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Hydrogeochemistry and extrapolation of end members in a mixed thermal water system, Vals, Switzerland

By FRANÇOIS-D. VUATAZ¹⁾, JEAN-F. SCHNEIDER²⁾, FELICE C. JAFFÉ³⁾
and EMANUEL MAZOR⁴⁾

ABSTRACT

A multisampling program has been carried out over two hydrologic cycles for seven different sources of water in the Vals thermal area, eastern Switzerland. Artesian thermal water flows out of a thrust-sliced area consisting of gypsum-bearing dolomites, and spreads into postglacial sediments filling the valley. The groundwaters sampled are Ca-SO₄ dominated (SO₄ = 200–1000 mg/l) and have temperatures of 8°–30 °C, both parameters varying with the well depths (10–96 m) and with time.

A correlation of oxygen-18 with SO₄ has been observed, indicating that the freshest and coldest water originates from the highest elevations, while the most mineralized and warmest water is recharged at lower elevations. Tritium concentration is negatively correlated to mineralization and temperature, yielding for mixing of thermomineral and cold fresh waters.

Seasonal variations have been recorded throughout the hydrologic cycle and have been attributed to the recharge-discharge system of the shallow aquifer and to variable pumping rates of the producing wells.

Mixing calculations based on mineralization variations as a function of pumping rate, tritium and oxygen-18, have been applied to deduce extrapolated values for an inferred deep warm and mineralized end member. According to the model and to the local temperature increase with depth, the drilling of a relatively deep well could tap Ca-SO₄-bearing thermal water with a maximum temperature of 42 °C and total dissolved solids of 2700 mg/l.

ZUSAMMENFASSUNG

Im Valser Thermengebiet (Graubünden, Schweiz) wurde während zweier hydrologischer Zyklen für sieben verschiedene Wässer ein hydrogeochemisches Untersuchungsprogramm durchgeführt. Das artesische Thermalwasser stammt aus einer stark zerscherten Überschiebungszone, die hauptsächlich aus gipshaltigen Dolomiten besteht, und fliesst in der postglazialen Talfüllung aus. Die Grundwasserproben werden durch Ca-SO₄ dominiert (SO₄ = 200–1000 mg/l) und haben Temperaturen von 8° bis 30 °C. Beide Werte hängen von der Brunntiefe (10–96 m) und der Zeit der Probenahme ab.

Ein beobachteter Zusammenhang zwischen Sauerstoff-18- und SO₄-Gehalt weist darauf hin, dass das am schwächsten mineralisierte und kälteste Wasser sein Einzugsgebiet in den grössten Höhen hat, während das mineralreichste und wärmste Wasser von geringeren Höhen stammt. Die Tritiumkonzentra-

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tion nimmt mit steigender Mineralisation und zunehmender Temperatur ab, was auf eine Mischung von warmen, mineralisierten Wässern mit kalten Oberflächenwässern hindeutet.

Die jahreszeitlichen Schwankungen, die während des hydrologischen Zyklus registriert wurden, konnten mit Änderungen des Wasserhaushalts des oberflächennahen Grundwasserleiters und mit unterschiedlichen Pumpraten der Förderbrunnen erklärt werden.

Mischungsrechnungen, die die Mineralisation als Funktion der Pumpraten und des Tritium- und Sauerstoff-18-Gehalts berücksichtigen, wurden dazu benutzt, geochemische Daten des in grösserer Tiefe vermuteten unvermischten Thermalwassers abzuschätzen. Aufgrund dieser Mischungsmodelle und der örtlichen geothermischen Tiefenstufe dürfte mit einer neuen tieferen Bohrung ein Ca-SO_4 -Wasser mit einer maximalen Temperatur von 42°C und einer Gesamtmineralisation von 2700 mg/l erschlossen werden können.

RÉSUMÉ

Sept types d'eau différents ont été échantillonnés au cours de deux cycles hydrologiques, à Vals (Grisons, Suisse). De l'eau thermale artésienne s'écoule d'une zone écaillée consistant principalement de dolomies gypsifères et se répand dans des sédiments postglaciaires remplissant la vallée. Les eaux souterraines échantillonnées sont à dominante Ca-SO_4 ($\text{SO}_4 = 200\text{--}1000\text{ mg/l}$) et atteignent des températures de 8° à 30°C , paramètres qui varient avec la profondeur des puits ($10\text{--}96\text{ m}$) et avec la période d'échantillonnage.

Une corrélation entre l'oxygène-18 et le SO_4 est décrite, montrant que les eaux les plus diluées et froides proviennent de l'altitude la plus élevée, alors que l'eau la plus minéralisée et chaude est originaire d'une zone de recharge à plus basse altitude. La concentration en tritium est négativement corrélée à la minéralisation ainsi qu'à la température, indiquant la présence d'un mélange entre l'eau thermominérale et les eaux diluées et froides.

Des variations saisonnières des caractéristiques de l'eau thermominérale ont été observées au cours du cycle hydrologique et ont été attribuées au système de recharge et vidange de l'aquifère superficiel ainsi qu'aux débits variables de pompage dans les puits de production.

Un modèle de mélange a été élaboré, basé sur les variations de la minéralisation en fonction des débits de pompage, du tritium et de l'oxygène-18, et a permis de déduire par extrapolation les caractéristiques de la composante chaude et minéralisée du mélange. Selon ce modèle et l'augmentation locale de la température avec la profondeur, le forage d'un nouveau puits plus profond permettrait de capter une eau thermale de type Ca-SO_4 dont la température maximum serait de 42°C et la minéralisation totale maximum 2700 mg/l .

1. Introduction

Vals is located in the canton of Graubünden, eastern Switzerland. The Vals valley, which is about 25 km long and has a north-south orientation, is perpendicular to the upper Rhine river valley. Thermal waters have been known and utilized at least since the 12th century, as recorded in old documents (WINTERHALTER 1945). Several shallow hand-dug catchments and wells were made in the past, to improve the temperature, discharge and quality of the thermal water.

Since the 1960's, a thermal spa and a mineral water bottling plant in Vals are using the Ca-SO_4 thermomineral water tapped from two production wells, namely Lower well and Upper well (Fig. 1). In the last years, more thermal water has been required and recently an exploration well has been drilled, called New well, which has given promising results.

The present study is part of a broader research project carried out on 19 thermal areas from Switzerland and adjacent alpine regions (VUATAZ 1982 and 1983). Its purpose is to acquire a better knowledge of the low enthalpy geothermal potential of Switzerland and to define the geochemical and hydrologic properties of the deep thermal systems (JAFFÉ et al. 1981).

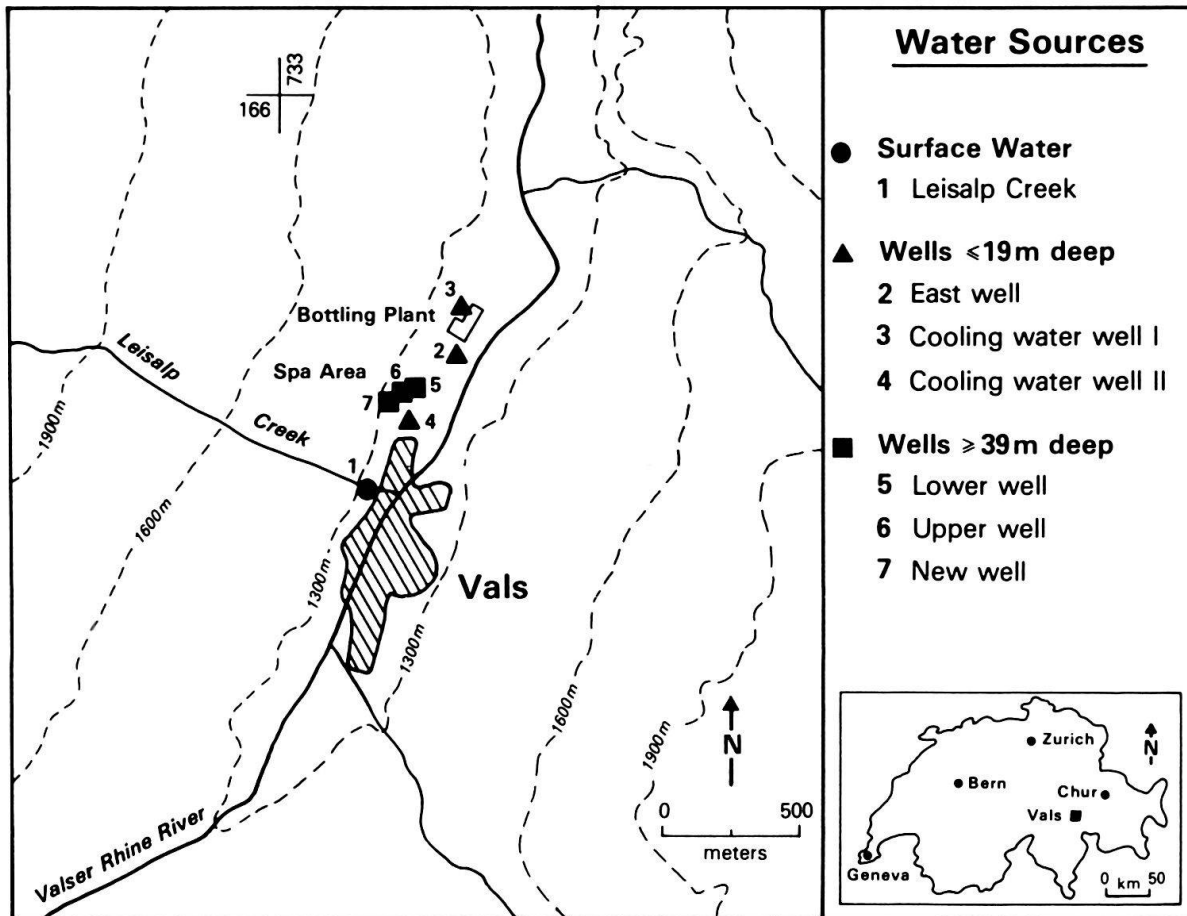


Fig. 1. Sampling points location in Vals.

The geochemical study of Vals thermal water system began with a multisampling and multitracing program (MAZOR 1976), carried out on the two existing production thermal wells, over a complete hydrologic cycle by eight sampling dates (VUATAZ 1978). At a second stage, additional detailed sampling of the different water sources was executed (VUATAZ 1980a). In 1981, after the drilling of the New well, a third series of samples was collected (SCHNEIDER 1981) and recently, the New well has been sampled again (Valser St. Petersquelle AG, 1982, written communication).

This geochemical study included the sampling of seven different water sources: surface water (Leisalp Creek), shallow cold water wells (East well, Cooling water well I and Cooling water well II) and thermal water wells (Lower well, Upper well and New well). Five wells are now used either by the Valser bottling company or by the thermal spa (Fig. 1), while the East well has been abandoned since October 1981.

2. Geologic and hydrologic setting

Vals is situated at the boundary between Adula and Bündnerschiefer overthrusts, in the Penninic belt of the Alps. In this area, the Adula overthrust is mainly composed of successive gneiss, micaceous schist and Triassic dolomite outliers.

North of this, a thrust-sliced zone formed by the Bündnerschiefer overthrust, is composed of calcareous shales, marbles, serpentines, dolomites and gneiss, piled into a series called the Vals thrust slices (NABHOLZ & VAN DER PLAS, 1967). A few kilometers north of Vals, the Adula overthrust is overlain by the Bündnerschiefer.

At the village of Vals, the bottom of the valley is filled by more than 80 m of moraine, postglacial alluvium and landslide deposits (KAPP & MÜLLER 1968a). Several mountain creeks that originate mainly from snowmelt, flow down on both sides of the valley into the Valser Rhine river. A shallow single or multilayered aquifer contained in the valley-bottom sedimentary fill is fed by these various streams. Some parts of the valley fill do not contain groundwater, while others are very permeable (3×10^{-4} m/s) and have a good yield (KAPP & MÜLLER 1968b). Several shallow wells were drilled in these sandy sediments and have been used as water supply wells for the village community and as cooling or rinsing water in the bottling plant.

The thermomineral water flows out of the bedrock, of Triassic dolomites, on the west flank and possibly also from the bottom of the valley. The thickness of the Quaternary sedimentary fill reaches at least 82 m in the west side and probably much more in the middle of the valley. Thermal water spreads up into this formation and mixes to various degrees with the shallow cold groundwater. Due to the complex thrust-sliced tectonics, the thermal water emergence should most probably be located along several bedrock fault swarms.

3. Main characteristics of the waters

Chemical parameters

All the groundwaters sampled at Vals have a common chemical feature (Table 1): the two main dissolved ions are SO_4 and Ca (Fig. 2), while the creek water is Ca- HCO_3 dominated (VUATAZ 1982). For the thermal water, Ca and SO_4 represent about 80% of the total dissolved ions. The second major cation and anion are Mg and HCO_3 . This water is very poor in alkaline cations and Cl.

All groundwaters, deep or shallow, seem to have a similar chemical pattern as shown in Figure 2. This may indicate that the uprising thermal water spreads into the recent sedimentary fill of the valley and mixes with the local cold groundwaters, even the shallowest ones (East well). The mixing pattern is further evident by the linear correlation of Ca, Mg, Na, Sr, HCO_3 , F, SiO_2 and Total Dissolved Solids (TDS) with SO_4 (Fig. 3).

It is not possible to calculate the deep reservoir temperature by chemical geothermometry, since the main dissolved mineral is gypsum and the concentration of alkaline cations like Li, Na and K is too low. Due to the absence of silicate rocks and to the dilution with fresh groundwaters, the silica content is also low and probably does not reach equilibrium with quartz or other silica phases (FOURNIER, in RYBACH & MUFFLER, 1981). As a matter of information, the highest analyzed silica content is 24 mg/l (Upper well) and gives a subsurface minimum temperature of 39 °C according to the chalcedony geothermometer, probably the only silica geothermometer which may be used for lukewarm water reservoirs.

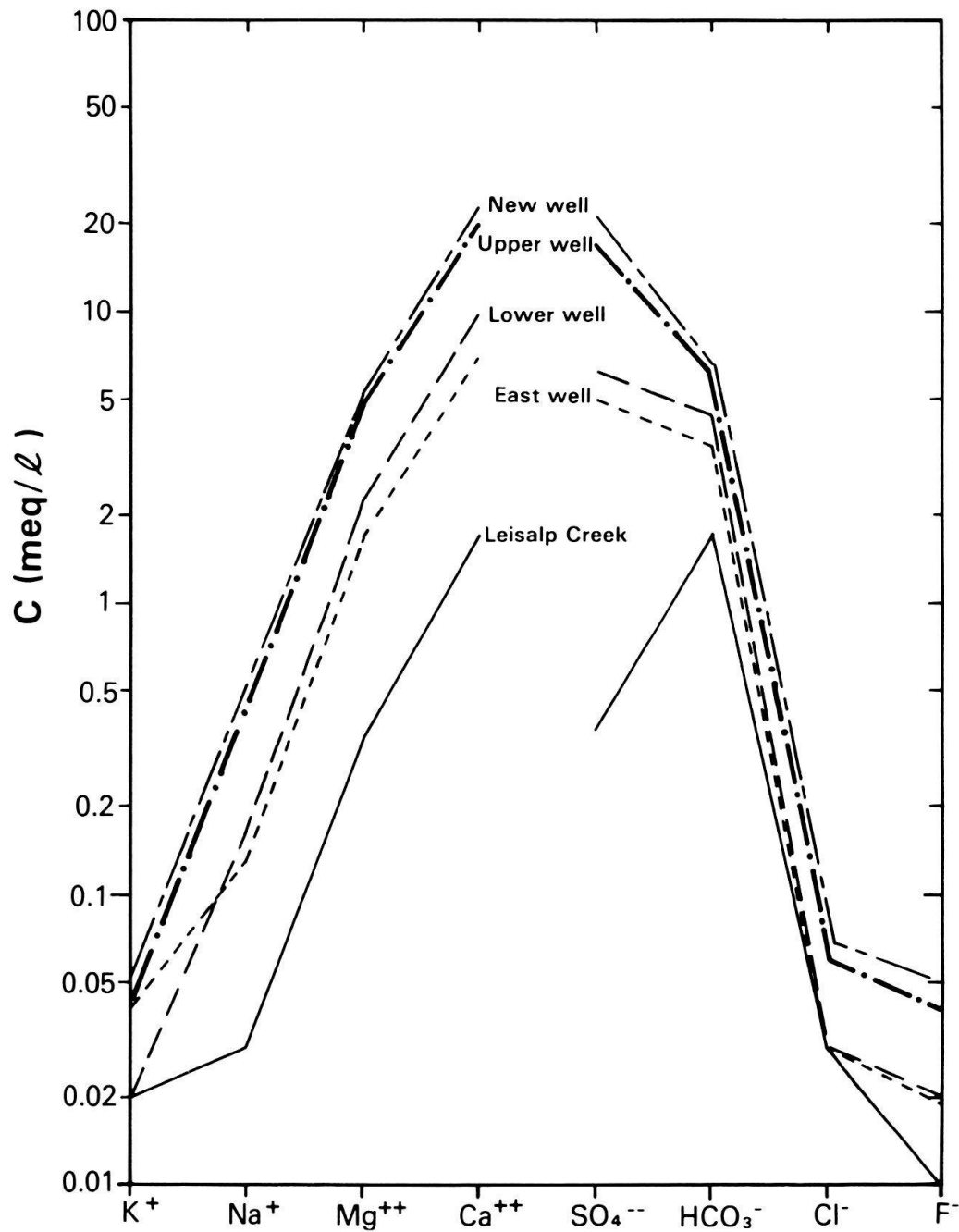


Fig. 2. Ionic composition diagram of the different types of water in Vals. From top to bottom, three thermal water production wells, one shallow groundwater and one surface water. All the samples were collected in November 1979 except the New well in April 1981. A mixing pattern is seen between mineralized and dilute waters.

Physical parameters

The mean annual air temperature for Vals at an elevation of 1250 m.a.s.l. should be $6 \pm 0.5^\circ\text{C}$, as computed from various mean air temperatures in other alpine areas (Annalen der Schweizerischen Meteorologischen Anstalt). From this value, one can estimate the normal average temperature of the shallow cold groundwater to be 1–

TABLE 1

Chemical, physical and isotopic parameters of the waters in Vals [chemistry was analyzed by F. D. Vuataz (1977-78-79) and by the Chemisches Laboratorium des Kantons Graubünden (1981-82); isotopes were analyzed by the Institute of Physics, University of Bern, the Institute of Radiohydrometry, Neuhenberg, West Germany (1977-78), and by the Weizmann Institute of Science, Rehovot, Israel (1979-81)].¹

Date	Leisalp creek					East well (10 m deep)			Cooling water well I (10 m deep)			
	11.1979	8.1977	10.1977	5.1979	8.1979	5.1979	8.1979	11.1979	4.1981	5.1979	11.1979	8.1979
Ca ⁺⁺ (mg/l)	33.1	33.8	40.8	42.6	37.6	109	126	139	189	209	205	
Mg ⁺⁺ "	4.02	3.89	3.69	2.75	3.89	15.6	16.6	20.1	24.0	26.5	26.0	
Na ⁺ "	0.63	0.43	0.46	0.35	0.63	2.53	2.63	2.94	4.20	3.88	3.44	
Sr ⁺⁺ "	0.25	0.12	0.17	0.22	0.33	2.09	2.29	2.58	3.41	3.74	3.62	
K ⁺ "	0.85	0.74	0.94	0.89	0.81	1.59	1.56	1.43	4.41	3.46	3.35	
Li ⁺ "	0	0	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.02	0.02	
SO ₄ ⁻⁻ "	18	16	15	8	19	170	210	240	63.6	300	330	338
HCO ₃ ⁻ "	103	104	117	129	123	183	190	213	165	265	278	262
Cl ⁻ "	1.15	2.5	2.5	1.33	1.24	1.33	1.60	1.15	0.88	6.03	3.99	5.14
F ⁻ "	0.21			0.11	0.14	0.32	0.35	0.39	0.28	0.33	0.29	
Total cations (meq/l)	2.04	2.05	2.39	2.40	2.25	6.92	7.86	8.81	11.78	12.95	12.69	
Total anions (meq/l)	2.11	2.11	2.30	2.32	2.45	6.59	7.55	8.54	10.77	11.56	11.49	
SiO ₂ (mg/l)	3.83	4.37	2.0	2.68	2.68	7.65	9.75	9.82	8.57	7.65	8.04	
TDS (mg/l) ²	165	166	183	188	189	493	561	630	805	867	855	
Temperature (°C)	6.2	10.2	7.5	8.3	8.3	10.0	10.9	10.9	8	8.6	16.5	10.1
pH	8.57	8.10	8.35	8.45	8.40	7.40	7.48	7.45	7.50	7.25	7.15	7.25
Discharge (l/min)	1500			1200	720	500	500	500	500	500	500	
Water level (m) ³						1.5	1.5		4.5		4.4	
δ ¹⁸ O (°/‰)	-13.9			-14.2	-13.9	-13.1	-13.5	-13.4	-13.9	-13.2	-13.3	
δ ² H (°/‰)	-96.0			-97.3	-95.3	-91.3	-95.7	-101	-94.0	-102	-96.8	
δ ³ H (TU)	107			94	104	82	83	80	76	72	79	81

TABLE 1 (cont.)

Date	Cooling water well II (19 m deep)				Lower well (39 m deep)												
	8.1979	5.1979	4.1981	11.1979	202	185	190	185	206	202	205	217	236	236	7.1978	3.1978	4.1981
Ca ⁺⁺ (mg/l)	105	106		250	202	185	190	185	206	202	205	217	236	236	230		
Mg ⁺⁺	5.10	5.10		30.3	26.6	24.3	24.8	26.6	26.1	25.2	26.4	26.9	30.9	30.3	32.5		
Na ⁺	9.45	9.61		5.11	3.61	3.09	3.09	3.24	3.13	3.31	3.66	4.16	4.35	4.54	4.34		
Sr ⁺⁺	1.31	1.24		5.06	4.03	3.72	3.72	3.87	3.95	3.97	3.98	4.58	5.49	4.95	5.61		
K ⁺	1.75	1.66		1.18	0.90	0.92	0.94	0.70	0.90	1.06	0.94	1.00	1.04	1.02	1.01		
Li ⁺	0.01	0.01		0.02	0.02	0.02	0.02	0.02	0.01	0.02	0.01	0.02	0.02	0.02	0.02		
SO ₄ ⁻⁻	100	105	402	438	300	320	320	340	340	363	390	400	450	450	460	713	
HCO ₃ ⁻	221	220	284	299	267	255	259	278	268	256	268	259	277	287	276	339	
Cl ⁻	9.22	10.6	2.02	3.19	1.15	3.5	3.0	3.5	3.5	1.15	1.75	0.89	1.75	2.5	1.75	1.86	
F ⁻	0.33	0.33		0.58	0.37	0.36		0.34		0.37		0.40	0.28	0.29			
Total cations (meq/l)	6.15	6.20		15.34	12.54	11.48	11.77	11.67	12.67	12.42	12.68	13.35	14.66	14.61	14.50		
Total anions (meq/l)	5.98	6.11		14.14	10.67	10.96	10.99	11.75	11.57	11.81	12.56	12.62	13.97	14.16	14.15		
SiO ₂ (mg/l)	4.46	5.36		13.8	10.7	11.3	8.91	10.2	9.64	9.81	10.8	10.0	10.9	12.3	11.0		
TDS (mg/l) ²	458	465		1046	816	807	813	851	861	866	911	925	1018	1029	1022		
Temperature (°C)	12.0	11.9	14.0	12.6	17.4	18.0	17.5	18.1	17.9	17.8	17.7	18.1	18.0	18.0	17.9	21.3	
pH	7.53	7.40	7.10	7.14	7.21	7.40	7.30	6.95	7.40	7.10	7.55	7.15	7.20	7.20	7.55	6.85	
Discharge (l/min)	0	0	100	400						150		100				250	
Water level (m) ³	4.5	4.0		5.4	21.9	16.4	14.8	16.1		19.0	15.0	17.5	17.8	19.1	19.9		
δ ¹⁸ O (‰)	-12.7	-12.6	-12.9	-13.1	-13.5	-13.8				-13.9		-13.2			-13.6	-12.7	
δ ² H (‰)	-91.3	-89.4		-98.5	-101	-99.1				-96.5		-94.3			-98.9		
δ ³ H (TU)	124	124	69	66	79	105				81		84			77	58	

TABLE 1 (cont.)

Date	Upper well (47 m deep)											New well (96 m deep)		
	5.1979	8.1979	6.1977	5.1977	8.1977	11.1979	10.1977	12.1977	4.1981	6.1978	7.1978	3.1978	4.1982	4.1981
Ca ⁺⁺ (mg/l)	338	364	375	377	400	408	394	423	445	452	439	436	446	
Mg ⁺⁺ "	44.8	47.7	52.2	53.6	52.9	56.2	53.1	53.5	57.2	58.4	61.3	54.3	57.5	
Na ⁺ "	7.84	8.11	8.83	9.16	8.31	10.0	9.21	9.61	10.5	11.0	10.7	10.1	11.4	
Sr ⁺⁺ "	7.79	8.14	8.45	8.46	8.54	9.52	8.31	8.29	11.4	9.99	11.3	9.10	9.5	
K ⁺ "	1.31	1.33	1.51	1.32	1.82	1.39	1.50	1.43	1.57	1.63	1.52	1.10	1.8	
Li ⁺ "	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.02	0.04	0.04	0.03	0.04	0.02	
SO ₄ ⁻⁻ "	725	750	800	800	800	825	850	900	925	950	1020	988	1020	
HCO ₃ ⁻ "	323	343	351	371	361	375	359	366	381	389	382	391	403	
Cl ⁻ "	0.71	1.42	3.5	4.5	4.0	2.30	4.0	2.5	2.0	3.25	1.75	2.38	2.50	
F ⁻ "	0.61	0.63	0.59	0.54		0.69			0.62	0.64		1.07	0.86	
Total cations (meq/l)	21.11	22.66	23.63	23.85	24.92	25.93	24.66	26.15	27.67	28.11	27.71	26.90	27.75	
Total anions (meq/l)	20.44	21.31	22.54	22.89	22.69	23.42	23.69	24.81	25.61	26.28	27.55	27.10	27.96	
SiO ₂ (mg/l)	15.5	18.8	23.7	20.7	19.3	21.4	18.9	19.1	22.9	24.4	21.9	22.0	22.5	
TDS (mg/l) ²	1467	1543	1625	1646	1656	1710	1698	1783	1858	1900	1950	1915	1975	
Temperature (°C)	22.0	22.6	24.2	24.1	24.2	24.1	25.2	24.9	23.4	25.2	24.9	30.1	29.6	
pH	7.00	7.15	6.95	6.70	6.95	6.90	6.95	7.35	6.77	6.95	7.15	6.33	6.70	
Discharge (l/min)	380	400							320			660	600	
Water level (m) ³	15.0	11.8	8.5	9.2		7.6	12.6	17.8	13.4	15.2	16.3	0	0	
18O (‰)	-12.4	-12.8	-12.9			-12.6			-12.6		-12.9		-12.3	
2H (‰)	-90.3	-91.2	-93.3			-95.6					-91.8			
3H (TU)	52	53	83			36			35		37		36	

¹ The water sources and the samples are arranged by increasing SO₄ concentration, except for Leisalp creek, which samples are arranged by increasing TDS.

The ion sequence is made by decreasing concentration of cations and anions, respectively, as observed in the most mineralized samples.

Precision: Chemical parameters $\leq \pm 10\%$; temperature = $\pm 0.2^\circ\text{C}$; pH (measured in the field) = ± 0.2 pH; discharge = $\pm 20\%$; water level = ± 0.1 m;

$\delta^{18}\text{O} = \pm 0.1\text{--}0.15\text{‰}$; $\delta^2\text{H} = \pm 1\text{--}2\text{‰}$; $^3\text{H} = \pm 10\text{--}15\%$.

² TDS (Total Dissolved Solids): sum of the chemical species listed in the table.

³ Water level: depth of the groundwater below surface in the six wells during sampling. All the wells were pumped except the New well, which is strongly artesian.

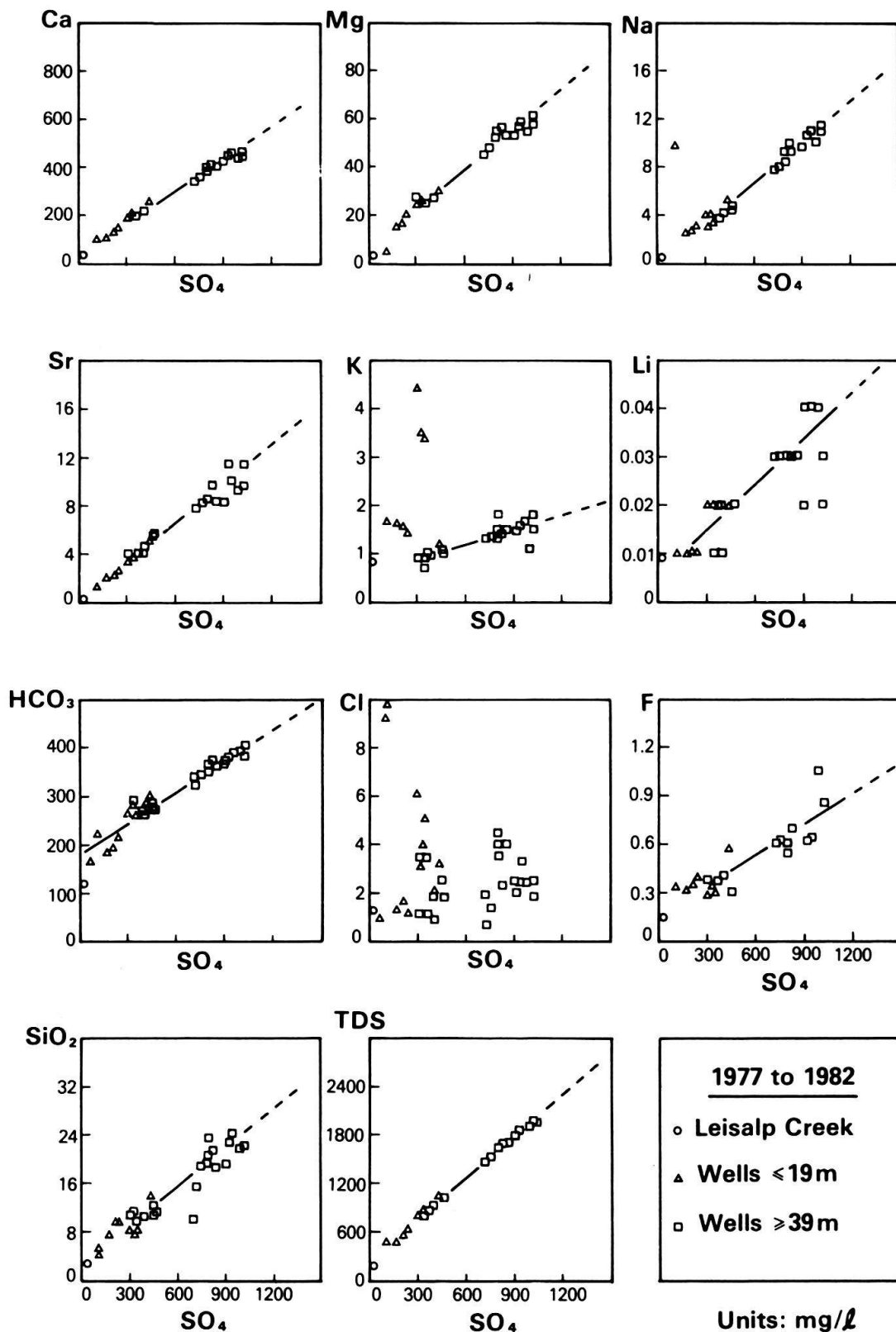


Fig.3. Major chemical parameters versus SO_4 . The group which is on the right side of each graph contains all the samples from Upper well and New well. The staircase like trend for Li is due to rounding off and the precision limit of the analytical method. Mixing trends are seen for all parameters except Cl.

1.5 °C higher than the mean annual air temperature, namely 7 ± 0.5 °C (WALTON 1970).

Observed temperatures however, show an average of 10 ± 1 °C for the two shallowest wells (Table 1). The exception of the 16.5 °C value recorded from the Cooling water well I, in November 1979, is very doubtful. This 3 °C difference between calculated and observed temperatures might be attributed to the spreading and mixing of thermal water into the shallow aquifer.

A plot of the emergence temperature versus well depth shows a positive correlation (Fig. 4). The upper line segment fits the maximum temperature values of the three shallow cold wells and the two thermal water production wells. Extrapolation of this segment towards surface gives 7 °C, which matches the theoretical temperature of the shallow aquifer, before any mixing with thermal water. Between the two deepest wells, the temperature increase is smaller, a common feature when changing from loose sediments to consolidated rocks. However, at least another point of measurement between the Upper and New wells or below the latter one would be needed, to confirm any trend of temperature increase with depth.

Isotopic parameters

Oxygen-18 and deuterium, especially from 1979, are poorly correlated and scatter along the meteoric water line $\delta^2\text{H} = 8 \times \delta^{18}\text{O} + 10$ (CRAIG 1961) (Fig. 5). They do not display any particular trend, which could be attributed to local climatic effects. In order to determine if one or none of the two stable isotopes can be used to calculate the recharge area elevation, the relations between oxygen-18 and SO_4 , and between deuterium and SO_4 , have been checked. The freshest waters have the lowest concentration in heavy isotopes. The linear regressions calculated with ^{18}O - SO_4 and with ^2H - SO_4 have respectively a coefficient correlation of 0.8 and 0.4, whereas they should be similar. It seems that the oxygen-18 data are reliable (Fig. 6), while the deuterium values are not.

River and spring waters collected in various regions of Switzerland allowed the establishment of a oxygen-18 gradient in terms of elevation (SIEGENTHALER 1979; SIEGENTHALER in HÖGL 1980; SIEGENTHALER & OESCHGER 1980; VUATAZ 1982), where $A(\text{m}) = -367 \times \delta^{18}\text{O} - 3110$, $A(\text{m})$ being the average elevation in meters above sea level of the recharge area. Due to the location of the calibration sampling points, this relation has the best precision for the elevations under 2000 m and the regions north of the Alps. The application of this gradient for the waters studied here gives a maximum extension of average recharge elevation from 1440 m for the thermal waters to 2100 m for the surface waters (Fig. 6).

Tritium values display a wide range of concentrations according to sampling periods and different water sources (Table 1) (FONTES in FRITZ & FONTES 1980). A decrease of tritium content is observed in two wells between 1977 and 1981, due to the decreasing tritium concentration of the rain and therefore of all the meteoric waters, since the end of the atmospheric nuclear tests. For a given well and hydrologic cycle, variable tritium values have to be explained by seasonal variations of the mixing ratio itself. During the study period, Leisalp Creek water had the highest

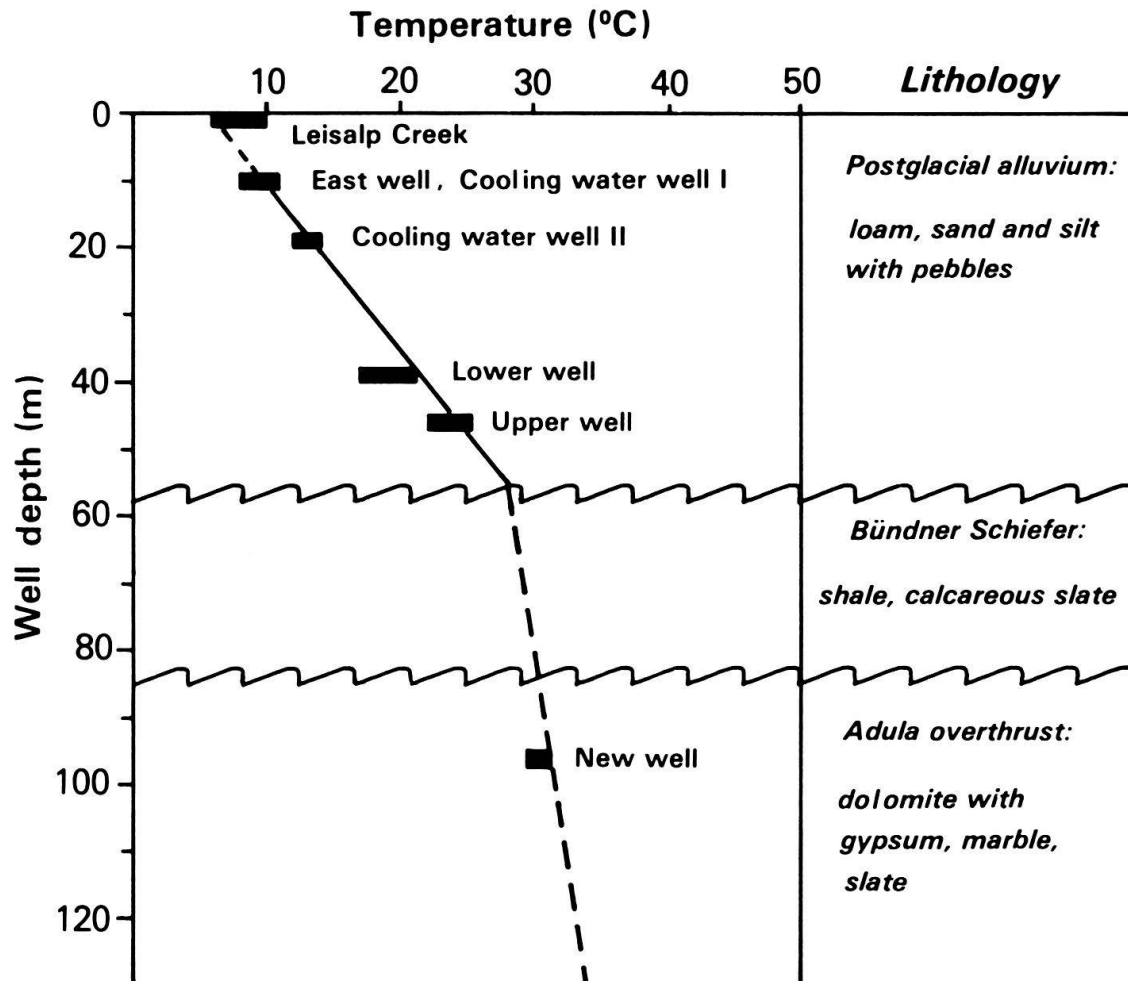


Fig. 4. Temperature versus depth and lithology of the wells in Vals. The range of temperature represents the variations observed during the years 1977 to 1982. The lithology corresponds to the profile made from the cuttings of the New well, and the thickness of the last formation is unknown (W. Nabholz, University of Bern, Switzerland, 1981, unpubl. data).

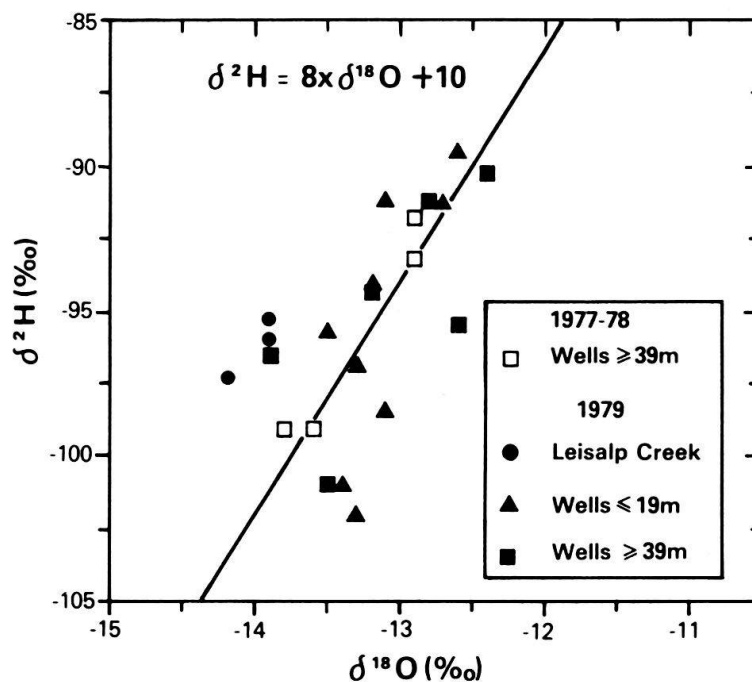


Fig. 5. Oxygen-18 and deuterium of the waters from Vals. The scatter of the points from the meteoric water line is assumed to be due to the lack of precision of the deuterium analyses in 1979.

tritium concentration with an average of 100 TU, shallow and cold groundwaters reached 80 TU and deep thermal waters ranged from 40 to 60 TU (Fig. 7).

The first two samples taken from the Cooling water well II in 1979 display anomalous chemical and isotopic characteristics in comparison to the East well and the Cooling water well I that tap local shallow groundwater. That water was very dilute but with twice higher Na and Cl contents. Tritium concentration of the Cooling water well II, with 124 TU, was higher than the shallow ground- or surface waters for the same period. These characteristics are explained by the fact that Cooling water well II had not been pumped for several years and the water which was taken with a downhole sampler, was stored in the widened part of the casing and probably stagnant. Moreover, the wellhead is at ground level and not tightly shut, and may directly collect some of the runoff waters around the nearby buildings and paved yards. For these reasons, the two samples taken from the Cooling water well II in May and August 1979 will not be used in the mixing models, because they do not represent the actual dynamic groundwater conditions.

4. Variations of the thermal water characteristics

Significant variations have been recorded in the physical, chemical and isotopic parameters of the thermal water wells of Vals (VUATAZ 1980b). Monthly chemical monitoring of Upper and Lower wells since 1972 has shown that the variations do not strictly follow a hydrologic cycle, probably due to the various pumping rates of these wells. From one year to another, various SO_4 concentrations are obtained at the same period of the year (Table 2). However, the influence of the seasons and runoff waters emerges: the minimum value of mineralization, here SO_4 the main anion, appears during the summer, which corresponds to the end of snowmelt recharge into the shallow aquifer (Fig. 8.) On the other hand, the highest SO_4 content is present during fall and at the end of the winter (no precipitation, or stored under snow cover).

Because the two production boreholes which have been observed for the longest time (Upper and Lower wells) do not reach the bedrock floor of the valley, it is most probable that the deep thermal water is more or less influenced (cooled and diluted) by the valley aquifer. According to the season, either discharge (late summer to early spring) or recharge (mid-spring to mid-summer) of the shallow aquifer by runoff waters changes the flowing conditions of the uprising thermal water in the valley fill. Due to the variable pumping rate conditions of the two production wells and their interactive behavior, natural seasonal variations are probably modified and masked. Unfortunately, the available data do not allow to differentiate quantitatively the influence of the natural and artificial changes on the dilution of thermal water by cold water. However, the global phenomenon will be discussed below with the mixing model.

Numerous data are available concerning the exploitation conditions, namely pumping rate, groundwater level, temperature and mineralization (Valser St. Petersquelle AG, personal communications, 1977 to 1982). Both Upper and Lower wells are artesian, but they must be pumped to provide enough water for spa and bottling plant requirements. It has been determined that under selected pumping conditions,

TABLE 2

Monthly values of SO_4 content (mg/l) for the Upper well during the period 1972-1979 [analyzed by the Laboratorium für Wasseruntersuchungen, Hannover, West Germany and by the Chemisches Laboratorium des Kantons Graubünden].¹

	1972	1973	1974	1975	1976	1977	1978	1979	Monthly average
January	1046	1048	1074	1035	863	963	960	809	975±96
February	1034	1031	801	1044	925	889	1005	824	944±98
March	--	1060	885	1027	974	954	1016	840	965±79
April	1042	1064	939	1036	991	983	1015	835	988±73
May	--	1040	--	970	962	915	1034	868	965±67
June	1043	1044	949	874	954	970	1019	785	955±89
July	896	--	908	961	859	839	1032	860	908±68
August	1007	--	823	882	907	962	1026	827	919±82
September	1044	1032	990	834	923	960	929	934	956±67
October	1045	1019	988	888	960	988	964	--	979±50
November	1019	949	1005	--	917	984	857	915	949±58
December	--	995	--	--	931	966	802	947	928±74
Yearly average	1020±52	1028±34	936±84	955±80	931±41	948±45	972±75	859±53	953±24

¹ This set of data is used for the observation of averaged seasonal variations (see Figure 8).

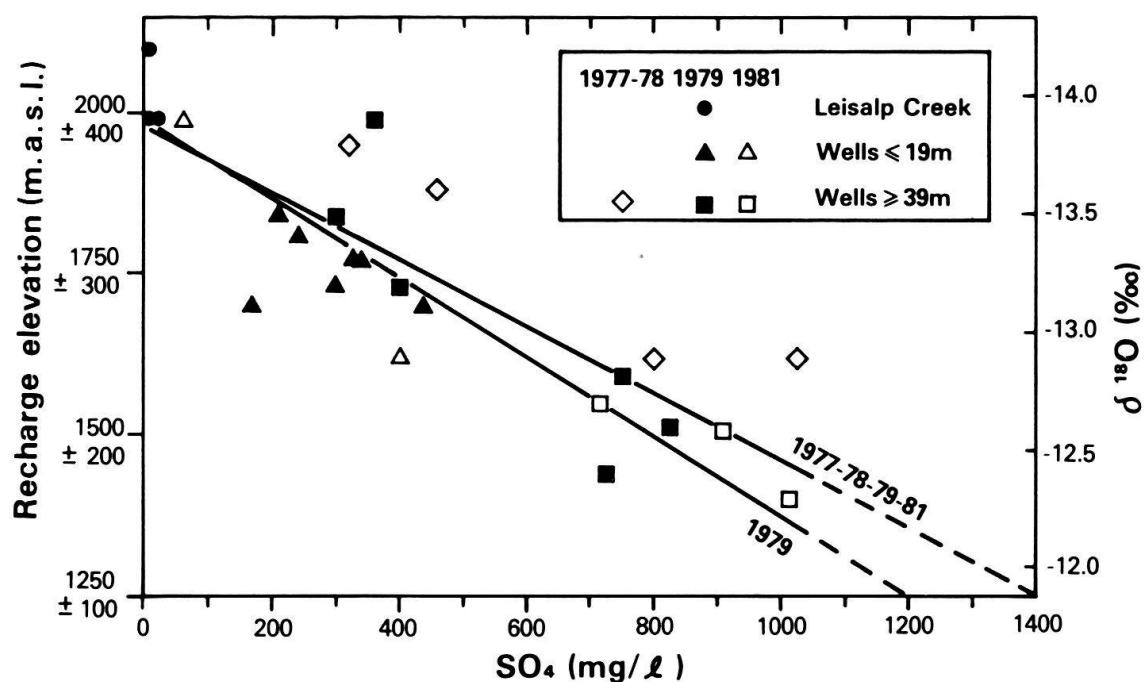


Fig.6. Oxygen-18-deduced recharge area elevation and SO_4 correlation. The two lines represent linear regressions computed from the 1979 and 1977 through 1981 samples. The dashed parts of the lines show the trend of the extrapolation towards the mineralized end member. For the lowest possible recharge area elevation (1250 m.a.s.l. = Vals elevation), the SO_4 content reaches 1300 ± 100 mg/l. The error of the recharge elevation is empirically increased from about 10 to 20% while the elevation goes from 1250 to 2000 m.a.s.l., because the oxygen-18 gradient with elevation used here is regional and not specific for Vals area.

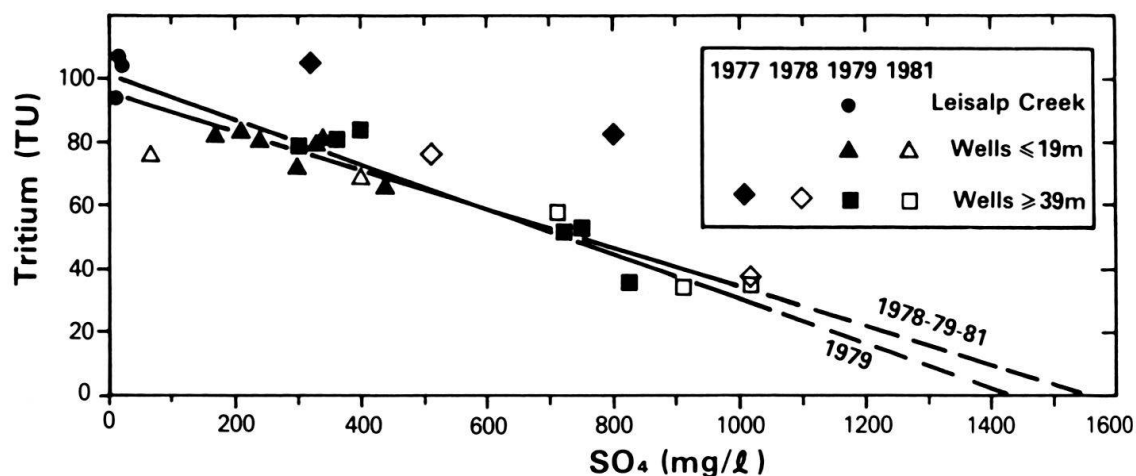


Fig. 7. Tritium and SO_4 correlation. The two lines represent linear regressions computed from the 1979 and 1978 through 1981 samples. The dashed parts of the lines show the trend of the extrapolation towards the mineralized end member. For a low or zero tritium content, the SO_4 value reaches 1500 ± 100 mg/l.

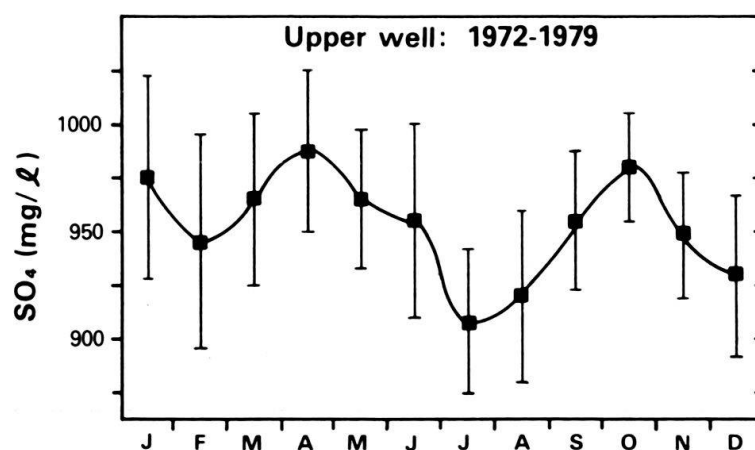


Fig. 8. Average monthly values of SO_4 content for the Upper well (1972-79). Error-bars represent half of the standard deviation around the average (see Table 2). Observed seasonal variations are likely to be modified and partially masked by irregular pumping rates.

the Lower well (depth = 39 m; temperature $\approx 18^\circ\text{C}$; TDS ≈ 850 mg/l) draws some of the shallow groundwater and reduces strong dilution of thermal water pumped by the nearby Upper well (depth = 47 m; temperature $\approx 24^\circ\text{C}$; TDS ≈ 1720 mg/l). The most favorable pumping rates to obtain this equilibrium are 100–200 l/min for the Lower well and 300–400 l/min for the Upper well.

The hypothesis of a warmer and more mineralized water flowing out of the valley floor was established on the basis of the first geochemical studies of seasonal variations (VUATAZ 1978, 1980a) and confirmed by drilling of the New well, reaching the Triassic dolomites and providing 600 l/min of artesian thermomineral water at 30°C with a TDS of 1970 mg/l (SCHNEIDER 1981; VUATAZ 1983). As the Lower and Upper wells are not any longer pumped, the New well yields 800 l/min of artesian water at 30°C with a TDS of 1900 ± 100 mg/l (Valser St. Petersquelle AG, 1982, written communication).

5. Mixing models

In order to determine if any mixing occurs in a thermal water system and to establish a quantitative mixing model, it is necessary to find a major ion which has distinct concentration in both thermal and fresh waters. This ion's concentration should also depend only on the degree of mixing and not on dissolution-precipitation reactions (MAZOR 1976). For most thermal systems, Cl or SO_4 is the so-called conservative ion.

Plots of SO_4 content versus the main chemical parameters display positive linear correlations (Fig. 3), as well as SO_4 versus oxygen-18 (Fig. 6), tritium (Fig. 7), flow rate (Fig. 9) and temperature (Fig. 10). This indicates that SO_4 is a conservative ion for the Vals system, according to the above conditions. Moreover, straight lines also show a mixing pattern between two end members: a mineralized warm water and a dilute cold one.

A major interest of a mixing model in a thermal water system is to extrapolate the chemical and physical characteristics of the unmixed deep end member (MAZOR et al. 1983), a useful method for predicting the water characteristics of future wells. For the thermal water system in Vals, three modes of extrapolation have been used, based on flow rate, tritium and oxygen-18 (VUATAZ 1978, 1980a and 1983).

Flow rate based extrapolation

This first extrapolation is established on the relation existing between pumping rate and SO_4 concentration for the main production hole (Upper well). Starting at the beginning of 1979, flowmeters were installed on the Lower and Upper wells (Table 3). Two different relations are shown between pumping rate and SO_4 in 1979 (Fig. 9): a positive linear relation (Lower well; $r = 0.75$) and a negative linear relation (Upper well; $r = -0.76$).

These two wells are interactive and the physical and chemical characteristics of the water are highly dependent of their respective pumping rates and of the combination of both. The two different observed behaviors are possibly due to the location and depth of these wells, although they are very close and have similar depths (39 and 47 m). A better correlation would probably exist between pumping rates and SO_4 , if the ratio of pumping between the Upper and Lower wells was stable. This ratio varies from 5 to 1, and sometimes one of the wells is shut down.

From the plot, one can observe that the Lower well is tapping more shallow dilute groundwater (low SO_4 for low pumping rates), while the Upper well is more influenced by the uprising thermomineral water (high SO_4 for low pumping rates). Using the negative correlation between pumping rates and SO_4 for the Upper well, it is possible to extrapolate the trend to a very small pumping rate, assumed to be the natural upward flow of thermal water to the well through the valley fill. It is then possible to determine the SO_4 concentration for the unmixed deep thermal water: with a flow rate of 0–20 l/min, the mineralized end member reaches a maximum SO_4 content of 1300 mg/l (Fig. 9).

Tritium based extrapolation

This extrapolation is established on the inverse relationship between tritium concentration and SO_4 (Fig. 7). In many thermal groundwater systems, deep thermomineral waters are virtually deprived of tritium, because the meteoric waters from which they originate, percolated in the underground before the first atmospheric nuclear tests in 1953. According to the study period (1977–81), this means a minimum underground transit time of 24–28 years. Frequently, thermomineral waters flow out of faults or fractures from consolidated rocks and spread into permeable shallow sediments, which are generally saturated with cold, young water. This shallow water may contain as much tritium as surface waters. If mixing occurs, the thermomineral water acquires tritium proportional to the mixing percentage.

In Vals, the two thermal water wells sampled in 1977 had a much higher tritium concentration compared to their SO_4 content, than during the years 1978 to 1981. It can be explained by a higher tritium background in the rainfall and subsequently in the uprising thermal water at that time, which has always been mixed with shallow groundwater. For this reason and because two values are not enough to establish any trend, the samples from 1977 will not be used for this tritium based extrapolation.

One mixing line has been computed between tritium and SO_4 , with the 1979 samples only ($r = -0.95$), because numerous tritium data are available within a period of five months (same tritium background content in the freshest water). A second mixing line calculated with the samples of 1978, 1979 and 1981 ($r = -0.94$), displays a similar trend to the first one. If the two lines are extrapolated to a low or zero tritium concentration, assumed to be present in the deep unmixed thermal water, the mineralized end member reaches a maximum SO_4 content of 1400–1600 mg/l (Fig. 7).

Oxygen-18 based extrapolation

This third extrapolation is established on differences in oxygen-18 concentrations and therefore, on differences in recharge area elevations, indicating various origins (Fig. 6). The freshest and coldest water has the highest recharge elevation of around 2000 m.a.s.l., while the thermomineral fluid originates from a lower elevation of around 1400 m.a.s.l. For this extrapolation also, two mixing lines between recharge area elevation and SO_4 have been calculated. One mixing line has been computed with the 1979 samples only ($r = -0.87$), for the same reasons explained in the tritium model. All the 1977 to 1981 oxygen-18/ SO_4 data have been used to calculate the second mixing line ($r = -0.85$). Both lines are taken into consideration and extrapolated to the lowest possible recharge area elevation, which theoretically could not be under the emergence elevation, namely 1250 m.a.s.l. According to these mixing lines, the mineralized end member reaches a maximum SO_4 content of 1200–1400 mg/l (Fig. 6).

Pumping rate, tritium, and oxygen-18 (recharge area elevation) allowed the establishment of three independent mixing models and the extrapolation of consistent SO_4 content for the deep mineralized end member (1200–1600 mg/l).

TABLE 3

Monthly values of SO_4 (mg/l) and flow rate (l/min) in 1979 for the two production wells [analyzed by the Chemisches Laboratorium des Kantons Graubünden].¹

Date	Lower well		Upper well	
	SO_4	Flow rate	SO_4	Flow rate
1.24	-	0	809	410
1.30	335	60	-	-
2.8	360	70	824	360
3.20	-	70	840	350
4.24	-	70	835	350
5.24	-	100	868	380
6.28	399	100	785	400
7.24	380	150	860	400
8.26	363	150	827	400
9.12	370	200	934	220
11.27	-	0	915	350
11.30	531	300	-	0
12.4	405	280	947	300

¹ This set of data was collected under steady pumping rate conditions and is used for the flow rate based extrapolation of the mineralized end member (see Figure 9). Other values taken at the beginning of new pumping rates were omitted.

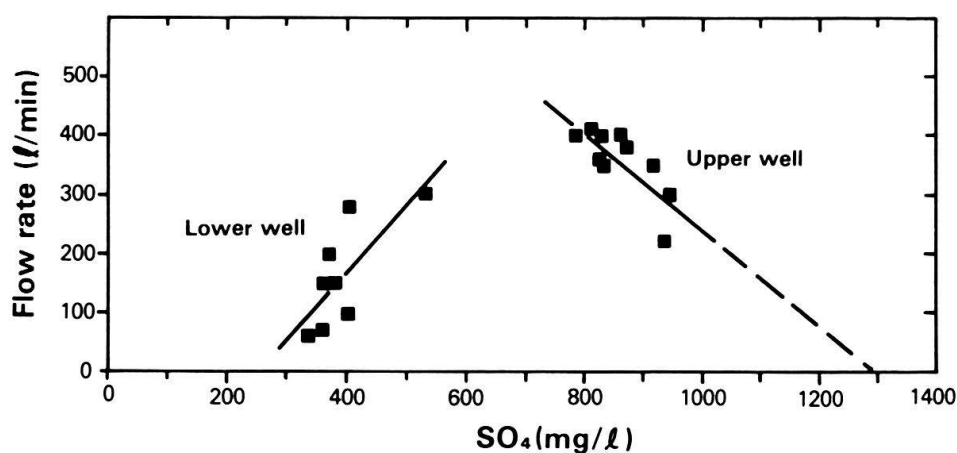


Fig. 9. Flow rate and SO_4 correlation. The two lines represent linear regressions computed with the 1979 samples for the Lower and Upper wells. The dashed part of the line for the negative correlation shows the trend of the extrapolation towards the mineralized end member. For a low or zero flow rate, the SO_4 value reaches a maximum of 1300 mg/l.

6. Composition of the end members and percentage of thermal water

Knowing the range and the probable maximum concentration of the main conservative ion (SO_4) obtained from the mixing lines, it is now possible to extrapolate all the parameters strongly correlated with SO_4 . A good positive linear correla-

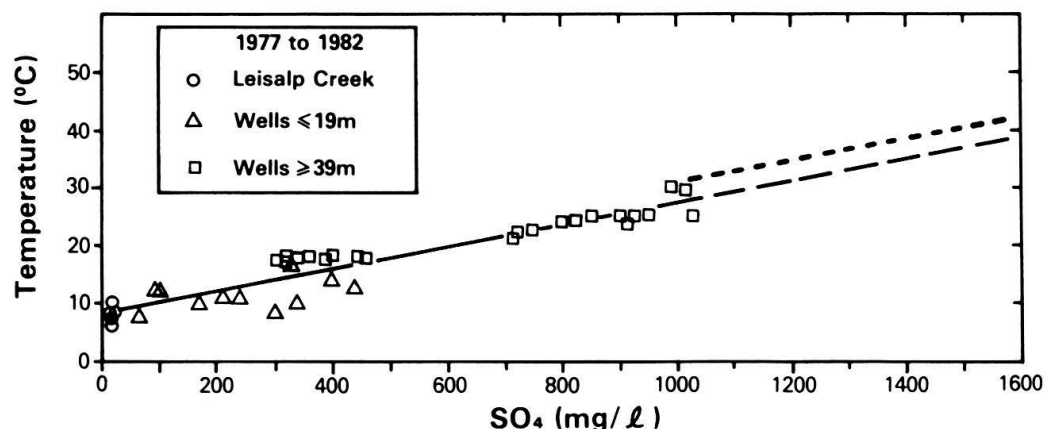


Fig. 10. Emergence temperature versus SO_4 . The linear regression was calculated with all the samples from 1977 to 1981. The dashed part of the line shows the trend of temperature increase towards the thermomineral end member ($T = 39^\circ\text{C}$ for $\text{SO}_4 = 1600 \text{ mg/l}$). The parallel dotted line represents the inferred temperature increase without conductive cooling (see text). In this case, the maximum possible temperature is of 42°C .

tion ($r = 0.94$) exists between emergence temperature of all the types of water and SO_4 (Fig. 10). This trend gives a range of temperature from 31° to 39°C for SO_4 content from 1200 to 1600 mg/l. However, the mixing line does not take into account possible conductive cooling occurring during water ascent. In the New well, a bottom hole temperature of 31°C has been measured, which is 3°C more than the linear regression for the corresponding SO_4 value (1020 mg/l). A parallel segment, 3°C higher than the mixing line displays a range of deep temperature from 35° to 42°C , according to SO_4 content, before cooling by conduction and dilution (Fig. 10).

The values or concentrations of the other chemical, physical and isotopic parameters can be deduced from the plots versus SO_4 for the warm and cold end members (Fig. 3). Most of the parameters are well correlated with SO_4 , except Cl. From the two SO_4 concentrations corresponding to the average surface water (15 mg/l) and to the average value between the three mixing models for the deep end member (1400 mg/l), one can read the values of the other parameters on the best-fit lines of the plots (Fig. 3 and Table 4). The cold end member is slightly more mineralized than the Leisalp creek water, but much less than the cold groundwaters sampled in the shallow wells. The latter ones are probably mixed with the uprising thermal water or have already dissolved minerals due to their underground residence time. The extrapolated cold end member may be the freshest shallow groundwater, just after surface water percolation.

Once the end-member compositions have been determined, it becomes possible to calculate mixing percentages for each sample. Examples for the three thermal water wells are given in Table 4. One can observe that the percentage of thermal water varies according to the parameters, but the calculated average using many parameters may give a better approximation of the mixing, which actually takes place. For example, it appears that the water tapped by the New well might be still mixed with dilute and cold groundwater up to 30%.

TABLE 4

Composition of the two extrapolated end members and percentage of thermal water in three production wells.¹

	Extrapolated cold end member		Extrapolated warm end member		Percentage of thermal water ²		New well (%)
	Lower well (%)	Upper well (%)	Lower well (%)	Upper well (%)	Lower well (%)	Upper well (%)	
Ca	50 (mg/l)	630 (mg/l)	31	67	68		
Mg	6 "	83 "	34	72	67		
Na	<1 "	16 "	22	65	69		
Sr	<1 "	15 "	33	74	61		
K	0.6 "	2 "	29	66	86		
Li	0.005 "	0.05 "	33	56	33		
SO ₄	15 "	1400 "	32	73	73		
HCO ₃	180 "	480 "	32	67	74		
Cl	1 "	2 "	(75)	75	(150)		
F	0.15 "	1 "	16	58	84		
SiO ₂	3 "	33 "	27	63	65		
TDS	240 (mg/l)	2670 (mg/l)	32	71	71		
Temperature	8 (°C)	38 (°C)	33	56	72		
pH	7.7	6.3	11	39	71		
Oxygen-18	-13.9 (δ ¹⁸ O ‰)	-11.9 (δ ¹⁸ O ‰)	15	50	80		
Deuterium	-98.1 (δ ² H ‰)	-90.8 (δ ² H ‰)	(-11)	86	--		
Tritium	100 (TU)	0 (TU)	23	63	64		
Average percentage of thermal water	0	100	27±8	65±11	69±12		

¹ The composition of the two end members is deduced from the plots of Figure 3 with the extrapolated SO₄ values: 15 mg/l for the cold end member and 1400 mg/l for the warm end member.

² The percentages of thermal water are based on the highest SO₄ content sample for each of the three wells. The percentage values in brackets are not considered as meaningful for the mixing model and have not been used for the calculation of the average and its standard deviation.

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