during summer and intermediate seasons. Similar conclusions are reached (fig. 6, tab. 2) if deuterium excess is plotted versus $\delta^{34}S$ (or versus the percentage of marine sulphate). The seasonal behaviour of these two parameters indicates that during winter, the air masses arrive on the peninsula after a long circulation over Europe and release precipitations affected essentially by continental contributions. Because the Adriatic Sea contributes little vapour to the atmosphere it is not able to change the geochemical and isotope signals of air masses.

On the basis of precipitation chemistry, it is believed that in Central Italy the air masses coming from the North have a constant percentage of marine sulphate (between 1 and 5 %) independent of the altitude as evidenced in the Maritime Alps (Bortolami et al., 1979 d).

2.4. Conclusions

The information provided by stable isotopes combined with geochemical and geographical parameters help in the interpretation of the global circulation of air masses over northern and central Italy.

This is of importance for a better definition of the meteorological input to the hydrogeological studies, which are:

1) Air masses crossing either the Alps or the Apennines are subjected to «mountain shadow effect», giving rise to a somewhat smoother isotope gradient on the lee side than on the sea side.

2) The major contribution of Atlantic Ocean humid air masses travelling over the continent appears, generally, during the summer in the Western Alps and during winter on the Eastern Alps side and in Central Italy.

3) Sulphur-34 content of dissolved sulphates offers a supplementary parameter for defining the annual geochemical cycle of precipitation.

3. Surface waters

The case of environmental isotopes in river systems has been undertaken in order to define the mutual contribution of surface waters to groundwaters. However, all rivers differ from each other in their geographical, climatological and geolithological patterns of their drainage basin.

These parameters regulate more than the

TABLE 2

Chemical and isotopic data of quarterly weighted precipitations samples from three meteorological stations in Central Italy

ANZIO	Cl^- p.p.m.	SO_4^{--} p.p.m.	SO_4^{--} marine %	^{34}S‰	d‰
dec-feb 72	6.08	8.64	10	+0.9	11.6
march-may 72	10.7	7.68	25	+4.1	13.5
june-aug 72	11.7	6.24	30	+5.2	15.3
sept-nov 72	10.7	7.20	21	+4.0	14.2
ANAGNI					
dec-feb 72	2.86	6.24	6	+0.2	11.5
march-may 72	4.81	5.28	13	+0.8	11.6
june-aug 72	4.88	4.80	14	+2.5	12.3
sept-nov 72	3.10	5.12	9	+0.7	11.5
ASCOLI					
dec-feb 72	3.41	7.20	7	-0.1	10.8
march-may 72	3.88	6.48	8	+0.6	11.0
june-aug 72	4.90	5.76	17	+2.2	12.2
sept-nov 72	3.13	5.95	7	+0.2	11.8

The chemical data are expressed in p.p.m.; the percentage is referred to marine sulphate as defined by MIZUTANI and RAFTER (1969); $\delta^{34}S$ refers to the international standard: *C.D.*; *d* is deuterium excess defined as: $d = D - 8\,\delta^{18}O$.

others the variation of isotopic composition during discharge.

3.1. CREEK AND RIVERS IN SMALL DRAINAGE BASINS

In small drainage basins, water storage reservoirs are very limited and the discharges from basins are strongly dependent on precipitation events.

In this context the magnitude of the annual cycle of the isotopic composition of the rivers is an inverse function to the size of the basin: the response to precipitation events is very fast. Is the case of Bacchiglione, Leogra-Astico and Chiampo in Venitian Prealps (BORTOLAMI and FONTES, 1974) and Corsaglia, Ellero, Maudagna and Pesio in Piedmont (AMBROGIO, 1975; SUSELLA, 1976; BORTOLAMI et al., 1978, 1979 d, 1982 b; ZAULI, 1978).

All the values reflect the mean altitude of the basin calculated with the isotopic gradient. During winter, if the catchment area is covered by snow, the stable isotopes content varies, as the drainage basin, affected by snow melt, becomes smaller; the seasonal $\delta^{18}O$ variations are probably resulting from both snow melt and variation of the isotopic composition of precipitations.

3.2. RIVERS IN MEDIUM DRAINAGE BASINS

3.2.1. *Alps systems*

In this group we consider the rivers under glacial regime as Dora Baltea, Sesia, Po (in Chivasso) and Adige (BORTOLAMI et al., 1983 b).

TABLE 3

$\delta^{18}O$ values in some rivers originating in the Italian Peninsula

River	n	sampling period	$\delta^{18}O$‰ vs SMOW max	min	$\bar{\delta}$	σ	Flow $m^3 \cdot s^{-1}$ max	min	Size of basin Km^2
PIAVE (Nervesa)	43	02/70-12/74	-7.6 (09/70)	-11.0 (04/72)	-9.78	0.70			2.100
ADIGE (S.Michele)	11	01/71-12/74	-11.4 (02/72)	-13.0 (09/72)	-12.21	0.61			1.700
ADIGE (Boara P.)	38	01/71-06/75	-10.3 (11/71)	-12.9 (06/72)	-11.96	0.59	808 (06/72)	78.5 (08/73)	11.956
BACCHIGLIONE (Padova)	17	08/71-12/72	-5.6 (11/71)	- 8.9 (02/72)	-7.83	1.06	194 (06/72)	6.9 (11/71)	1.384
BRENTA (Padova)	40	02/70-09/75	-6.8 (07/70)	-11.6 (05.72)	-10.03	0.73	470 (06/72)	11.0 (01/73)	1.862
PO (Pontelagoscuro)	43	10/71-10/75	-9.2 (11/73)	-10.9 (05/74)	-9.98	0.32	3410 (02/72)	525 (08/74)	70.091
SILE (Treviso)	41	04/70-06/74	-7.4 (11/70)	-10.2 (01/72)	-9.33	0.69			1.500
PO (Chivasso)	4	03/75-06/76			-12.77	0.71			18.970
SESIA (Borgosesia)	4				-12.56	0.70			750
ELVO (Salussola)	4				-9.75	1.00			75
CERVO (Biella)	4				-10.57	0.55			100
DORA B.(Borgo Revel)	4				-13.34	0.70			4.000
TICINO (Castelletto)	4				-9.64	0.31			6.600
NERA (Triponzo)	12	10/71-09/72	-9.8 (04/72)	- 9.1 (08/72)	-9.55	0.11			
TRONTO (Acqua Santa)	12	10/71-09/72	-10.0 (03/72)	- 9.2 (09/72)	-9.62	0.19			
VELINO (Borgo Velino)	12	10/71-09/72	-10.7 (06/72)	- 8.4 (10/71)	-9.48	0.29			
ANIENE (Tivoli)	12	10/71-09/72	-8.4 (04/72)	- 7.6 (07/72)	-8.12	0.09			

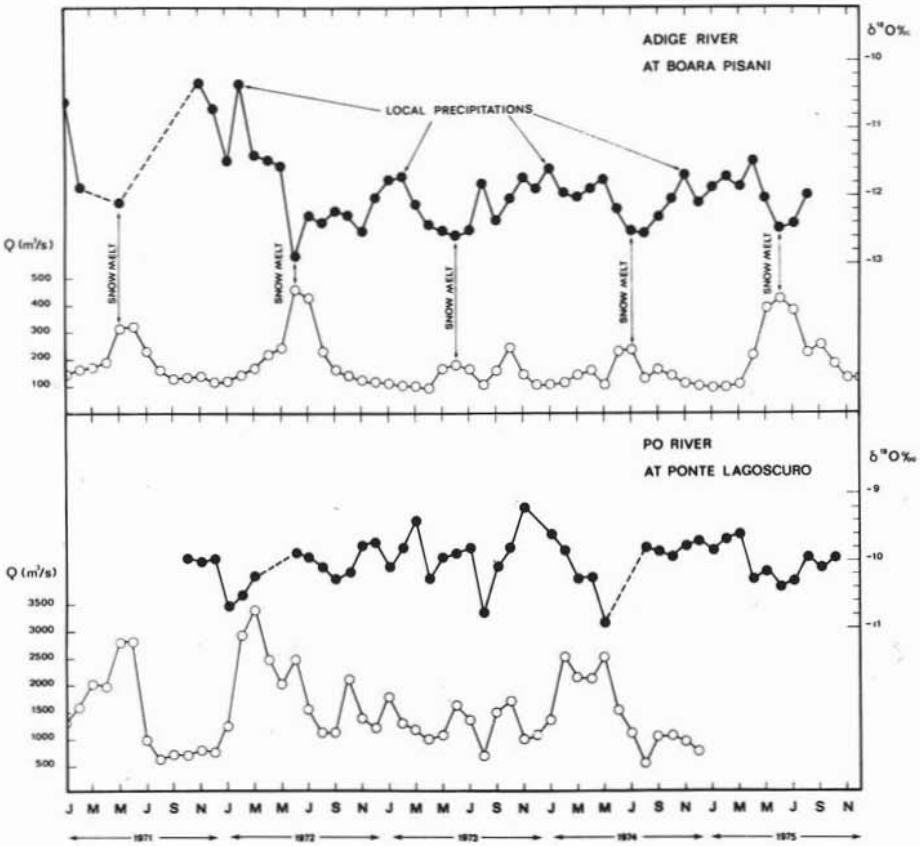

Fig. 7. — Seasonal variation of $\delta^{18}O$ in Adige and Po rivers respectively at Boara Pisani and Pontelagoscuro. Note the base flow variations which underly the sharp response to precipitations and snow melt for Adige and the random variation of Po. Filled and emplay circles are referred to oxygen-18 content and to the rate flow respectively.

We can consider them as indirect runoff dominated systems. Because of the storage of winter precipitations in snow covers and the presence of ice masses and their respective melting during warmer seasons, the isotopic sycles are reversed or, at least, shifted in time. This is shown in table 3 and in fig. 7 by the Adige River. Note that the less negative $\delta^{18}O$ in samples collected in winter (average from two winter samples: —11.3‰) is compared to the average value of —12.6 ‰ for five summer samples (FRITZ, 1981; BORTOLAMI et al., 1983 b).

3.2.2. *Prealps systems*

The Brenta and Piave show a quite constant oxygen-18 composition. They are not affected by seasonal snow melt and the seasonal meteorological signals are completely smoothed out (FRITZ, 1981). It appears that in the Piedmont area, groundwater discharges provided the only supply to the rivers.

3.2.3. *Apennine systems*

The influence of the Karst on the rivers isotopic composition is clearly described by oxygen-18 content in Aniene, Nera, Tronto and Velino rivers (ZUPPI, unpublished data; TISSIER, 1976).

Base flows supplied from the large karstic aquifers with long transit times (see below) do not show any seasonal variations during the annual cycles. However waters slightly depleted in heavy isotope are present during spring as result of direct runoff from the highest altitude in the catchment area possibly lineed to snow melt.

Nevertheless the main contribution of river flow comes from the greatest karstic springs, with a quite constant oxygen-18 content.

These observations are valid only in those rivers with carbonatic deposits. In contrast the Reno River (CARLIN et al., 1975) and Arno River (GONFIANTINI et al., 1973) with their drainage basin essentially on impervious sediments could be considered as direct runoff dominated systems. In this case, higher concentrations during summer and lower ones during winter are found.

3.3. RIVER IN LARGE DRAINAGE BASINS

3.3.1. *Homogeneisation by groundwaters*

The Po plain is covered, essentially, by Quaternary sediments, with some local exception (i.e. Moncalieri - Casale Monferrato area, where Tertiary deposits outcrop).

Aquifers are sometimes in hydraulic equilibrium with Po tributaries and piezometric data indicate that a continuous exchange with groundwaters takes place.

Po tributaries coming from Alps and Apennines are subjected differents climatological conditions. However the very constant isotopic composition of Po waters at Pontelagoscuro (about 50 km from Adriatic Sea): reflects the unique « buffering » role of groundwater reservoirs (fig. 7). Thus the Po River does not exibit, as other large rivers in Europe i.e. Rhine River, etc. (MOOK, 1970) or in America i.e. Mississippi River (FRIEDMAN et al., 1964) and Amazzonia (MATSUI and al., 1976), cyclic variations in response to the available discharge from subdrainage basins.

3.3.2. *Homogeneization by surface reservoirs*

The constancy of isotopic content in Ticino river samples collected near Magenta is due to the influence of the large reservoir of Lago Maggiore and others lakes of the Ticino drainage area (Lugano, Orta, etc.).

Mixing within lake masses is caused by the smooth yearly cycle of oxygen-18 (BORTOLAMI et al., 1982).

3.4. CONCLUSIONS

The examples quoted above show that:

1) The cyclic fluctuations of river waters isotopic composition are mainly governed by the hydrogeological and geopedological conditions of drainage basins: large Karstic areas and large porous media basins tend to control river supplies smoothing out the meteorological signals.

2) The meteorological signals can be recognized only in runoff dominated systems. In this case, it is possible to find two groups: one « direct », controlled by meteorological events, and another « indirect », controlled essentially by the storage of precipitations on snow and ice covers.

4. Groundwaters

4.1. AQUIFERS IN POROUS MEDIA

Two large areas of the Po Valley have been studied in detail in the Piedmont Region (BORTOLAMI et al., 1980 b; BORTOLAMI and ZUPPI, in prep.) and Venetian Plain (BORTOLAMI et al., 1973).

4.1. *Piedmont fresh groundwaters*

Piezometric data indicated that seepage between rivers and aquifers could occur. Both chemical and isotope measurements were computer processed (BORTOLAMI et al., 1980 a) permitting semiquantitative estimates which could not have been obtained with classic hydrological means (fig. 8).

It was shown that Dora Baltea loses water to aquifers from the end of Aosta Valley up to its confluence with Po River; other very important seepages occur below Ivrea morenic hills along fluvioglacial deposits. The Dora Baltea underground water flows eastward; near Vercelli the direction of this subsurface movement changes southward. At the same time prealpine reliefs (Elvo, Cervo, Rovasenda basins) and Turin Hills provide further infiltration to groundwaters and gradually mask the initial isotopic signal.

The Sesia River receives waters from aquifers on the right bank and loses waters on the left one. The influence of this river can be followed for several kilometers up to Novara, where a contribution from the Ticino River occurs. The Lomellina region, south of Novara, may be considered as a mixing area, where all the Alpine contributions (Po, Dora Baltea, Sesia and Ticino rivers), are mixed with the local ones (from

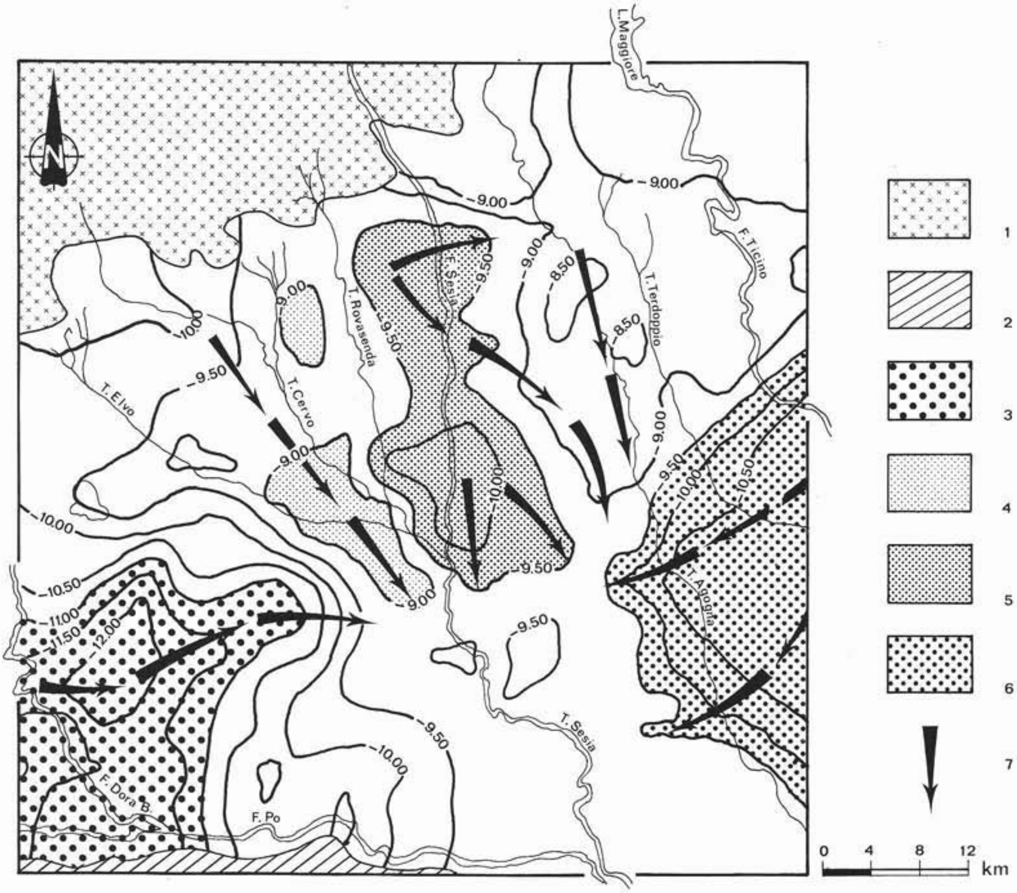

Fig. 8. — Areal variation of $\delta^{18}O$ in the Po Plain (eastern Piedmont). One can observe the influence of Dora Baltea and Sesia rivers. The isotopic signal is completely masked in the Lomellina region which could be considered a mixing area. 1) Alps: generally crystalline rocks; 2) Turin and Monferrato Hills: sedimentary rocks; 3) underground extensions of Dora Baltea waters; 4) underground influence of Cervo waters; 5) underground extensions of Sesia River; 6) underground influence of Ticino waters; 7) groundwater flow directions.

Monferrato Hills and from the extensive canal network) and with the Apennine supplies (Tanaro River). The uniformity of oxygen-18 content, about —9.50 ‰, does not permit then to estimate the origin of waters.

4.1.2. *Piedmontmineral groundwaters*

In the southern region of Lomellina and in the Turin-Monferrato Hills an important phenomenon occurs: an interface between fresh and saline waters is found at depths ranging from subsurface (in Monferrato Hills) to 500 meters (South of Lomellina) (Bortolami et al., 1979 a; Bortolami et al., 1983 b; I.R.S.A., 1982; Piovesana, 1977).

The seepage between aquifers is marked with an increase in salinity and a relative enrichment in heavy isotopes. Plotting deuterium versus oxygen-18 contents in the diagram (fig. 9) one notes a mixing triangle. The extreme lines intercept the local meteoric line at values, in oxygen-18 of —11.0 ‰ and —9.0 ‰, indicating respectively an « alpine zone of recharge » and a « local zone of recharge ».

The intercept of these two lines is defined by δD = —5.0 ‰ and ^{18}O + 2.00 ‰; the latter values correspond to the isotopic composition of the original deep paleosaline water enriched in heavy isotopes possibly by ultrafiltration in clay rich deposits.

The sulphates sulphur-34 content ($\delta^{34}S$

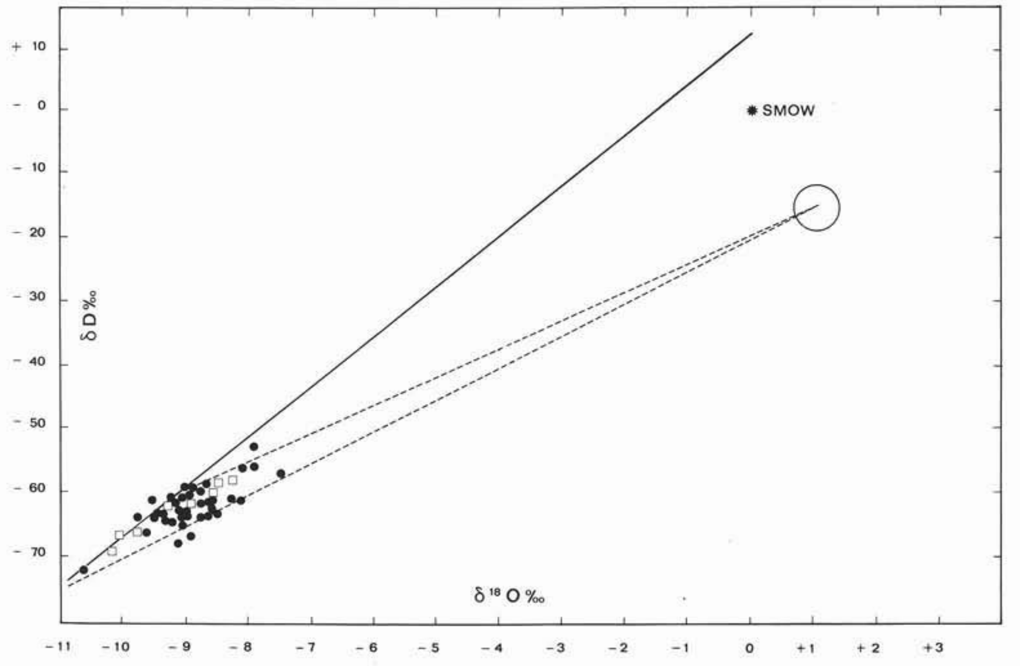

Fig. 9. — δD versus $\delta^{18}O$ for Monferrato (circles) and southern Lomellina areas (squares). All the isotopic results are delimited by two lines defining a « mixing area ». The lines intercept the local meteoric line at values in $\delta^{18}O$ of —11.0 ‰ and —9.0 ‰ indicating respectively an « alpine zone of recharge » and « local zone of recharge ». The intercept of the two mixing lines should indicate the isotopic composition of the original saline water.

ranging from +19.8 ‰ in Monferrato Hills to +16.5 ‰ in South Lomellina) suggest one source of sulphur to the system: a heavy sulphur component, which could be of marine origin, either from oceanic aqueous sulphate (Monferrato) or from dissolution of Messinian evaporite sulphate (Lomellina, where buried structures with Messinian lithotypes are frequent). The mean $\delta^{18}O$ values of dissolved sulphate ($\delta^{18}O = +10.1 \pm 0.6$ ‰) supports the hypothesis of an oceanic origin.

4.1.3. *Venice Plain*

In the Venice Plain (fig. 10) the stable isotope contents show the presence of two groups of deep waters ($\delta^{18}O$ = —10.0‰ and —12.0 ‰) both correlated to different recharge areas. These waters are clearly different from those of the unconfined shallow aquifers ($\delta^{18}O$ = —8 ‰). The deep supplies can be respectively correlated to the recharge basins of the prealpine rivers Brenta and Piave with similar geomorphologic characteristics ($\delta^{18}O$ = —10 ‰) on one hand, and on the other hand to the Adige River ($\delta^{18}O$ = 12.0 ‰).

The underground extension of Alpine water is geographically delimited by its isotopic fingerprint, as reported in fig. 10 between the zone of Venice Lagoon and the southwestern part of the plain. The prealpine type water is located under the central part of the plain.

In the Abano Terme district, where a number of warm water points occurs, $\delta^{18}O$ values range from —10.0 ‰ and —12.0 ‰ (Bortolami et al., 1973; Panichi et al., 1976). The first of these two values corresponds to that of groundwater recharged to that of Adige seepage which might occur North of Verona at the beginning of the Lessini Mountains.

Some other areas of the Venice Plain subjected to the influence of small prealpine drainage basins are found in the Vicenza Province (associated with the catchment area of Leogra and Astico rivers).

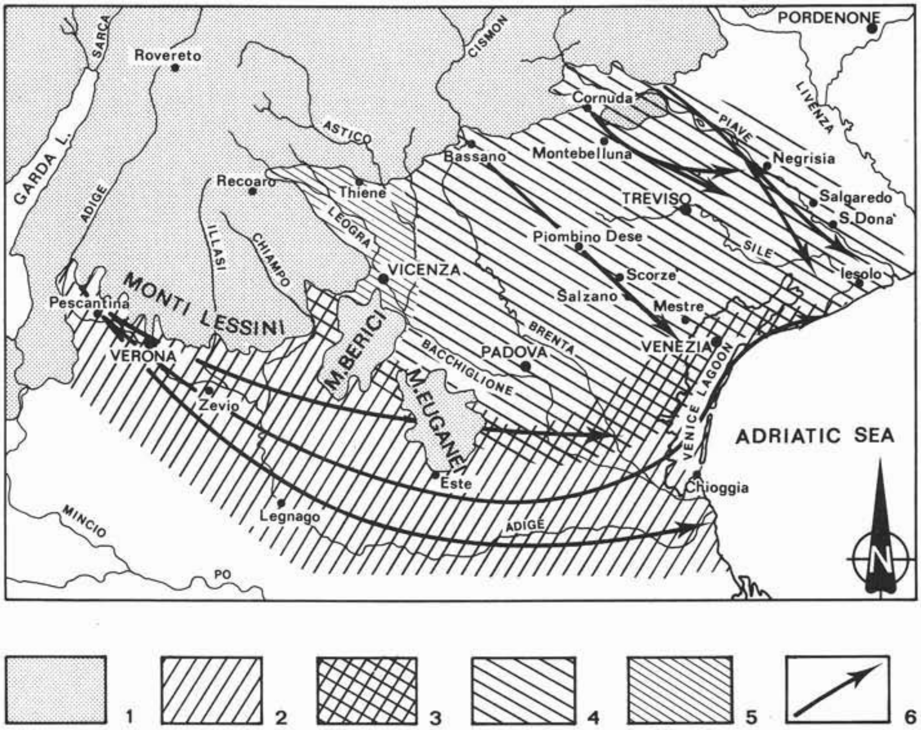

Fig. 10. — Areal variation of $\delta^{18}O$ in the Venice Plain groundwaters. Deep supplies can be respectively correlated to the Adige River on one hand, and to recharge basins of the prealpine rivers on the other hand. 1) Alpine and prealpine areas; 2) underground extension of Adige waters; 3) mixing area between alpine and prealpine waters; 4) underground extension of Brenta and Piave waters; 5) underground influence of Astico-Leogra rivers.

However their down stream extension is small due to the greater influence of other main river supplies.

Unconfined shallow aquifers show, generally, a local meteoric recharge. However one can find, in connection with the canal network, wells with water of prealpine or alpine type recharge. Seepages from canals are very frequent and volume lost trough seepage is probably important.

In the Mestre-Marghera areas sea water intrusion in shallow aquifers is very usual and increases with water withdrawal.

4.2. Karstic circulation

4.2.1. *Piedmont*

The information that stable isotopes can provide about the source of water such as altitude of recharge and seasonal variation of the input can be combined with geochemical parameters for interpretation of Karst flows. In the whole area of Marguareis-Mongioie Massif two different types of karst groundwaters occur: one « intra massif » (i.e. Bossea, Caudano, Pis del Pesio, Vene del Tanaro, etc.) and another one « extra massif » (Beinette).

1) In the first case, the groundwater flow patterns are, generally, quite short and fast. At the end of winter the snow melt occurs at a progressively increasing altitude. Therefore the isotopic composition of water in springs becames similar to that of snow melt, which, in this season, is a major component of spring discharge. Two different types of groundwater flow occur:

a) a deep one, isotopically and chemically homogeneous, representing the base flow, oversaturated with respect to calcite;

b) a shallow and faster one, isotopically varying according to the increasing altitude at which snow melt occurs, with low T.D.S. and undersaturated with respect to calcite.

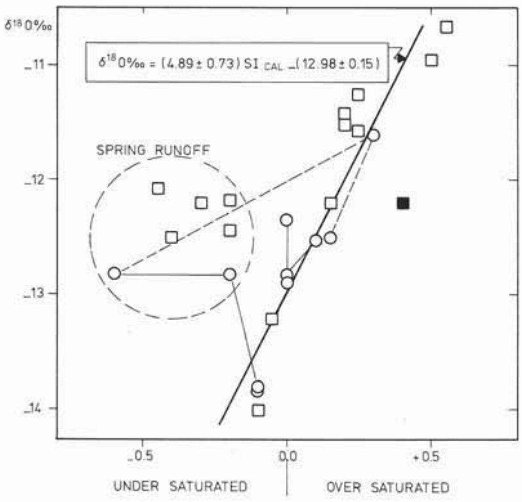

Fig. 11. — $\delta^{18}O$ versus calcite saturation index in some « perched » karstic systems of Piedmont. The plot describes the following hydrological regime: a shallow, fast and non-dispersive groundwater circulation following spring runoff and later, deeper subsurface flow dominated by isotopically and chemically homogeneous base flow. For base flow conditions the relationship is:

$$\delta^{18}O‰ = 4.81 \; SI_{calc.} - 12.98$$

with a coefficient of determination of 0.91 and the estimated standard error of 0.14.

The mixing, or at least the contribution of the superficial circulation, is thus recognizable through parallel, seasonal variation of the isotopic and chemical composition of water (fig. 11).

2) Groundwater flows are long and slow; all the year long the flow is always homogeneous and dispersive and meteoric input variations are not distinguished. Stable isotopes, as well as the saline load are inclined to be rather constant and independent from low discharge variations.

4.2.2. *Latium*

As in Piedmont the carbonatic sequences of the Central Apennines show two groundwater flow patterns. In the spring located inside of the carbonatic structures as Triponzo (Umbria), Antrodoco, Fontana Liri, Pompeo, Tufano, Capo d'Acqua di Trevi, Valle dell'Inferno, Marano, etc. (Lazio) it is possible to recognize a deep component isotopically homogeneous and a shallow one isotopically variable. The water localities on the border of the structures (Canetra, Santa Susanna, Cassino, Ninfa, Laghi del Vescovo, Tivoli 1) indicate an homogeneous flow representing the base flow; the local contributions are, in general, less than 10 %). The isotopic composition of base flow is coherent with the mean altitude of the whole karstic system i.e., 850 m for Cassino (mean altitude of Simbruini-Ernici Mt). 550 m for Ninfa (Lepini Mt.). It is interesting to note that isotopically, the base flow of the « intra massif system » is very close to that of the general system (fig. 12).

These observations, and those of the Piedmont karst systems introduce the concept of « perched Karst » and « basal Karst ». The systems inside carbonatic structures are perched, whereas the systems outside are basal.

4.2.3. *Central Italy mineral springs*

The intensive tectonics favour the presence, in the carbonatic relief, of several springs with salt and temperature anomalies. Variations in isotopic composition of the water can be interpreted as dilution between deep, well homogeneized karstic groundwater and deep saline waters rising through the fault systems.

The ^{34}S content of the associated sulphides and sulphates indicates the origin of sulphur from evaporitic triassic sediments except for Tivoli 2 and Vescovo, where sulphur isotope contents indicates a mixture of two sources of aqueous sulphur: one marine (triassic for Tivoli 2 and recent sea water for Vescovo), and another one of deep perivolcanic sulphur (ZUPPI et al., 1974; FONTES and ZUPPI, 1976).

In addition sulphides and sulphates are limited by a redox mechanism as suggested by Eh variations. ^{18}O content of sulphates shows the same characteristics.

With these data is calculated temperature reaction through the oxygen-18 fractionation between sulphates and water (LLOYD, 1968), at least accounting for the dilution between the two components (Mc KENZIE and TRUESDELL, 1977). Calculations give generally low temperatures (less than 100° C, compatible with the basal temperature of the system, under normal geothermal gradient). Tivoli 2 and Vescovo give higher temperatures (130° C and 150° C respectively) compatible with the geothermal anomaly of Albano volcanic system.

A particular case is Acqua Santa, where the comparative pattern of salt and oxygen-18 suggests that the discharge is made of at least three, components (FONTES and ZUPPI, 1976). The sulphur-34 and oxygen-18 contents of sulphates give an elevated temperature of about 150° C. Therefore for the high chloride content and for the presence of Pliocene deposits, Acqua Santa could be considered as a product of mixing between karstic systems and old marine water (fig. 13). The latter trapped in depth could have the same origin of that found in the Po Valley and would be the consequence of the variation of the Mediterranean Sea in the Upper Miocene.

4.3. CIRCULATION IN CRYSTALLINE ROCKS

4.3.1. *Mont Blanc Massif*

Thanks to the construction of the 11.6 km long Mont Blanc Tunnel it is possible to collect water that has drained through cracks in the rock.

The heavy isotope concentrations indicate that infiltration is essentially vertical and occurs over the topographical profile above the tunnel. Moreover the stable isotope contents show that groundwater circulations are independent and vertical and that a good homogeneization occurs in each single system (FONTES et al., 1978; BORTOLAMI et al., 1979 b). The variable deuterium excess indicates that some waters (those at a higher temperature, about 30° C with respect to a mean temperature of 10° C) have undergone a kinetic evaporation. Mont Blanc can be considered an excellent natural laboratory for the survey of fracture flow in crystalline rocks. This is a subject of importance for the evaluation of nuclear wastes storages in hard rocks.

4.3.2. *Piedmont and Aosta Valley*

Generally crystalline rocks are considered as impermeable or semi-impermeable. In Mont Blanc Massif BORTOLAMI et al. (1979 b) using tritium distribution calculated a permeability of $5 \cdot 10^{-7}$ m $\cdot$ s^{-1} and and effective porosity close to 1 %. However, often it is possible to recognize local ground-

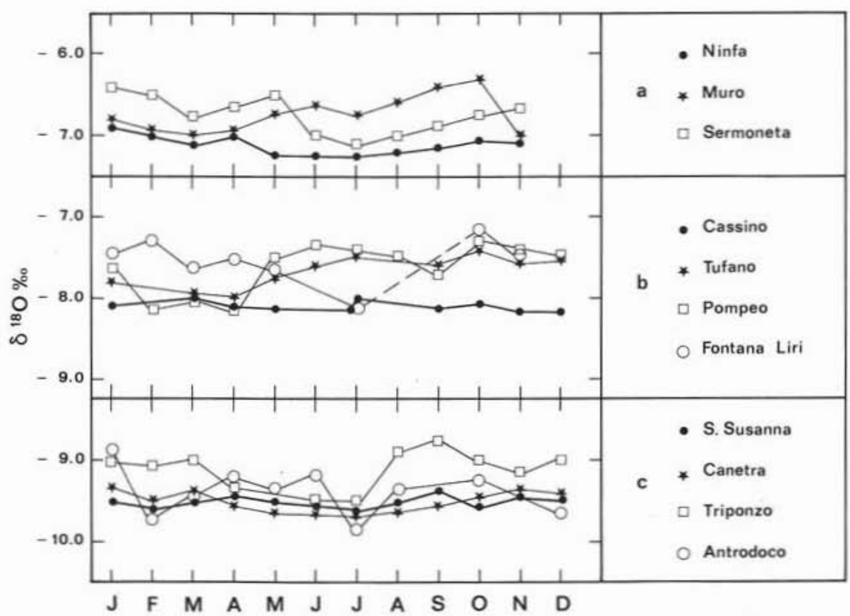

Fig. 12. — Seasonal variation of $\delta^{18}O$ in some karstic areas of Central Italy: *a*) Lepini Mountains system; *b*) Simbruini-Ernici Mountains system; *c*) Sibillini and Reatini Mountains system. Note the base flow variation which underly the sharp response to meteoric signals for the « inside massif » springs (in general fed by « perched karstic systems ») and the constancy of isotopic signal content for the « outside massif » water points (fed by « basal karstic groundwaters »).

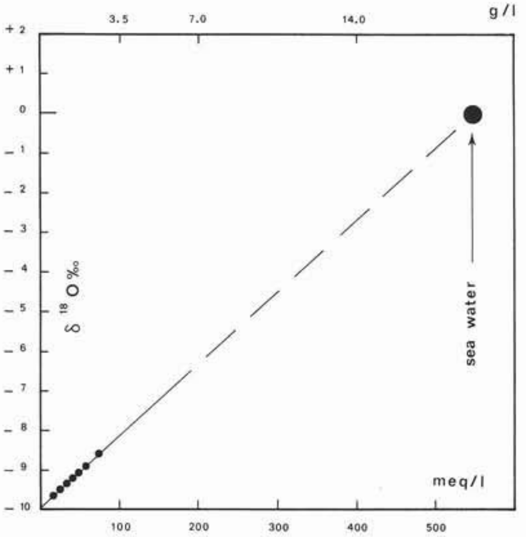

Fig. 13. — $\delta^{18}O$ versus chloride content in Acqua Santa T. (Ascoli Piceno). The line could be considered as a mixing line between karstic groundwaters and old marine water.

water infiltration. In the western Alps several water points have been investigated in order to shed new light on the water circulation in the impervious crystalline rocks. Two different types of groundwater flow occur: one very fast and generally short (i.e. Abrau, Aragnera, Barale (Val Pesio), etc.) and another slow and normally deep (i.e. Saint Vincent, Vinadio, Valdieri, Acqui T.).

1) In fig. 4 where deuterium excess is plotted versus chloride all the pairs cluster on the characteristic line of the local precipitations. Thus the isotopic content and the chemical load of the springs discharge from crystalline rocks follow the isotopic and chemical composition of the meteorological events.

This suggests that the subterranean flow paths are very short and similar to subterranean runoff with small shift in time, particularly during the snow melt (spring season).

All the considered water points are associated with small fault systems and the discharge varies during the year.

2) Corresponding to the main tectonic lines anomalies in salt content and in temperature are observed. In the diagram deuterium versus oxygen-18 the points fall on a correlation line with a slope of 6 indicating that waters are slightly affected by evaporation. The temperature, quite constant and always higher than the mean environmental temperature, account for a deep circulation. Therefore the salt content is very high and chloride is predominant. Since it impossible that such a high chloride content (more than 1 g l^{-1}) is due to silicate alteration, a secondary source of water under a regional profile must be considered.

As mentioned in section 4.1.2., at different depths of the Po Valley, a saline water level occurs. It is possible that during tectonic movement the saline water has been squeezed up along faults. The presence of deep, saline water inside of the Alpine area is of great importance because it extends the area of the fossil saline waters beyond the already well-known areas of the Po Valley and of tertiary Ligurian-Piedmont Basin, to the crystalline alpine basement. It is therefore evident that the evaporation line becomes a mixing line as observed in figure 9.

A more complete example is obtained from the Acqui Terme district where the water points are fed with different proportional mixing between meteoric waters and a fossil sea water (BORTOLAMI et al., 1979 c, 1982 b, 1983). The contribution of the surface waters to the dilution of the saline waters would range between 93 and 98 %. The recharge zone of meteoric waters either shallow or deep, has been fixed in the Voltri-Savona Massif between Ligurian Apennines and Alps. The reservoir temperature has

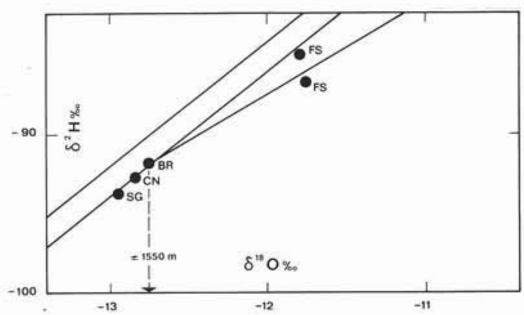

Fig. 14. — δD versus $\delta^{18}O$ in Saint Vincent thermal spring. Even in this case one must consider line below the global meteoric line as a mixing line between local fresh groundwaters, with a isotopic altitude of recharge of about 1500 meters, and deep saline water. The mixing line is described by the following equation: $\delta D = 6\,\delta^{18}O - 15.5$.

been estimated on the basis of chemical and isotopical data to be about 200° C. This high value permits to be consider the Acqui district as the more important geothermal reservoir in northern Italy, where no other indication of significant temperature has been obtained from numerous geothermal researches.

5. Conclusion

The application of environmental isotopes, jointly with chemistry, in aquifer studies, permitted:

- to define the zone and amount of groundwater discharge in porous media;
- to improve the knowledge on the concept of transit and transfer in the seepage between river and aquifers and between aquifers themselves;
- to clarify some problems of the Karst hydrodynamic identifying two karstic systems: one, inside of investigated carbonatic structures, generally perched; a second one, outside of these structures, generally basal;
- to estimate the flow contributions of different reservoirs to a single water point;
- to extend the influence of deep saline waters to the heart of the Alps structure.

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