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The S. Andrea Bagni Waters (Province of Parma): Origin, Mixing with High-Salinity Waters and Inferences on Climatic Microvariations

Le acque di S. Andrea Bagni (Parma): caratteri chimici e isotopici, mescolamento con acque saline e inferenze su microvariazioni climatiche

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ABSTRACT - Waters from the S. Andrea Bagni and neighbouring areas (Salsomaggiore, Monticelli, Fontevivo) of the Province of Parma have been investigated for their chemical and stable isotope imprinting. The monitoring of the water composition covered a period ranging from four to thirteen months (182 new data for $\delta^{18}O$ and $\delta^{2}H$, 60 new data for pH, specific conductivity, total alkalinity, chlorine). The waters undergo long-term circulation at depth as suggested by constance in the isotope data during the year and low values of tritium. The low-salinity waters (conductivity < 1500 $\mu S\ cm^{-1}$) of S. Andrea Bagni have a meteoric origin plotting very close to the present-day precipitation line of Northern Italy. They show largely variable chemical composition (Na/carbonate, Na-Mg/carbonate, Na-Ca-Mg-/carbonate, Mg-Na/carbonate, Mg-Ca/carbonate). The intermediate to strongly-saline waters (conductivity from 1900 ≈ to ≈ 40,000 $\mu S\ cm^{-1}$) are Na/carbonate-chloride to Na/chloride ($CaCl_2$-bearing); they plot away from the precipitation line, in that definitely differing from the low-salinity waters. In the diagrams Na-Cl and $\delta^{18}O$-$\delta^{2}H$, these intermediate to high-salinity waters from S. Andrea Bagni define straight lines which indicate mixing between low-salinity and high-salinity waters. Chemical and isotopic mass balance suggests that the high-salinity waters/brines from Salsomaggiore, Monticelli and Fontevivo cannot represent an end-member of the mixing. The end-member is unknown or represented by the Purgativa forte water. The very low $\delta^{18}O$ and $\delta^{2}H$ of some waters (e.g. Lidia) indicate infiltration under climatic conditions which, on average, were slightly different from the present ones.

KEY WORDS: Underground Waters, Chemistry, Oxygen and Hydrogen Isotopes, Water Mixing, Climatic Variations, S. Andrea Bagni, Emilia-Romagna Region, Italy.

RIASSUNTO - Si è compiuta un'indagine sui caratteri chimici e la distribuzione degli isotopi stabili nelle acque di S. Andrea Bagni e delle aree limitrofe (Salsomaggiore, Monticelli, Fontevivo) in Provincia di Parma. La composizione delle acque è stata controllata periodicamente in un intervallo di tempo variabile da quattro a tredici mesi (182 nuovi dati di $\delta^{18}O$ e $\delta^{2}H$, 60 nuovi dati di pH, conducibilità specifica, alcalinità totale, cloruro). Le acque hanno una prolungata circolazione profonda come indicato dai bassi valori del tritio e dalla costanza dei dati isotopici durante il periodo di indagine. Le acque a bassa salinità (conducibilità < 1500 $\mu S\ cm^{-1}$) di S. Andrea Bagni hanno un'origine meteorica e cadono molto vicine alla linea delle precipitazioni attuali dell'Italia settentrionale. La loro composizione chimica è estremamente variabile (Na/bicabonato, Na-Mg/bicarbonato, Na-Ca-Mg/bicarbonato, Mg-Na/bicarbonato, Mg-Ca/bicarbonato). Le acque da mediamente a fortemente saline (conducibilità da ≈ 1,900 a ≈ 40,000 $\mu S\ cm^{-1}$) sono da Na/bicarbonato-clorurate a Na/clorurate (con $CaCl_2$); queste acque si discostano assai dalla linea delle precipitazioni e quindi differiscono significativamente dalle acque a bassa salinità. Nei diagrammi Na-Cl e $\delta^{18}O$-$\delta^{2}H$ le acque da mediamente a fortemente saline di S. Andrea Bagni giacciono su linee rette, ciò che suggerisce *mixing* tra acque a bassa salinità e acque a elevata salinità. Il bilancio di massa chimico e isotopico indica che le acque a elevata salinità/salamoie di Salsomaggiore, Monticelli e Fontevivo non possono rappresentare un estremo composizionale del mixing. L'estremo composizionale è sconosciuto o potrebbe essere rappresentato dall'acqua Purgativa forte. I valori estremamente bassi di $\delta^{18}O$ e $\delta^{2}H$ di alcune acque (es. Lidia) indicano infiltrazione di acque in condizioni climatiche medie leggermente differenti da quelle attuali.

PAROLE CHIAVE: Acque sotterranee, Chimismo, Isotopi ossigeno e idrogeno, Mixing di acque, Variazioni climatiche, S. Andrea Bagni, Regione Emilia-Romagna, Italia.

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1. - INTRODUCTION

The Emilia-Romagna region (Northern Italy) is rich in natural waters suitable for medical purposes and for bottling. Among them, the waters of the Rio Fabbro valley, WNW of S. Andrea Bagni (Province of Parma) have been well known since the second half of the nineteenth century for their medical use (drinking, bath, inhalation, mud bath). The beginning of spa activity is dated 1888; this activity assumed particular relevance starting from 1923. Also the Nobel prize Marie Curie verified the curative properties of the waters for renal calculosis, cystitis and neuritis. At present, some waters are also widely traded as mineral waters (e.g.: S. Andrea, Lidia). Most waters are taken from wells, which may reach high depth (up to about 490 m) and were mainly drilled during the last century.

The Rio Fabbro and neighbouring areas are characterized by the occurrence of well known sedimentary rocks of Serravalian age (*Gisolo stream formation*, SERVIZIO GEOLOGICO D'ITALIA, 1999). The folding form the Salsomaggiore anticline dipping SE to SSE of about 22-30° (FINETTI, 1958). The Serravalian rocks stratigraphically rest on Langhian sediments (*Ghiara stream formation*, see SERVIZIO GEOLOGICO D'ITALIA, Sheet 198 Bardi, 1999) and, at the NE side of the area, they are covered by Late Messinian hypoaline clastic deposits (BERIOLI *et alii*, 1993; IACCARINO & PAPANI, 1980; ARTONI, 2003).

The Serravalian sediments mostly consist of sand, sandstone and silt strata with clay-silt intercalations; conglomerates cemented by calcite are also present. Sands mainly consist of dominant quartz, muscovite, feldspars, minor biotite and chlorite, and accessory minerals; calcite is mostly present in the groundmass (SPINELLI, 1964).

The Serravalian sediments probably are more porous than the underlying Langhian formation; thus, the former are the site of aquifers, the latter acts as aquitard. The stratigraphic sections of the numerous wells drilled in the area, indicate that waters are mostly related to the sandy beds. No reliable determinations of the permeability coefficients (k) has been performed on the lithologies of the Serravalian formation; an approximate evaluation performed by MEZZADRI (1978), gives $k \approx 10^{-5}$ m s^{-1}.

2. - ANALYTICAL METHODS

The waters were filtered using 0.45 μm nylon-glass fiber filters and stored in HDPE bottles at 4°C. Temperature, pH and conductivity were determined in the field. Alkalinity was determined by Gran titration (GRAN, 1952) within twelve hours after sampling. Chloride determinations were performed by colourimetric method (mercury (II) thiocyanate and and iron (III) nitrate: Spectroquant Merk 1.14755). Hydrogen and oxygen stable isotope of water were analysed by a FINNIGAN GLF 1086 automatic equilibration device and a DELTA PLUS FINNIGAN mass-spectrometer. Pure hydrogen for δ^2H evaluation was obtained equilibrating directly hydrogen with water at 18°C by means of a catalyser; measurement of δ^{18}O was performed on CO_2 equilibrated with the water at 18°C (EPSTEIN & MAYEDA, 1953). The standard error is within ±0.05‰ for δ^{18}O and ±1‰ for δ^2H. High-salinity waters/brines were previously distilled at 370°C for isotope analyses.

3. - WELLS AND WATER CHEMISTRY

Local denominations of waters are listed in table 1. The Ducale well is located at the NE margin of the Rio Fabbro valley; all the others along the valley. Generally, in the single well, the water is collected from several aquifers, starting from a depth of about 20-70 m to avoid pollution from the surface. The waters exhibit largely variable chemical composition and most of them are sulphide-bearing (tables 2, 3). Moreover, a revision of the data from the literature, suggests that each water has practically maintained very similar composition also for several tens of years. High coefficient of variation is frequently shown by K, Ca and Cl when present in very low amount (< 1 mEq/L); this is probably mostly due to analytical errors. The Purgativa forte water, however, exhibits large variation of Mg values (about 65 mEq/L in 1976 against 31 mEq/L in 1979 and 1991). The Lidia water shows small variation in alkalinity, Ca and Mg (fig. 1) which indicate mixing with Ca-Mg-carbonate water in the past 30 years. This could be due both to small variation of the water pathways at depth or to excessive exploitation for drinking use.

Ducale, Lidia, Magnesiaca and S. Andrea waters have low salinity (< 25 mmole/L), whereas Purgativa leggera, well F12 and purgativa forte are saline to highly saline (546-1064 mmole/L). The Villa Vignali water is more saline than Ducale, Lidia, Magnesiaca and S. Andrea.

Ducale and Lidia are Na-carbonate waters of extreme/nearly extreme composition in having Na/[Na+K+Ca+Mg] ≥ 0.85 and alk/(alk+Cl+SO_4) ≥ 0.80 (as equivalents). The origin of the Na-carbonate waters have been discussed in seve-

Tab. 1 - *Classification of the investigated waters of S. Andrea Bagni and physical conditions of the wells.*
- Classificazione delle acque studiate di S. Andrea Bagni e descrizione delle condizioni fisiche dei pozzi.

Local denomination	**Water type**	**Presumed well depth (m)**	**Depth of catchment (m)**	**Approximate water discharge (L/hour)**
Low-salinity waters				
Ducale	Na/Bicarbonate S(-II)	128	> 22	700
Lidia	Na/Bicarbonate S(-II)	433	> 80 ?	3000-3500
Magnesiaca	Na-Mg/Bicarbonate S(-II)	1		?
Fontechiara	Na-Ca-Mg/Bicarbonate	450	> 70 ?	2800-3500
S. Andrea (nine wells)	from Mg-Na/Bicarbonate to Mg-Ca/Bicarbonate S(-II)	470 (maximum)	> 60-70 ?	12000
Ferruginosa	Na-Ca-Mg/Bicarbonate-Sulphate	60	> 33.5 ?	1300 ?
Intermediate waters				
Villa Vignali	Na/Bicarbonate-Chloride S(-II)	180	?	?
Saline waters				
Purgativa leggera	Na/Chloride ($CaCl_2$)	15	?	20-30
Well F12	Na/Chloride ($CaCl_2$) S(-II)	?	?	very small
High-salinity waters				
Purgativa forte	Na/Chloride ($CaCl_2$)	15	> 12	35

S(-II), sulphide-bearing waters

ral papers (e.g. VENTURELLI *et alii*, 2003). They originated through long-term interaction of common carbonate waters with rocks containing Na-silicate; the process is commonly accompanied by oxygen and carbon dioxide consumption, reduction of sulphur and nitrogen and precipitation of calcite, which proceeds up to nearly complete subtraction of calcium. Figure 2 reports the Na and Cl distribution in the low-salinity waters: Ferruginosa, Magnesiaca waters are characterised by higher Cl content suggesting mixing with very low quantities of chlorine-rich waters. This is also true for the intermediate water from Villa Vignali, which has even more high Cl value (10.3 mEq/L).

Purgativa forte, well F12 and Purgativa leggera are Na-chloride waters of $CaCl_2$-type (i.e.: $Na+K+Mg-Cl < 0$, as equivalents; see table 2) with Na/Cl very close (0.89 ± 0.04, mole ratio) to that of the marine water (0.86). Worldwide, $CaCl_2$ waters and brines (BEIN & DUTTON, 1993) are frequently associated to deposits or surface emissions of hydrocarbons. This is also the case of S. Andrea Bagni and many other places in the northern side of the Apennine and in the Po plain (CONTI *et alii*, 2000), where wells were drilled for hydrocarbons research or to obtain saline waters for curative purposes. As discussed below and in agreement with figure 3, the Purgativa leggera and Purgativa forte waters could represent the product of mixing of low-salinity waters with high-salinity waters/brines of uncertain composition, but located, in any case, along or close to the regression line reported in figure 3.

4. - ISOTOPIC AND CHEMICAL MONITORING

For a period ranging from four to thirteen months, many waters from S. Andrea Bagni have been monitored for oxygen and hydrogen stable isotopes, and for alkalinity, conductivity, chloride and pH. Results are reported in table 3a.
Moreover, during the recent past years, many isotopic analyses have been carried out on other high-salinity waters (Salsomaggiore, Monticelli and Fontevivo, Province of Parma; table 3b) occurring not far from S. Andrea Bagni.

The $\delta^{18}O$ and $\delta^{2}H$ data for the low-salinity waters are reported in figure 4. Their distribution along the precipitation line obtained for Northern Italy (LONGINELLI & SELMO, 2003) indicates a clear meteoric origin. The intermediate water from Villa Vignali, Purgativa leggera and Purgativa forte fall away from this meteoric trend.

Tab. 2 - *Composition of the waters of S. Andrea Bagni and neighbouring localities.*
- Composizione delle acque di S. Andrea Bagni e di località limitrofe.

Well/Spring	Date	pH	Alk	Cl^-	SO_4^{2-}	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+	Salinity	Na+K+	Na/Cl
		at 20°C	mEq/L	mEq/L	mEq/L	mEq/L	mEq/L	mEq/L	mEq/L	mEq/L	(mmole/L)	+Mg-Cl	
S. Andrea Bagni													
Low-salinity waters													
DUCALE	15/10/1992	9,1	10,6	0,31	1,32	12,3	0,06	0,04	0,03	0,011	23,9	12	40
	11/05/1992	9,25	9,70	0,23	1,42	10,3	0,90	0,08	0,03	0,033	22,0	11	45
	16/04/1991	9,15	9,60	0,17	1,35	10,2	0,77	0,08	0,02	0,022	21,5	11	60
LIDIA S	27/03/2001	8,90	8,10	0,31	1,78	7,40	0,04	1,05	1,15	0,064	17,9	8,3	24
	16/09/1998	9,25	7,21	0,22	1,46	8,09	0,02	0,22	0,22	0,078	16,6	8,1	37
	10/10/1996	9,40	7,45	0,24	1,41	8,61	0,03	0,24	0,24	0,000	17,3	8,6	36
	06/06/1994	9,40	7,80	0,32	1,40	9,01	0,04	0,20	0,28	0,050	18,2	9,0	28
	16/04/1991	9,35	7,40	0,23	1,60	8,74	0,04	0,30	0,10	0,028	17,4	8,7	39
	01/03/1978	9,00	8,06	0,34	1,63	8,09	0,06	0,73	0,69	0,057	18,1	8,5	24
FONTE CHIARA	08/08/2002	7,60	5,80	0,28	2,76	3,39	0,08	2,40	2,47	0,078	13,4	5,7	12
	27/03/2001	7,70	5,90	0,21	2,45	3,35	0,07	2,47	2,39	0,128	13,3	5,6	16
	16/09/1998	7,55	5,80	0,25	2,55	3,26	0,07	2,69	2,50	0,133	13,4	5,6	13
	06/06/1994	7,54	5,70	0,31	2,48	3,56	0,09	2,46	2,38	0,089	13,4	5,7	12
	25/05/1987	7,65	6,03	0,28	2,21	3,48	0,14	2,45	2,44	0,116	13,6	5,8	12
	15/10/1982	7,55	6,14	0,27	2,15	3,50	0,09	2,50	2,36	0,103	13,6	5,7	13
MAGNESIACA	18/04/1991	7,80	9,00	2,40	3,33	8,61	0,13	1,58	4,36	0,083	24,9	11	3,6
S. ANDREA (lower well 1)	21/09/1994	7,70	6,80	0,24	2,17	2,80	0,08	2,04	4,56	0,067	14,4	7,2	12
S. ANDREA ("spring" well)	17/10/1994	7,35	6,30	0,59	2,58	2,31	0,09	3,08	4,36	0,094	14,4	6,2	3,9
S. ANDREA (new well 2)	21/09/1994	7,50	7,30	0,21	2,35	2,47	0,08	2,32	4,86	0,094	14,9	7,2	12
S. ANDREA (upper intermediate well 3)	21/09/1994	7,35	8,50	0,21	3,23	1,99	0,12	3,93	5,84	0,022	17,3	7,7	9,4
S. ANDREA (upper well 4)	21/09/1994	7,40	8,70	0,20	3,10	2,11	0,12	3,71	6,11	0,067	17,7	8,1	10,7
S. ANDREA (lower intermediate well 6)	17/10/1994	7,20	8,00	0,21	2,43	1,62	0,11	2,70	6,04	0,072	15,6	7,6	7,7
FERRUGGINOSA	11/05/1992	7,40	6,10	1,92	5,21	4,98	0,14	4,80	3,39	0,072	19,9	6,6	2,6
	16/04/1991	7,40	6,00	2,00	5,62	5,07	0,15	4,91	3,32	0,083	20,2	6,5	2,5
	11/09/1979	7,30	7,15	1,64	6,59	4,85	0,15	4,52	4,29	0,000	21,5	7,6	3,0
Intermediate-salinity waters													
VILLA VIGNALI	30/09/1998	9,17	8,85	8,75	3,91	21,1	0,07	0,12	0,17	0,11	40,9	13	2,4
Saline waters													
PURGATIVA LEGGERA	18/04/1991	7,75	2,10	278	0,12	259	1,28	16,6	12,6	0,67	556	-5,3	0,93
	11/09/1979	8,20	2,45	274	0,35	253	2,17	13,4	14,2	0,42	546	-4,6	0,92
POZZO F12	30/09/1998	7,81	3,36	305	0,22	278	0,68	16,7	13,6	0,0	602	-12	0,91
High-salinity waters													
PURGATIVA FORTE	18/04/1991	7,50	1,80	526	0,04	457	1,53	37,5	31,4	0,83	1021	-36	0,87
	11/09/1979	7,60	1,95	519	0,14	464	2,94	41,8	30,9	0,97	1026	-21	0,89
	14/05/1976	7,55	1,80	552	0,10	459	0,20	33,4	63,2	2,12	1064	-29	0,83
High-salinity waters/brines from neighbouring localities													
SALSOMAGGIORE (1)	30/10/1974	6,71	4,05	2531	2,43	2133	4,48	267	111	10,9	4873	-282	0,84
SALSOMAGGIORE (2)	1974	6,70	4,05	2569	2,86	2142	5,09	284	120	11,6	4935	-301	0,83
FONTEVIVO	02/02/1934	7,7		2693	4,18	2098		356	235	9,3	5097	-360	0,78
MONTICELLI (well 2)	22/04/1938	5,74		2270		1571		374	298	9,8	4187	-401	0,69
MONTICELLI (well 6)	22/04/1938	5,71		2307		1595		373	306	8,8	4251	-406	0,69
MONTICELLI (well 7)	22/04/1938	5,7		2271		1590		357	287	10,7	4194	-393	0,70
MONTICELLI (well 8)	22/04/1938	5,72		2286		1661		333	262	10,1	4255	-363	0,73
MONTICELLI (well 9)	22/04/1938	5,75		2233		1656		313	228	14,9	4175	-349	0,74
VARANO MARCHESI	10/04/1938	6,7		583		421		106	40	14,4	1092	-122	0,72

SO_4^{2-} = total sulphur as SO_4^{2-}; S(-II) = sulphide-bearing waters. Data from: FARRUGGIA *et alii* (1970), and references therein; ARTUSI *et alii* (1977) and references therein; TOSCANI *et alii* (2001);
Terme di S. Andrea Bagni and Spumador Co., internal reports.

Tacking into account the analytical errors, we may state that, in general, the analysed waters are not influenced by the annual isotope variation of the precipitation. In other words, the mean residence time of the waters at depth is in the order of magnitude of several years. Figure 5 reports an example of $\delta^{18}O$ distribution for S. Andrea (spring well) and Lidia as a function of sampling period. Minor isotope variations during the year are observed in Purgativa forte (from July 2003 to January 2004, $\delta^{18}O$ decreases smoothly from 0.86 to 0.53‰). Since the Purgativa forte water is collected at shallow depth, this small variation could be due to evaporation during summer or to slight dilution by autumn/winter precipitation.

Long-term circulation for the investigated waters is also supported by tritium determination which have been carried out on some water samples: Lidia, Fontechiara and S. Andrea (lower well) with 1 ± 1 TU, Purgativa leggera, Purgativa forte and Magnesiaca with 2 ± 1 TU (Laboratory of Isotopic Geochemistry, Department of Earth, Environmental and Marine Sciences, University of Trieste); moreover, the well F12 gave a value of 0.05 ± 0.02 TU (Institute of Geological and Nuclear Sciences, Lower Hutt, New Zeeland). In the Reno river (Bologna), not far from the area of our interest, the tritium concentration was higher than about 70 TU during 1972-1973 (Carlin *et alii*, 1975); assuming that these values approximate the concentration in precipitation at that time, the present-day values would be 12-13 TU. These

Tab. 3 - *a) Chemical and isotope data of the S. Andrea Bagni waters; b) strongly saline waters from neighbouring areas.* - a) Dati chimici e isotopici delle acque di S. Andrea Bagni e b) delle acque estremamente saline di aree limitrofe.

a)

Waters	Sampling period for chemical parameters	N° of data	pH	Cond µS cm^{-1}	Alk mEq/L	Cl$^-$ mEq/L	Sampling period for oxygen and hydrogen stable isotopes	N° of data	$\delta^{18}O$ V-SMOW ‰	δ^2H V-SMOW ‰
Low-salinity waters										
Ducale	07/2003-01/2004	7	8.8±0.4	935±15	10.13±0.03	0.404±0.006	02/2003-01/2004	12	-9.70±0.01	-65.9±0.7
Lidia	07/2003-01/2004	7	8.5±0.2	776±19	7.47±0.10	0.480±0.045	01/2003-01/2004	13	-10.50±0.04	-72.1±0.7
Magnesiaca	07/2003-01/2004	7	(6.5±0.8)	1408±43	9.23±0.08	6.29±0.40	07/2003-01/2004		-9.35±0.08	-63.1±1.5
Fontechiara	07/2003-01/2004	7	7.1±0.2	671±5	5.90±0.08	0.333±0.008	02/2003-01/2004	12	-9.90±0.02	-67.6±0.7
S. Andrea (lower well)	07/2003-01/2004	7	7.2±0.1	679±6	6.46±0.03	0.333±0.003	02/2003-01/2004	12	-9.55±0.02	-64.5±0.5
S. Andrea (spring well)	07/2003-01/2004		7.2±0.1	678±5	5.88±0.05	0.347±0.008	02/2003-01/2004	12	-9.77±0.02	-66.2±0.7
Ferruginosa	07/2003-01/2004	7	6.9±0.2	993±18	6.38±0.08	1.23±0.08	07/2003-01/2004	7	-9.60±0.02	-65.8±1.0
Intermediate waters										
Villa Vignali	10/2003-01/2004	4	8.9±0.1	1891±23	8.78±0.03	10.3±0.2	01/2003-01/2004	13	-9.50±0.02	-65.9±0.7
Saline waters										
Purgativa leggera	07/2003-01/2004	7	7.9±0.3	21,740±1070	2.41±0.16	295.7±10.2	07/2003-01/2004	7	-4.99±0.10	-45.8±1.4
High-salinity waters										
Purgativa forte	07/2003-01/2004	7	7.2±0.2	39,700±910	1.90±0.05	574.5±14.4	07/2003-01/2004	7	0.76±0.12	-21.2±1.5

Cond = specific conductivity; **Alk** = total alkalinity; ±, standard deviation; ( ), less reliable data depending on abundant presence of *Beggiatoa* in the water pool.
Standard error for $\delta^{18}O$ and δ^2H is 0.05 ‰ and 1 ‰ respectively. Isotope analyses for Purgativa forte and Purgativa leggera have been performed on samples of water previously distilled at 370°C.

b)

Localities	Sampling period	Depth (m)	N° of data	$\delta^{18}0$ (‰) V-SMOW	$\delta^{2}0$ (‰) V-SMOW
Fontevivo	06/02/2003 (*)	≈980	1	4.68	-14.6
Monticelli (well 10)	12/2002-12/2003	135	12	-0.30 ± 0.31	-10.4 ± 1.0
Monticelli (well 13)	01/2003-12/2003	192	11	-0.22 ± 0.20	-9.30 ± 1.32
Salsomaggiore (well 8)	03/2001-005/2002 (*)	989	21	10.19 ± 0.65	-13.3 ± 2.7
Salsomaggiore (well 21)	05/06/2003-19/06/2003 (*)	601	20	11.96 ± 0.21	-13.2 ± 1.5
Salsomaggiore (well 27)	05/06/2003-19/06/2003 (*)	1258	22	10.19 ± 0.23	-13.0 ± 1.6

(*) Including periods of water pumping; ±, standard deviation. Data are obtained on samples previously distilled at 370°C.

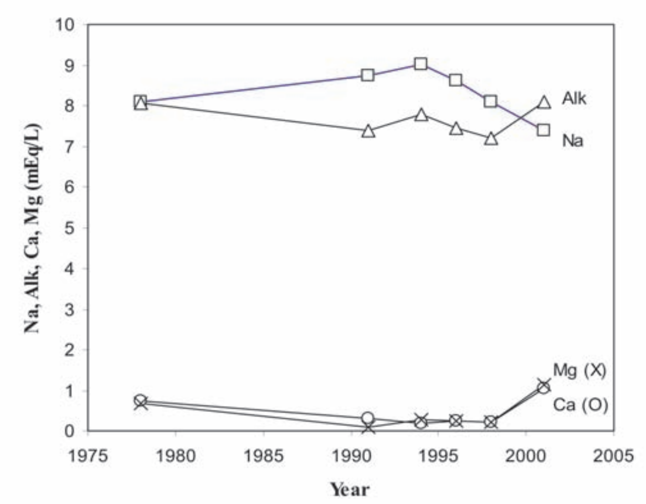

Fig. 1 - Lidia water: variation in time of the chemical composition. From 1998 to 2001, Ca, Mg and alkalinity (Alk) (mEq/L) increase indicating some mixing of the Na water with Ca-Mg waters.
- Sorgente Lidia: variazione della composizione chimica nel tempo. Dal 1998 al 2001, Ca, Mg e alcalinità (Alk) (mEq/L) aumentano indicando l'esistenza di un mixing *tra l'acqua sodica e le acque Calcio-Magnesiache.*

concentrations are much higher than those found in the investigated waters. Reasonably, the tritium characters indicate an average time of water infiltration higher than about 40 years, i.e. before the tritium climax related to the atomic weapon experiments in the atmosphere. This age contrasts with the estimates reported in previous technical reports (e.g. MEZZADRI, 1978).

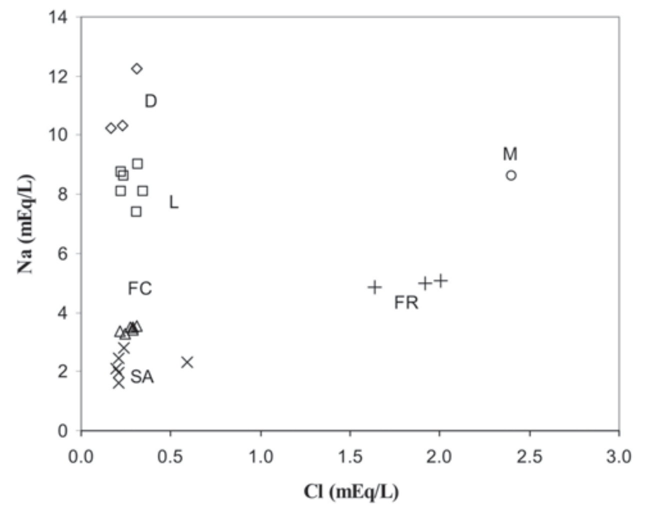

Fig. 2 - Distribution of Na and Cl in the low-salinity waters of S. Andrea Bagni. D = Ducale, L = Lidia, FC = Fontechiara, SA = S. Andrea, FR = Ferruginosa, M = Magnesiaca (cf. table 2).
- Distribuzione di Na e Cl nelle acque a bassa salinità di S. Andrea Bagni. D = Ducale, L = Lidia, FC = Fontechiara, SA = S. Andrea, FR = Ferruginosa, M = Magnesiaca (cf. tabella 2).

4.1. - MIXING OF LOW-SALINITY WITH HIGH-SALINITY WATER-BRINES

In figure 6 isotopic data for intermediate to high-salinity waters from S. Andrea Bagni are compared with high-salinity waters from neighbouring areas (Salsomaggiore, Fontevivo and Monticelli in the Province of Parma). The Purgativa forte and Purgativa leggera waters and the water from Villa Vignali are very well aligned suggesting variable mixing with waters with isotopic characteristics located along this line at values major or equal to those which characterize the Purgativa forte water. We will test the hypothesis that they are intermediate between low-salinity waters and strongly saline waters of Salsomaggiore ($\delta^{18}O \cong 10.8‰$ and $\delta^{2}H \cong -13.2‰$, averages)-Monticelli ($\delta^{18}O \cong -0.27‰$ and $\delta^{2}H \cong -9.9‰$, averages) types.

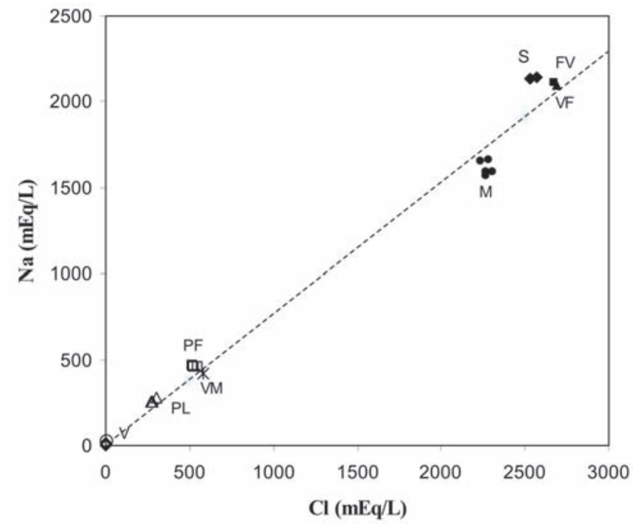

Fig. 3 - Distribution of Na and Cl in the intermediate to high-salinity waters of S. Andrea Bagni and neighbouring areas. S. Andrea Bagni: V = Villa Vignali, PL = Purgativa leggera, PF = Purgativa forte; the low-salinity waters essentially coincide with the origin of the diagram. Neighbouring localities: VM = Varano Marchesi, M = Monticelli, VF = Vicofertile, FV = Fontevivo, S = Salsomaggiore. The regression line is referred to all data: Na = 0.76 x Cl + 9.9, R = 0.996.
- Distribuzione di Na e Cl nelle acque con salinità da intermedia ad alta di S. Andrea Bagni e aree limitrofe. S. Andrea Bagni: V = Villa Vignali, PL = Purgativa leggera, PF = Purgativa forte; le acque a bassa salinità cadono all'origine del diagramma. Località limitrofe: VM = Varano Marchesi, M = Monticelli, VF = Vicofertile, FV = Fontevivo, S = Salsomaggiore. La retta di regressione che considera tutti i dati è la seguente: Na = 0.76 x Cl + 9.9, R = 0.996.

The intercept between the line (1) and (2) and between the lines (2) and (3) (fig. 6) of coordinates $\delta^{18}O \cong -10.1‰$, $\delta^{2}H \cong -69.2‰$ and $\delta^{18}O \cong 3.22‰$, $\delta^{2}H \cong -10.9‰$, respectively, define potential low-salinity and high-salinity end-members for the mixing. Taking into consideration these data and the average $\delta^{18}O$ values for the analysed

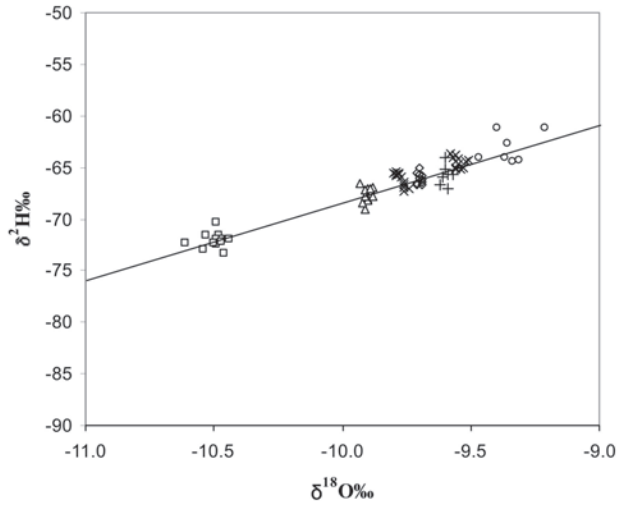

Fig. 4 - Oxygen and hydrogen isotopes in low-salinity waters. Square = Lidia, triangle = Fontechiara, X = S. Andrea (spring well, with low $\delta^{18}O$; lower well, with high $\delta^{18}O$), diamond = Ducale, cross = Ferruginosa, circle = Magnesiaca. For these waters, the regression line $\delta^2H = 7.73\ \delta^{18}O + 9.10$, (R = 0.914) is very similar to the one obtained for precipitations in Northern Italy: $\delta^2H = 7.71\ \delta^{18}O + 9.40$ (LONGINELLI & SELMO, 2003).
- Isotopi dell'ossigeno e dell'idrogeno nelle acque a bassa salinità. Quadrato = Lidia, triangolo = Fontechiara, X = S. Andrea (emergenza pozzo con basso $\delta^{18}O$; pozzo in profondità con alto $\delta^{18}O$), rombo = Ducale, croce = Ferruginosa, cerchio = Magnesiaca. Per queste acque, la retta di regressione $\delta^2H = 7.73\ \delta^{18}O + 9.10$, (R = 0.914), è molto simile a quella ottenuta per le precipitazioni dell'Italia settentrionale: $\delta^2H = 7.71\ \delta^{18}O + 9.40$ (LONGINELLI & SELMO, 2003).

waters, the contribution of the high-salinity end-member to Vignali, Purgativa leggera and well F12, and Purgativa forte is about 5%, 39% and 82%. A similar estimation has been performed by using the conservative element Cl. The average content at Monticelli and Salsomaggiore (about 2412 mEq/L of Cl) has been used for the high-salinity end-member; for the low-salinity component the Cl content has been practically assumed to be zero. The mass balance calculation gives in this case < 1%, 13% and 24% for Vignali, Purga-tiva leggera and well F12, and Purgativa forte, respectively. Because of the large disagreement between the two sets of results, the hypothesis of mixing with waters having chemistry and isotopic features similar to those from Salsomaggiore and Monticelli must be disregarded. For a main chemical composition corresponding to the average Salsomaggiore-Fontevivo-Monticelli, extrapolation along the straight line (2) (fig. 6) gives $\delta^{18}O \cong 11‰$ and $\delta^2H \cong 23‰$. Unfortunately, the isotopic data reported in the literature for brackish waters/brines of the Po plain and Apennine piedmont are very scarce and the hydrogen data are mostly lacking. It is noteworthy, however, that in the literature waters with $\delta^{18}O$ around 10‰ and, contemporaneously, δ^2H around 20‰ have not been yet found (see data reported in CONTI *et alii*, 2000). Thus we may conclude that the mixing occur with high-salinity waters similar to Purgativa forte or with more saline, not-sampled waters of undefined composition, but, in any case, plotting close to line (2) and Na-Cl line of figure 3.

4.2. - CLIMATIC MICROVARIATIONS

Ground waters of low salinity which remain for long time at depth reflect time-averaged values of precipitation; thus, comparison of ground waters with long-term averaged precipitation may potentially furnish indication of climatic variations in the catchment area (ROZANSKI *et alii*, 1997). In our case, the lack of annual variation in the isotopic composition of all the waters investigated at S. Andrea Bagni must indicate complete mixing of groundwaters derived from precipitation of several years.

Unfortunately, data on precipitation along the northern Apennines watershed down to the piedmont areas of our interest are very scarce in time and space because of the low number of sampling sites and only recently sampled. The only stations which have some relevance for our considerations are S. Pellegrino in Alpe (close to the Apennine watershed) and Parma. They, however, are not necessarily representative of precipitation in the whole area of interest. Moreover, data for Parma are only available from 1995 to 2004 and for S. Pellegrino in Alpe from 1993 to 1999, and also data related to rivers and mountain springs are very few and randomly collected.

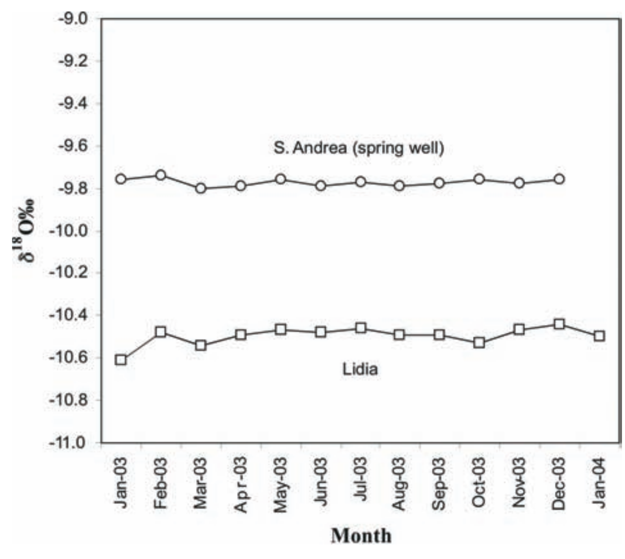

Fig. 5 - Oxygen isotope distribution in the Lidia and S. Andrea ("spring" well) waters during the period January 2003- January 2004.
- Distribuzione degli isotopi dell'ossigeno nelle acque Lidia e S. Andrea (pozzo "sorgente") nel periodo Gennaio 2003- Gennaio 2004.

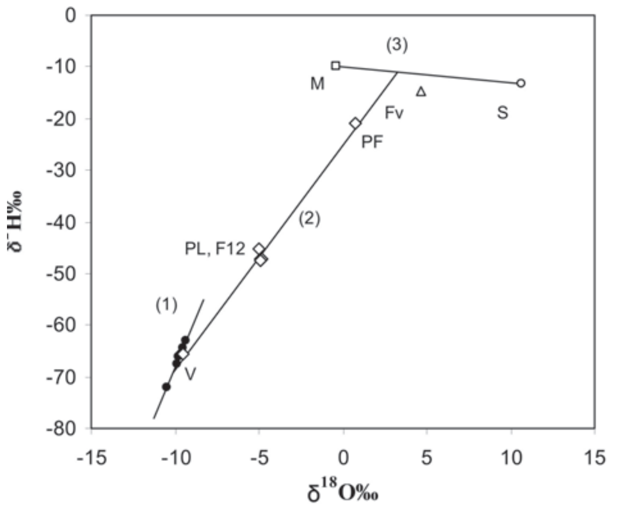

Fig. 6 - Oxygen and hydrogen isotope distribution in the investigated waters from S. Andrea Bagni (filled circle) and in high-salinity waters from neighbouring localities. V = Villa Vignali, PL = Purgativa leggera, well F12, PF = Purgativa forte, M = Monticelli, S = Salsomaggiore, FV = Fontevivo. (1), (2) and (3) refer to regression lines: (1) $\delta^2H = 7.84\ \delta^{18}O + 10.2$; (2) $\delta^2H = 4.37\ \delta^{18}O - 25.0$; (3) $\delta^2H = -0.298\ \delta^{18}O -9.98$.

- Distribuzione degli isotopi dell'ossigeno e dell'idrogeno nelle acque di S. Andrea Bagni (cerchio nero) e nelle acque ad elevata salinità delle località limitrofe. V = Villa Vignali, PL = Purgativa leggera, well F12, PF = Purgativa forte, M = Monticelli, S = Salsomaggiore, FV = Fontevivo. (1), (2) and (3) si riferiscono alle rette di regressione: (1) $\delta^2H = 7.84\ \delta^{18}O + 10.2$; (2) $\delta^2H = 4.37\ \delta^{18}O - 25.0$; (3) $\delta^2H = -0.298\ \delta^{18}O -9.98$.

The annual averages for precipitation of Parma varied largely during the last years depending on the variable relationship between the amount of precipitation and its isotopic values; for instance, starting from 1995, the lowest and highest annual mean $\delta^{18}O$ was -10.2‰ in 2003 and -6.5‰ in 2000 (LONGINELLI & SELMO, 2003; ANGLESIO, 2004) and the overall average $\delta^{18}O$ much lower that that reported in LONGINELLI & SELMO (2003). Due to these large variations, comparison between recent precipitation and old ground waters to obtain indication on climatic changes could be only done when data on precipitation are collected for many years; unfortunately, this is not the case of Parma. Nonetheless, some approximate inferences may be carried out also using the available data. Mobile weighted average $\delta^{18}O$ for the monthly precipitation at the Parma station (data from 1995 to 2004) gives practically a constant value of $\delta^{18}O$ for at least one year if the period of the mobile average is higher than four years. Assuming that this period is approximately valid for all the S. Andrea catchment area, we can conclude that only climatic microvariations of the order of many years could be recognized using the investigated waters from S. Andrea Bagni.

For the station of Parma, the mobile average with a period of four years gives $\delta^{18}O$ values ranging about from -7.5‰ to -8.9‰. Moreover, as inferred from the characteristics of rapid-flow springs occurring SW of the Apennine ridge along the line S. Pellegrino-Castelnuovo Garfagnana (Serchio valley; MUSSI *et alii*, 1998), the precipitation at different elevation exhibit the approximate trend $\delta^{18}O \cong [(-1.57\pm0.08)\ z - (6.13\pm0.09)]$‰ (R = 0.987), where ± denotes the standard error, R is the correlation coefficient and z the inferred average altitude in km of the catchment areas: for the elevation of the Apennine ridge the calculated $\delta^{18}O$ is higher than about -9.2‰. Surprisingly enough all the isotope data on local precipitation are higher than those which characterize several S. Andrea Bagni waters.

Summarizing, we may tentatively state that, on the basis of the available data, a comparison between recent precipitation and the long-term circulating waters at depth cannot give reliable quantitative estimation of climate microvariations since the data on precipitation are too uncertain. However, very probably, the S. Andrea waters with the lowest $\delta^{18}O$ values (e.g. Lidia with average $\delta^{18}O$ = -10.5‰) infiltrated during a period which, on average, was colder than the last ten years.

5. - CONCLUSIONS

The waters of S. Andrea Bagni, commonly well drawn, exhibit a strongly variable composition. The Na-carbonate type is dominant among the low-salinity waters, whereas saline and high-salinity waters are of the Na-chloride and $CaCl_2$-bearing type.

The water chemical composition remains constant or changes only slightly during the years indicating long-term circulation at depth.
This is in agreement with the oxygen and hydrogen stable isotope as well as the tritium content, which indicate that the low-salinity waters represent meteoric precipitation which infiltrated some tens of years before present (probably more than forty years).

The origin of the saline/high-salinity waters is more complex. They probably represent the product of mixing between more saline waters and the low-salinity types. However, both chemical and isotopic compositions exclude the possibility that the saline/high-salinity waters of S. Andrea Bagni are generated by mixing with waters comparable the high-salinity waters occurring at Salsomaggiore, Monticelli and Fontevivo.

In the area of interest, isotopic data on precipitation are very scarce; thus comparison with underground waters with the aim of obtaining indications on possible climatic microvariations is risky. It is noteworthy, however, that some low-salinity waters (e.g. Lidia) exhibit average delta values lower than those found till now in the precipitation of the Emilia region; that is in agreement with infiltration during slight different climatic conditions. However, more chemical and isotope data on precipitation and river waters are needed to obtain a reliable picture of the relationships between surface and underground waters in the investigated area.

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