Thermal and mineral waters in north-eastern Slovenia

Peter Kralj · Polona Kralj

Abstract The Mura basin in north-eastern Slovenia is made up of two depressions, developed during the Late Neogene and Early Pliocene all within a widespread system of Pannonian basins. Both depressions are characterized by the occurrence of thermal waters of somewhat different hydrogeochemical character. Radgona depression is in the northern part of the basin and reaches depths of about 2 km. Thermal waters are generally dominated by sodium-bicarbonate, not related to the age of an aquifer, its wallrock composition, the type of porosity or total concentration of dissolved solids. Locally, sulphate-rich waters are encountered, and they are related to the presence of gypsum in the rocks of pre-Tertiary basement. The adjacent Ljutomer depression is over 4 km deep and comprises compartments with stagnant or semi-stagnant aquifers. Herein saline waters predominate, even in the aquifers of carbonate composition and abundant CO_2 gas. In shallower, unconsolidated, intergranular aquifers sodium-bicarbonate waters predominate. Thermal aquifers of this type are very important to the economy of the region, but they are also subjected to overexploitation which is reflected in time-dependent changes of dynamic pressures, temperature, conductance, salinity, pH and concentration of major ions, trace elements, dissolved gasses, and total organic carbon. Mineral waters occur in shallow aquifers or springs in marginal areas of the Radgona depression. Bicarbonate waters are dominated by calcium, or both calcium and sodium. Some mineral waters are formed mainly by penetration of CO_2 gas into shallow aquifers and consequent water–rock interaction. Composition of some mineral waters indicate their possible evolution from thermal waters which have risen from central parts of the Radgona depression along deep-seated faults, and have been modified by cooling and mixing processes.

Key words Sedimentary aquifers · Thermal water · Mineral water · Water chemistry

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Introduction

North-eastern Slovenia is characterized by an abundant occurrence of thermal and mineral waters. During the last five decades, the area has been extensively explored to discover new resources of oil and gas, however wells commonly tapped thermal water instead.

Until the present, only low-enthalpy resources have been exploited. Thermal water, with a temperature of 50–70 °C, is abstracted from an intergranular aquifer of the Upper Pliocene age, named Termal I. It is widely used in balneology and, in the town of Murska Sobota, also for local district heating. Because of its importance, hydrodynamic properties and water chemistry have been monitored in some exploitation wells more or less regularly since the beginning of production. The results indicate that Termal I is subjected to overexploitation, reflected in a constant decrease of static pressures, and in Murska Sobota also in time-dependent regular changes of hydrodynamic pressures. Efficient re-injection of thermally used water seems to be the only solution to preserve this natural resource for future generations.

Mineral waters are also important to the economy of north-eastern Slovenia. Radenska bottling company is renown in many European countries as a producer of high-quality mineral and potable waters. However, Radenci is not the only location in NE Slovenia where mineral waters occur, but also many other smaller sources exist, and some of them might be interesting for bottling.

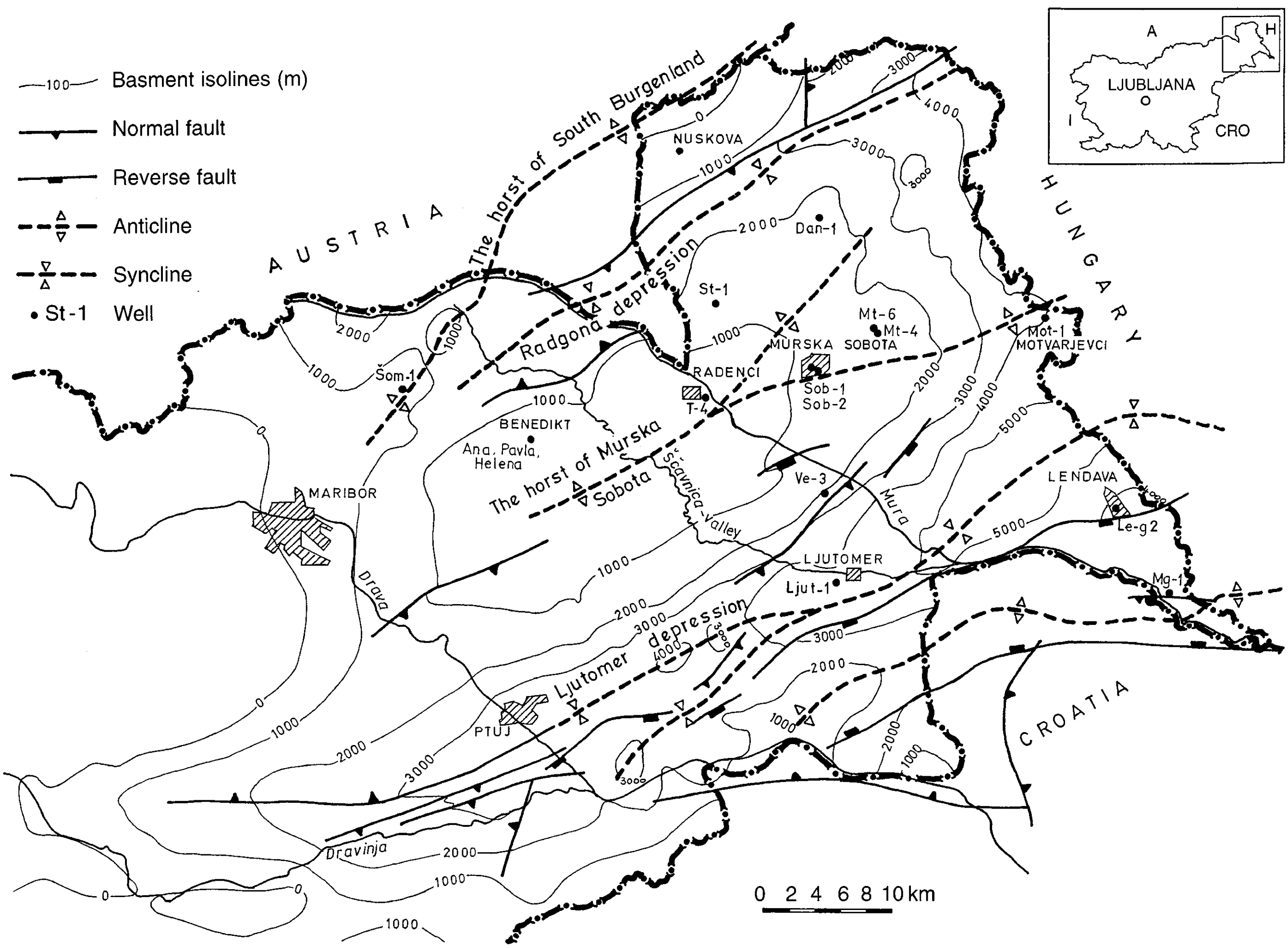
High-enthalpy resources also exist in north-eastern Slovenia, but they have not yet been exploited. In a deep well, Ljut-1, located at Ljutomer, a brine having the temperature of 173 °C, has been captured in the pre-Tertiary carbonate basement. The studies have shown that this aquifer is a potential source for future production of electric power from geothermal steam (Kralj 1994).

The present contribution deals mainly with the geological occurrence of thermal and mineral aquifers in north-eastern Slovenia, the water types or hydrogeochemical facies encountered, and the changes in chemical properties of composite water, which are related to overexploitation of the Sob-1 well in the town of Murska Sobota.

Geological setting

North-eastern Slovenia (Fig. 1) is a transitional region between Pannonian lowland in the east, and Southern Alps in the west. The most important tectonic structure is the Mura basin, which is infilled with clastic sediments of the Tertiary and Quarternary age. The Mura basin forms a part of a much larger Zala basin, which extends from south-western Hungary to northern Croatia, and belongs to a widespread system of Pannonian basins (Royden 1988).
Although the formation of Mura basin began as early as the Carpathian stage of the Tertiary age, the main subsidence occurred during Late Pliocene and Quarternary. This subsidence was closely related to tectonic activity which produced deep-seated strike-slip faults. Two of them are particularly important: the northeast–southwest trending Radgona fault in the north, and the east–west trending Ptuj-Ljutomer fault in the central part. Along the faults two depressions developed, separated by the horst of Murska Sobota (Fig. 1). They were named after the faults – the Radgona and Ljutomer depressions.
The major part of the Radgona depression is situated in Austria, and only southern margins extend on the territory of north-eastern Slovenia. In the north, it is separated from the adjacent Graz basin by the horst of South Burgenland, where the pre-Tertiary metamorphic basement outcrops. In the Radgona depression, the basement consists of Mesozoic carbonates overlying metamorphic rocks at a depth of about 2 km (Oberhauser 1980). The carbonates are a thermal aquifer with mineral water of essentially sodium-dominated bicarbonate type.
On the horst of Murska Sobota, the pre-Tertiary metamorphic basement rises to depths of about 500 m below the surface (Fig. 2). In the north-easterly direction, the horst spreads, but also deepens. Away from the horst of Murska Sobota, towards the Ljutomer depression, the

Fig. 1
Structural map of north-eastern Slovenia



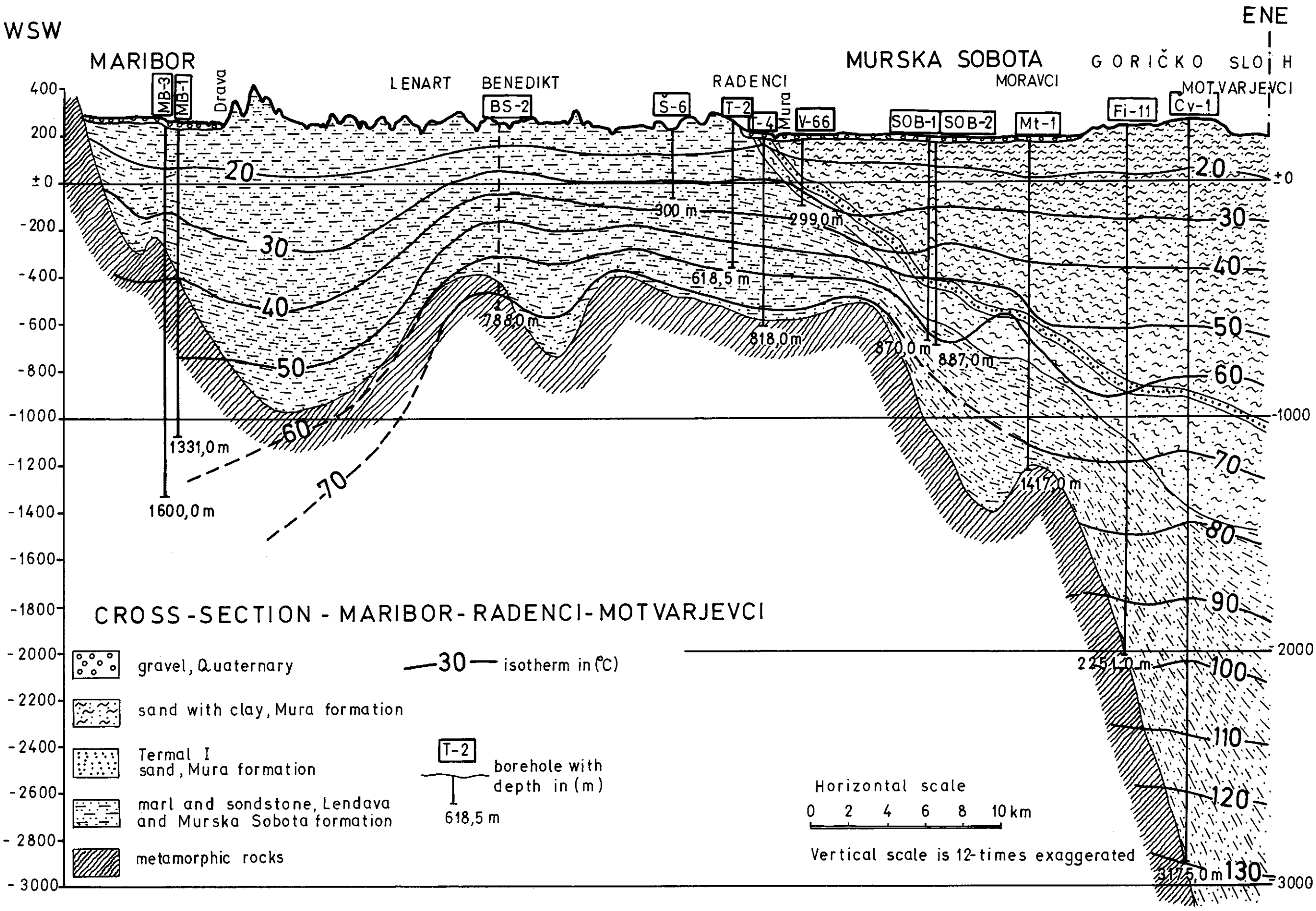


Fig. 2
Idealized cross-section through Mura basin in WSW–ENE direction

pre-Tertiary metamorphic basement deepens rapidly, and attains a depth of about 4 km in its central part. Here, some remains of Triassic dolomites overlie metamorpic rocks, forming an aquifer containig a brine and abundant CO_2 gas.

Tertiary sediments in the Radgona depression were deposited in a marine environment during Carpathian, Badeninan and Sarmatian stage (Pleničar 1968). Except for Badenian, they are developed as clastics – clays, marls, silts and sands. During Pannonian and Early Pontian, brakish conditions prevailed. In Late Pontian and Quarternary, the environment changed into continental – fluvial and limnic. Pliocene and Quarternary deposits are relatively thin, and probably, extensively eroded. CO_2 gas is abundant in marginal areas of the Radgona depression, penetratrating along deep faults from the pre-Tertiary basement. Nuskova, Radenci, Benedikt, and the Ščavnica valley are the sites of mineral water occurrences, either in shallow aquifers or as natural springs. CO_2 enters aquifers, mixing with, and dissolving in the water enhancing its agressiveness, and consequent water-rock interaction. On the horst of Murska Sobota and in the Ljutomer depression, Tertiary sedimentation began in the Sarmatian stage in a marine depositional environment. A thin layer of basal breccia is overlain by the sequences of interstratified clays, marls, shales, sands and sandstones (Fig. 2). Sarmatian sediments are united into the Murska Sobota formation. They are moderately to well lithified by compaction and cementation processes. Aquifers are commonly of poor capacity, unless fractured.

The overlying Pannonian and Lower Pontian sediments are fine-grained clays, silts and silty sands, deposited in a brakish environment. Their thickness attains up to 100 m. The sediments are united into Lendava formation. They are well compacted and partially lithified. The aquifers have poor capacity, but may be locally fractured, and characterized by the presence of CO_2 gas.

Upper Pontian and Quarternary sediments are continental and united into the Mura formation. Owing to rapid subsidence of the Radgona and Ljutomer depressions, rapid sedimentation occurred, the transport direction being from northwest to southeast. In the northern margin of the Radgona depression, along the horst of South Burgenland, systems of alluvial fans developed, and further on, they evolved into braided rivers. In the river channels, sands and pebbly sands accumulated, whereas in the adjacent flood basins, fine-grained sediments and organic matter deposited. During burial, the sediments stacked in horizontal and vertical directions forming a widespread

thermal aquifer – Termal I. Termal I underwent some compaction, nevertheless, it still preserved much of the primary porosity. For this reason, CO_2 does not occur as free gas, but only penetrates in the aquifer from the underlying formations, and dissolves in the water forming the set of inorganic carbon species.
The Radgona and Ljutomer depressions can be regarded as small artesian basins. Under compaction, waters rise from the depression centers towards the marginal areas, undergoing modifications due to elevated temperature and pressure conditions. Elevated lithostatic pressure may exceed hydrostatic pressure, and pore waters will tend to squeeze out through the low permeability horizons eventually producing an ion filtration (Albu and others 1997). The presence of CO_2 may cause considerable changes in chemical composition due to the enhanced agressiveness of the water. Finally, tectonic displacements which are more abundant in marginal areas of both depressions, can be responsible for the passage of water from different aquifers, producing the effects of mixing.

Hydrogeochemical facies

Hydrogeochemical facies, encountered in the thermal aquifers of the Mura basin, are shown in Table 1. The division is based on over 400 chemical analyses performed during hydrodynamical and hydrogeochemical monitoring of the aquifer – Termal I. Some data (G. Barič, unpub. data), obtained during oil and gas exploration are also incorporated. At first glance, it can be seen that sodium is the prevalent cation, whereas anion composition is variable, comprising chloride, bicarbonate or sulfate ions.
Mineral waters show the opposite compositional trend; they are essentially bicarbonate waters, dominated by calcium or calcium and sodium cations. Hydrogeochemical facies, encountered in mineral aquifers of the Mura basin are shown in Table 2. The division is based on 18 chemical analyses.

Table 1
Hydrogeochemical facies recognized in thermal aquifers of the Mura basin

Na-Cl	Sodium – chloride
$Na-HCO_3$	Sodium – bicarbonate
$Na-Cl-HCO_3$	Sodium – chloride – bicarbonate
$Na-HCO_3-SO_4-Cl$	Sodium – bicarbonate – sulphate – chloride
$Na-SO_4-HCO_3-Cl$	Sodium – chloride – sulphate – bicarbonate

Table 2
Hydrogeochemical facies recognized in mineral aquifers of the Mura basin

$Na-Ca-HCO_3$	Sodium – calcium – bicarbonate
$Ca-(Na)-HCO_3$	Calcium – sodium – bicarbonate
$Ca-Mg-(Na)-HCO_3$	Calcium – magnesium – bicarbonate

The Radgona depression

Thermal aquifers in the basement

Composition of water, abstracted from the pre-Tertiary carbonate basement in the Slovenian part of the Radgona depression, is generally dominated by sodium and bicarbonate. However, sulphate ions may become abundant locally, particularly if the carbonate rocks contain gypsum. Chloride is present in subordinate concentrations with respect to bicarbonate (Table 3).
The aquifers were tapped by deep oil wells St-1, Dan-1 and Šom-1, located along margins of the Radgona depression in the NE–SW direction (Fig. 1). The well St-1, Strukovci, penetrated the pre-Tertiary carbonate basement at a depth of 1645 m. Water, abstracted from the depth interval between 1645–1660 m, contained 6551 mg/l of total dissolved ions, and belongs to the $Na-HCO_3$ hydrogeochemical facies (Table 3). Concentrations of chloride ions were less than 1% of dissolved anions. The Dan-1 well, located at Dankovci, penetrated the pre-Tertiary basement at a depth of 2000.5 m. Water abstracted from the depth interval between 2188.5–2000.5 m contained 9858 mg/l of total dissolved ions, and belongs to $Na-HCO_3-SO_4-Cl$ hydrogeochemical facies (Table 3). Chloride amounts to 12.8% of the total anions. In the Šom-1 well, located at Šomat, the pre-Tertiary basement occurs at a relatively shallow depth of 895 m. The basement consists of carbonate, metamorphic and clastic rocks. Water, abstracted from the 895–914-m depth-interval, contained 5495 mg/l of total dissolved ions, and belongs to $Na-SO_4-HCO_3-Cl$ hydrogeochemical facies. Chloride amounted to 17.8% of the total dissolved anions.

Thermal and mineral aquifers in Badenian and Sarmatian sediments

Thermal water abstracted from Badenian and Sarmatian sediments is characterized by the dominance of sodium and bicarbonate. Mineralization is strongly dependent on the CO_2 gas available, which substantially increases water–rock interaction. In marginal parts of the Radgona depression CO_2 gas is abundantly encountered in thermal and mineral aquifers, but also in moffetes and underground traps.
The T-4 well, located at Radenci spa, penetrated the pre-Tertiary basement at a depth of 800 m. Thermal water is abstracted from the aquifers in Badenian and Sarmatian sediments between 400–450 m in depth; the water temperature is 43 °C, and dissolved ions amount to 10,946 mg/l (Table 3). The composition of water is dominatad by sodium and bicarbonate. Chloride and sulphate are relatively low, amounting to 2.9% and 0.8% of the total dissolved anions, respectively.
Shallow aquifers in Badenian and Sarmatian sediments commonly yield mineral water. The waters are dominated by calcium or calcium and sodium bicarbonate. In Benedikt (Fig. 1) three shallow boreholes – Helena, Pavla and Ana, reached a depth of 30 m, 60 m and 100 m, respectively. The chemical composition of abstracted water (Ta-

Table 3
Composition of thermal water in the aquifers of Radgona depression

Well depth (m) Formation, rock type	Units[a]	St-1 1645–1660 Carbonate basement	St-1 1652–1655 Carbonate basement	Dan-1 2188–2000 Carbonate basement	Šom-1 895–914 Carbonate basement	T-4 400–540 Murska Sobota
Na^+	mg/l	1414	750	2550	1570	2087
	meq/l	61.51	32.6	110.92	68.29	90.72
	%	78.6	90.6	90.5	91.2	72.1
K^+	mg/l	122	11	125	39	440
	meq/l	3.12	0.28	3.2	1.0	11.25
	%	4.0	0.8	2.61	1.3	9.1
Ca^{2+}	mg/l	181	42	145	66	233
	meq/l	9.03	2.1	7.24	3.29	11.63
	%	11.5	5.8	5.9	4.4	9.2
Mg^{2+}	mg/l	57	12	14	28	147
	meq/l	4.65	0.99	1.14	2.3	12.1
	%	5.9	2.8	0.9	3.1	9.8
Cl^-	mg/l	5	149	567	479	133
	meq/l	<0.	4.2	16.0	13.5	3.75
	%	<0.	11.6	12.8	17.8	2.8
HCO_3^-	mg/l	4199	1915	4874	1512	7633
	meq/l	68.82	31.4	79.9	24.78	125.13
	%	95.2	86.6	63.8	32.8	93.6
SO_4^{2-}	mg/l	203	31	1410	1795	233
	meq/l	4.32	0.65	29.3	37.37	4.85
	%	5.8	1.8	23.4	49.4	3.6
TDI	mg/l	6551	2669	9858	5495	10 946

[a] Percentages refer to separate sums of cations and anions

ble 4) shows an increase in total concentration of dissolved ions with respect to the borehole depth ranging from 951 mg/l in Helena, to 2391 mg/l in Ana. The most obvious is the increase in calcium and bicarbonate, but the other cations – magnesium, sodium, potassium and amonium – also become more abundant. Trace elements – silicon, barium, cesium, rubidium, lithium and strontium – increase in waters from deeper aquifers. Chloride ion is low, but tends to decrease with depth, and it is probably leached from the soil horizons.
The borehole Helena in the shallows has significant recharge, and aquifers are subjected to pollution from the surface. The water from the borehole contains up to 0.03 mg/l of nitrite, and a part of sulphate, boron, arsenium, bismuth, cobalt, copper, chromium, tungsten and zinc was derived from recharge waters. Traces of some organic compounds as octyl-, and nonil-phenoles, phtalates and many others, undoubtedly originate in the surface (Vončina, unpub. data). The borehole has been capped.
Waters from mineral springs are rather diverse in total concentration of dissolved solids, which range from 2–5 g/l. The water composition is dominated by calcium and bicarbonate, although some types may also contain sodium in equal or higher amounts as calcium. The sodium-rich mineral waters commonly contain substantially higher amounts of chloride than the others, indicating possible partial origin in highly mineralized thermal waters that underwent cooling and mixing processes during their rise to the surface. Rare earth element (REE) distribution normalized to chondrite values for thermal water from the T-4 well shows a flat curve indicating rather limited fractionation of heavy (HREE) and light (LREE) rare earth elements, and very small positive europium anomaly (Fig. 3a). All analyzed mineral waters from Benedikt and the Ščavnica valley show a pronounced positive europium anomaly; furthermore, the normalized europium values are practically the same as in thermal water from T-4, whereas LREE and HREE are considerably lower (Fig. 3b). When trivalent REE can undergo fractionation process due to precipitation, induced by the change in Eh, pH and the temperature. A great part of europium may persist in dissolved divalent state according to the reaction:

$$Eu^{3+} + Fe^{2+} = Eu^{2+} + Fe^{3+}$$

This can happen if the reaction equilibrium is shifted to the right side in a solution containing higher concentrations of Fe^{2+} (Michard and Albarede 1986) what is the case in all studied samples of mineral and thermal water.

The Horst of Murska Sobota and Ljutomer depression

Thermal aquifers in the basement

Aquifers in the pre-Tertiary basement can be stagnant and diverse in wallrock composition, nevertheless, Na-Cl hidrogeochemical facies predominates.

Table 4
Composition of mineral waters captured in shallow wells in Benedikt, Nuskova and Ščavnica valley

	Benedikt, Helena	Benedikt, Pavla	Benedikt, Ana	Ivanjševci	Očeslavci	Stavešinci	Nuskova	Špindler
Amount (mg/l)								
NH_4^+	0.52	1.74	4.98	3.07	0.90	0.86	0.19	0.44
Na^+	11	36	51	104	685	162	276	30
K^+	1	8.8	21	15	65	13	3	4.8
Ca^{2+}	172	420	800	487	417	375	328	570
Mg^{2+}	80	94	180	203	69	32	47	23
Fe^{2+}	0.99	8.4	7.2	6.66	1.22	2.67	0.92	0.84
Mn^{2+}	0.610	0.340	0.170	0.143	0.178	0.359	0.428	0.540
J^-	<0.01	0.05	<0.05	0.02	0.21	0.05	0.02	<0.01
F^-	<0.01	0.13	0.04	<0.1	0.78	0.22	0.40	0.22
Cl^-	14	5.0	3.5	7	170	25	32	8
N[a]	0.03	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
N	<2	1.3	1.3	<2	<2	<2	<2	<2
HCO_3^-	643	1800	3400	2590	2970	1690	1790	1620
SO_4^{2-}	26	14	23	2	118	19	68	37
CO_2	143	1918	1830	2500	3800	3300	3300	2600
P	0.034	0.015	<0.015	0.016	0.058	0.023	0.041	0.180
SiO_2	5	27	43	18	15	17	11	30
TOC	2.4	1.7	1.3	0.9	0.8	0.6	0.9	0.8
TDI	951	2391	4536	3420	4499	2321	2547	2295
pH	6.82	6.00	6.37	6.22	6.22	6.02	6.00	6.22
Amount (ppb)								
As	4.8	3.6	0.2	0.1	0.7	0.5	0.5	1.9
B	200	60	80	100	1400	200	1400	34
Ba	97	230	520	640	63	210	62	170
Be	0.2	0.1	0.4	0.5	0.3	0.2	0.1	0.2
Bi	0.05	<0.01	<0.01	0.02	<0.01	<0.01	<0.01	<0.01
Cd	0.08	0.04	3.1	0.21	0.13	0.01	0.05	1.3
Co	9.4	2	2	0.8	0.5	1.1	0.8	<0.1
Cr	1.7	1	0.4	6.7	5.5	0.7	0.7	0.3
Cs	0.06	0.13	1.5	0.88	11.5	0.01	0.29	8.3
Cu	4.2	9.1	2.2	<0.1	10	1.4	0.5	5.4
Ga	0.21	0.02	4.4	0.01	<0.01	0.04	0.02	0.09
Ni	26	14	24	32	20	25	32	1.9
Pb	0.08	0.36	0.06	0.22	0.12	0.01	0.01	0.04
Rb	2.6	24.8	106	53.4	346	61.2	27.7	213
Sc	12	7.7	13.4	25.9	23.2	9.3	9.6	1.9
Se	<0.1	0.9	0.5	0.7	9.4	1.8	3.4	2.1
Sn	<0.01	0.01	0.02	0.04	0.07	0.01	0.02	<0.01
Sr	358	1120	2330	8180	1090	2170	1000	876
U	0.75	0.5	0.2	<0.1	1.8	0.2	0.7	0.1
V	2.1	0.5	0.2	<0.1	1.8	0.2	0.7	0.1
W	1.1	<0.01	<0.01	0.01	0.01	1.4	<0.01	0.23
Y	1	0.87	0.24	0.7	0.03	1	0.28	0.02
Zn	62	7.6	2.8	3.5	3.5	5.1	4.6	2000
Zr	0.1	1.9	1.6	0.1	0.1	0.1	0.3	0.2
Pd	0.3	0.1	0.7	7.5	0.8	0.2	0.1	<0.1
La	0.75	0.29	0.07	0.02	<0.1	0.1	0.11	<0.01
Ce	1.25	0.52	0.14	0.01	0.01	0.15	0.19	<0.01
Pr	0.19	<0.01	0.02	<0.01	<0.01	0.02	0.02	<0.01
Nd	1.06	0.33	0.08	<0.01	0.09	0.12	0.1	<0.01
Sm	0.18	0.07	0.06	<0.01	0.02	0.02	0.02	<0.01
Eu	0.04	0.08	0.17	0.21	0.04	0.08	0.03	0.03
Gd	0.16	0.09	0.01	0.01	<0.01	0.05	0.02	<0.01
Tb	0.02	<0.01	<0.01	<0.01	<0.01	0.01	0.01	<0.01
Dy	0.11	0.1	0.02	<0.01	0.01	0.08	0.02	<0.01
Ho	0.3	0.02	<0.01	<0.01	<0.01	0.02	<0.01	<0.01
Er	0.06	0.07	0.3	0.01	0.01	0.07	0.04	<0.01
Yb	0.08	<0.01	0.02	<0.01	<0.01	0.05	0.02	<0.01

[a] N as nitrite

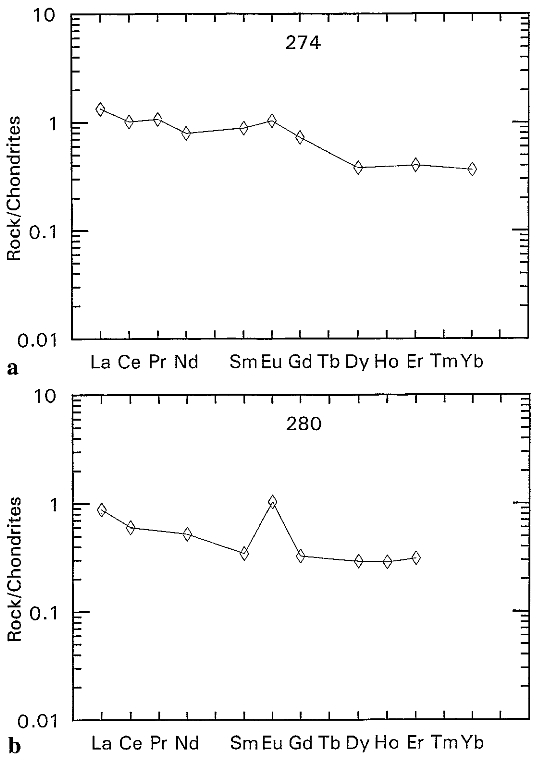


Fig. 3
Distribution of REE abundances normalized to chondrite values for mineral waters from the Radgona depression. **a** Sample from the T-4 well in Radenci, **b** sample from a shallow well in Stavešinci

The deep Ljut-1 well at Ljutomer, penetrated Mesozoic dolomites and dolomite breccias at a depth of 4004 m. The well tapped a stagnant, overpressurized aquifer with the fluid having the temperature of 173 °C, and mineralization amounting to 22,448 mg/l. Carbon dioxide was abundant.

Despite carbonate composition of the aquifer and abundant CO_2, the water was a brine (Table 5). Sodium and chloride ions amounted to almost 90% of total concentration of dissolved ions. The water is possibly marine in origin, being leached into the pre-Tertiary basement from the overlying marine sediments of the Murska Sobota formation, and later, modified by complex hydrogeochemical processes. The presence of carbon dioxide cannot substantially enhance mineralization of brines as saturation of carbonates is reached, and they tend to precipitate from the solution (Mazor 1991).

Aquifers in the Murska Sobota formation

The Murska Sobota formation includes stagnant aquifers, and confined aquifers with some phreatic parts. They bear thermal and mineral waters of rather diverse chemical composition.

A stagnant-type aquifer was tapped in the deep well Mot-1 at Motvarjevci, between 2828–2832 m in depth (Table 5). The water was a brine with total dissolved ions amounting to 26,995 mg/l. The dominant ions were sodium and chloride, with very subordinate bicarbonate and sulfate. In deper levels of the same well Mot-1 (3626.5–3630.5 m), another aquifer was encountered, with

Table 5
Composition of water from deep-seated aquifers in the Ljutomer depression

Well depth (m) Formation, rock type	Units[a]	Ljut-1 4005–4023 Carbonate basement	Mot-1 2828–2832 Murska Sobota	Mot-1 3626–3630 Murska Sobota	Mg-6 3727–3744 Murska Sobota	Mt-4 1176–1263 Murska Sobota
Na^+	mg/l	8214	10037	5700	4435	4960
	meq/l	350.4	436.3	247.93	192.91	215.7
	%	97.5	96.4	96.4	90.9	94.5
K^+	mg/l	230	138	318	185	250
	meq/l	5.77	3.53	8.13	4.73	6.39
	%	1.6	0.8	3.2	2.2	2.9
Ca^{2+}	mg/l	36	210	38	260	95
	meq/l	1.8	10.49	0.97	12.97	4.74
	%	0.1	2.3	0.4	6.1	2.
Mg^{2+}	mg/l	13	29	1.65	20	16.7
	meq/l	1.06	2.38	0.14	1.64	1.37
	%	0.1	0.6	<0.1	0.8	0.6
Cl^-	mg/l	11735	15619	8288	5404	5574
	meq/l	324.3	440.46	233.46	152.41	157.0
	%	90.5	97.1	90.8	71.3	67.9
HCO_3^-	mg/l	2082	607	805	2474	4249
	meq/l	33.48	9.96	13.2	40.56	69.99
	%	9.3	2.2	5.1	19.	30.3
SO_4^{2-}	mg/l	128	146	505	1001	196
	meq/l	2.66	3.04	10.52	20.84	4.08
	%	0.2	0.7	4.1	9.8	1.8
TDI	mg/l	22448	26995	15750	14210	15520

[a] Percentages refer to separate sums of cations and anions

Table 6
Composition of water from Termal I (Mura formation). Admixtures of waters from the Lendava fromation increase concentrations of almost all ions and trace elements

Well	Units[a]	Le-g	Ve-3	Mt-6	Sob-2	Sob-1
depth (m)		2813–1493	1111–1467	720–974	600–854	557–856
Formation		Mura	Mura	Mura, Lendava	Mura, Lendava	Mura, Lendava
Samples		3	18	25	46	71
Na^+	mg/l	280	363	335	733	755
	meq/l	12.18	15.79	14.55	32.85	33.71
	%	95.2	96.6	96.7	94.4	89.3
K^+	mg/l	8	9	7	44.0	71.0
	meq/l	0.2	0.24	0.18	1.14	1.8
	%	1.6	1.6	1.3	3.3	4.8
Ca^{2+}	mg/l	5	5	5	10	32
	meq/l	0.25	0.25	0.25	0.5	4.2
	%	1.9	1.5	1.7	1.4	1.6
Mg^{2+}	mg/l	8	1	1	4	8
	meq/l	0.66	0.08	0.08	0.33	0.66
	%	1.3	0.3	0.3	0.9	1.7
Cl^-	mg/l	3	18	132	122	149
	meq/l	0.09	0.46	3.72	3.44	4.2
	%	0.6	2.7	24.5	10.1	10.6
HCO_3^-	mg/l	856	970	696	1898	2125
	meq/l	14.03	15.96	11.41	31.12	34.83
	%	99.1	97.2	75.4	89.8	87.8
SO_4^{2-}	mg/l	2	<5	<5	<5	32
	meq/l	0.04				0.67
	%	0.3				1.6
TDI	mg/l	1173	1468	1187	2736	3189
CO_2	mg/l	15	178	227	411	550
pH		7.30	7.96	7.9	7.03	6.85
T	°C	58.3	54.5	58.8	47.6	49.0

[a] Percentages refer to separate sums of cations and anions

thermal water of the same Na-Cl type, but with lower total concentration of dissolved ions amounting to 15,750 mg/l. Water of similar mineralization and type was also tapped in the well Mg-6 (Murski gozd) in depths between 3726.7–3743.5 m (Table 5).

In Moravci spa, the Mt-4 well tapped some aquifers of Sarmatian and Badenian age, composed of fractured sandstones, which bear thermal water with the temperature of 71 °C, and abundant CO_2 gas. Concentration of total dissolved solids amounts to 15,520 mg/l. The water is dominated by sodium and chloride ions, although bicarbonate amounts to about 30% of the total dissolved anions (Table 5).

Aquifers in the Lendava and Mura formations

Aquifers in the Lendava and Mura formations are characterized by the dominance of sodium-bicarbonate hydrogeochemical facies. However, none of the wells in the Pomurje region abstracts only the water from Lendava formation, and for this reason, the exact chemistry is unknown. It can only be estimated from the composition of mixtures with the water from Termal I; in general, concentration of total dissolved solids and the temperature are higher, and CO_2 abundantly occurs as undissolved gas.

The aquifer – Termal I – is composed of several water-bearing sandy layers, interbedded with silts and clays, up to 60 m thick. Concentration of total dissolved solids averages to 1276 mg/l for 46 of analyzed samples (Table 6). In the water from Le-g2 well, located at Lendava, the average sodium concentrations amount to 280 mg/l, which means 96.7% of the total dissolved cations, and in the water from Ve-3 in Banovci spa, to 363 mg/l or 97.9% of total dissolved cations. Concentrations of bicarbonate average to 856 mg/l and 970 mg/l or 99.3% and 97.2% of total dissolved anions, respectively.

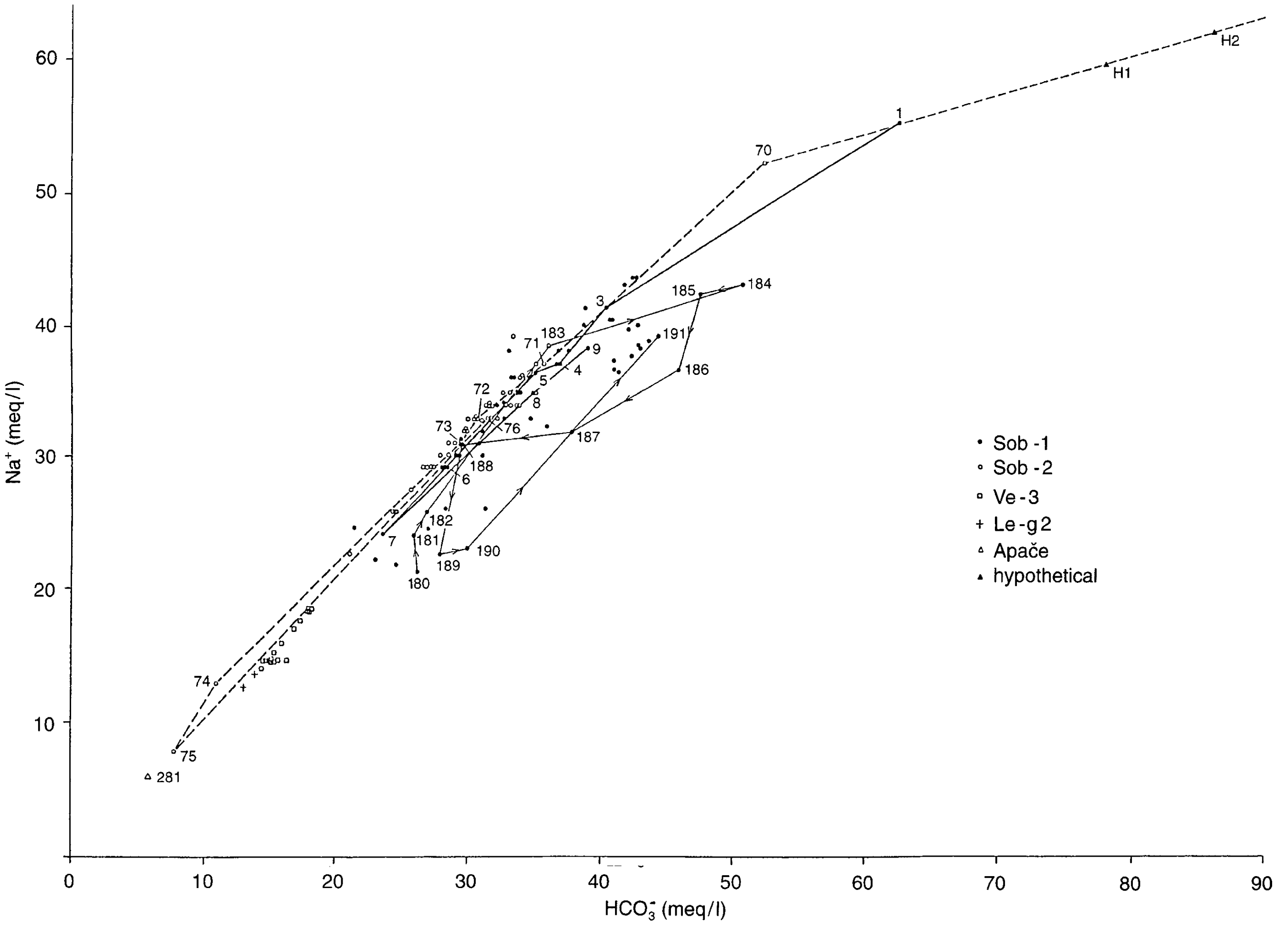
The wells Sob-2 and Sob-1, located in the town of Murska Sobota, also abstract the water from Termal I, but also some water from the Lendava formation. Consequently, concentrations of total dissolved solids considerably increase, as well as the amount of CO_2 gas (Table 6). The wells are about 317 m apart and are hydraulically interconnected. Sob-1 penetrated about 151 m of the Lendava formation, and Sob-2 only 129 m due to tectonic displacements. The presence of the water from the Lendava formation in the abstracted composite water, increased total concentration of dissolved solids to 2736 mg/l in Sob-2 and to 3189 mg/l in Sob-1. Sodium is still the dominant cation, averaging 733 mg/l in Sob-2, and 755 mg/l in Sob-1, and bicarbonate the dominant anion, averaging

1898 mg/l, and 2125 mg/l, respectively. With the increasing proportion of water from the Lendava formation, potassium and calcium tend to increase, along with chloride, sulphate and many other ions and trace elements. The composite character of abstracted water is particularly important in an aquifer subjected to overexploitation. In Fig. 4, the relationship between two major ions, Na^+ and HCO_3^- is shown for the studied water samples from the wells Le-g2 (crosses), Ve-3 (open squares), Sob-2 (solid circles) and Sob-1 (open circles). The majority of samples is clustered in a straight line which extrapolates to the zero points, and indicates dilution of relatively high concentrated sodium-bicarbonate waters with a fresh-water end member. The second, broken line connects the samples 1 and 70 which represent water composition in the beginning of exploitation of Sob-1 and Sob-2. Calculated from these values are H1 and H2, two possible compositions of intermixing water from the Lendava formation. Intitial concentrations of sodium and hydrogencarbonate are the highest recorded, and have never been attained during the well operation. The reason is in the largest proportion of water from the aquifers of Lendava formation, they have been overpressurized in the beginning of exploitation due to the presence of undissolved CO_2 gas. The Sob-1 began with operation in December 1987, and the Sob-2 in June 1988. In both wells sodium and bicarbonate have been in constant decrease until October 1992 (the samples 7 and 75), when they reached the lowest concentrations. After this period they increased in both wells, but started to vary. The samples from 180 to 192 show variations in water composition within 70 min, recorded in November 1997.

Variations in water composition caused by overexploitation of the Sob-1 well

Changes of dynamic pressures and temperatures in the Sob-1 well have been monitored by Leutert PT gauge

Fig. 4
Correlation of sodium with bicarbonate for the waters of Termal I. *Thicker solid line* connecting the samples 1–9 represents the trend of constantly decreasing concentration of Na^+ and HCO_3^- since the beginning of operation in December 1987 until January 1993 when they increased, but also began to vary. The *thinner solid line* connecting the samples 180–191 shows the change in concentration within 70-min cycle observed in November 1997. The *thicker broken line* connecting the samples 70–76 and represents the trend of constantly decreasing concentrations of the two ions in the well Sob-2 since the beginning of operation in June 1988 until November 1992 when they increased significantly. H1 and H2 are two hypothetical compositions of water from aqifers of the Lendava formation



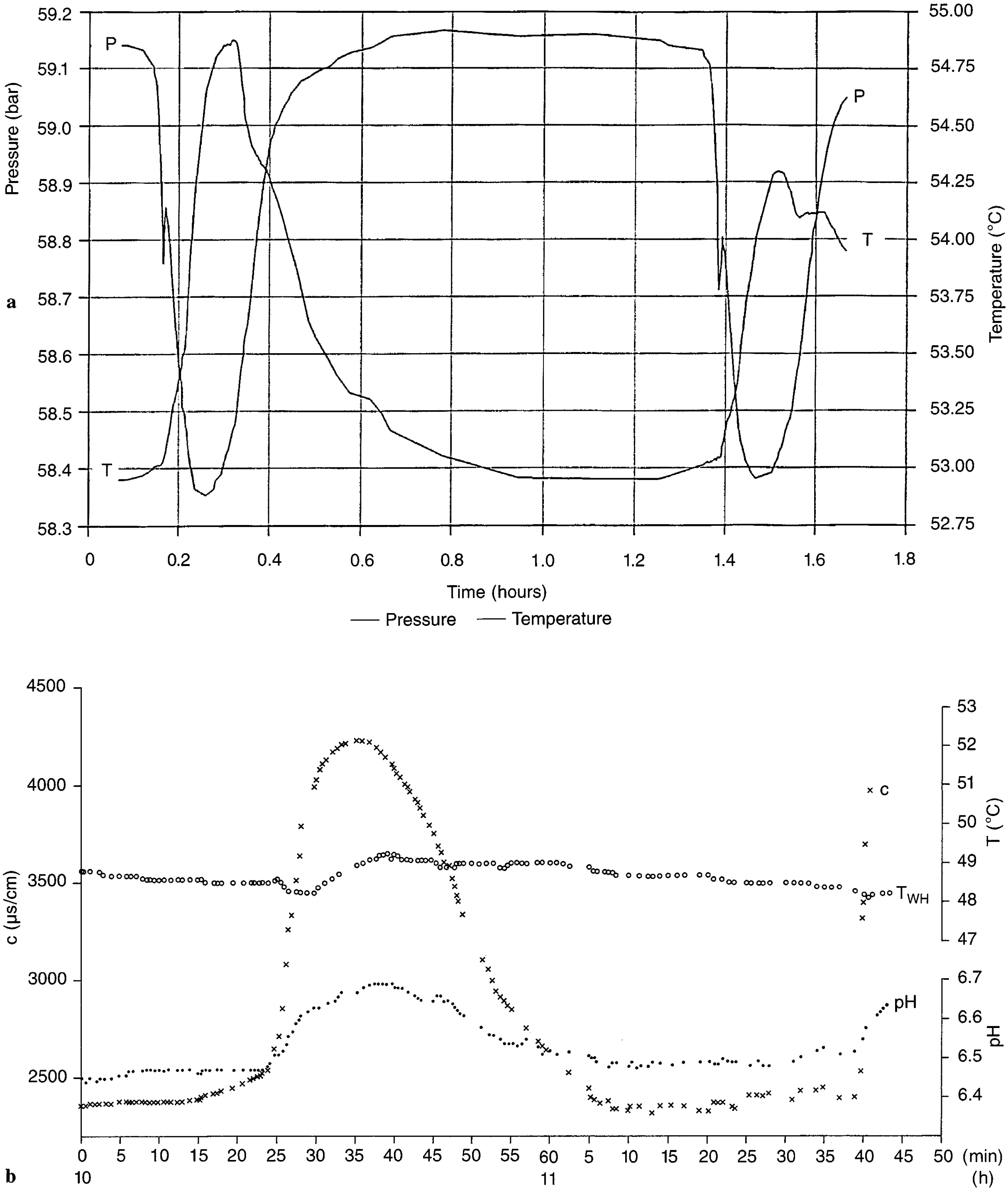
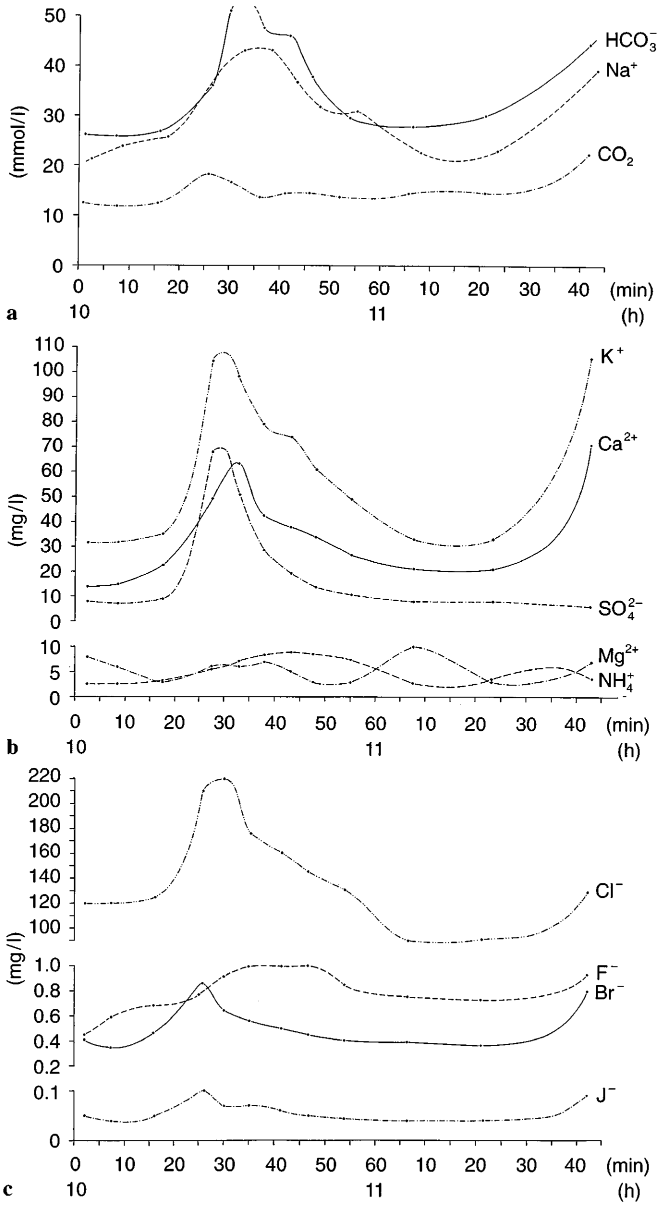


Fig. 5a
Time-dependent variations in pressure and temperature in the Sob-1 well, **b** the changes in conductance, salinity, pH and the water temperature at the well-head

during a one week period four times a year since the beginning of exploitation. The measurements have been taken every 10 s with computer-managed data output. Water samples were collected in the same 1-week period.

The water level has been in constant decrease since the beginning of exploitation. The water pressure varies regularly, most commonly within a time amplitude of about 70 min (Fig. 5a). Under more intensive exploitation, the time periods tend to be shorter and amount to about 30 min. When the pressure increases, the temperature decreases and when the pressure decreases, the temperature increases. The maximum difference in pressure amounts to 0.8 bar, and the maximum difference in temperature to 2.5 °C. Conductance, salinity and pH of water increase



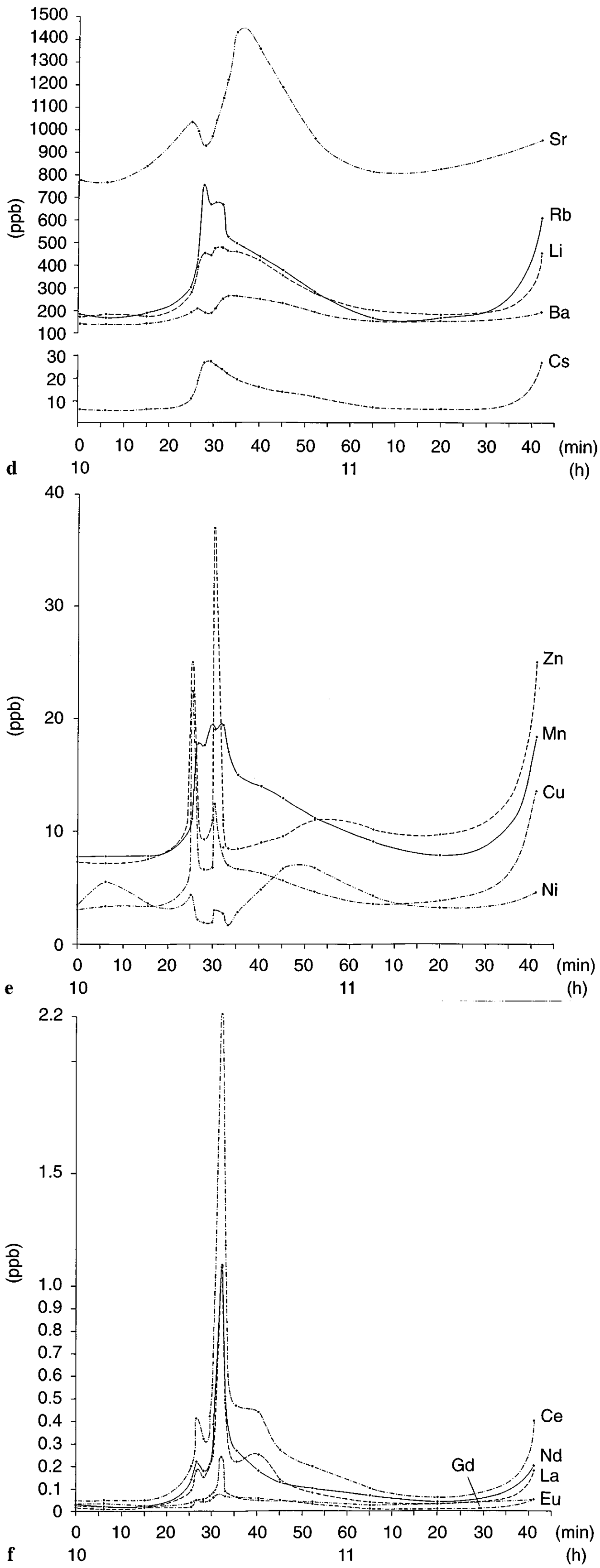


Fig. 6
Variations in abundances of various ions, trace elements and undissolved gasses in water from the Sob-1 well in a 70-min time interval in November 1997 **a** Na^+, HCO_3^- and undissolved CO_2, **b** K^+, Ca^{2+} and SO_4^{2-}, **c** Cl^-, Br^-, J^-, **d** Sr, Rb, Li, Ba, Cs, **e** Zn, Mn, Cu, Ni, **f** REE

proportionally with the temperature (Fig. 5b). The lowest measured conductance value is 2300 μS/cm, and the highest 4400 μS/cm. Salinity increases from 1.1 % to 2.2%, and pH from 6.34 to 6.69. The increase in temperature, conductance, salinity and pH in the abstracted composite water is related to a higher proportion of the water from the underlying Lendava formation. When the pressure in the aquifer – Termal I – decreases, the amount of water from the Lendava formation increases in the abstarcted composite water. When the pressure in the aquifer –Termal I – recovers and supplies more water

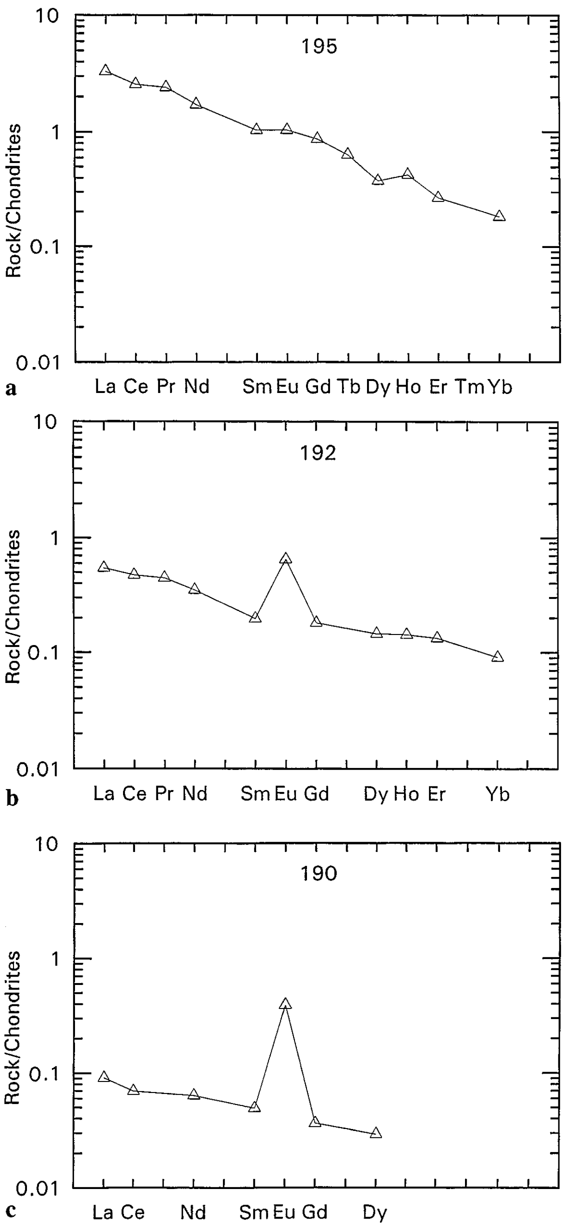


Fig. 7
Rare earth element abundances normalized to chondrite values in the water from the Sob-1 well, **a** water mixture with the highest mineralization, **b, c** water mixtures with lower mineralization

with a lower mineralization, the proportion of water from the Lendava formation becomes lower, as well as the overall chemical composition of the abstracted composite water.
The water from the Lendava formation is highly mineralized and even small amounts influence appreciably chemical composition of the abstracted composite water. An increase in concentration of almost all ions, dissolved gasses and trace elements – Na^+, HCO_3^- and CO_2 (Fig. 6a); K^+, Ca^{2+}, SO_4^{2-} (Fig. 6b); Cl^-, Br^-, J^- (Fig. 6c); Sr, Rb, Li, Ba, Cs (Fig. 6d); Zn, Mn, Cu, Ni (Fig. 6e); and REE (Fig. 6f) – occurs simultaneously with the decrease in pressure. Monitoring of the chemical composition within 70-min or 30-min cycles has shown, that the plots of changes in concentraton versus time are continuous and regularly repeating wave-like curves.
The maximum increase in concentration with respect to the lowest values is not the same for all of the ions and trace elements. For example: in a 70-min cycle, sodium concentrations increase from the lowest value of 490 mg/l to the highest value of 990 mg/l, which means about twice. At the same time, potassium increases from 32 mg/l to 104 mg/l, which is over three times; calcium increases from 14 mg/l to 63 mg/l, which is over four times, and sulphate increases from 8 mg/l to 68 mg/l, which is over eight times. A similar high increase in concentration was observed for light rare earth elements, particularly cerium (over eight times) and lanthanum (over ten times). The abundances of rare earth elements, normalized to chondrite values clearly indicate dilution patterns (Fig. 7). The only exception is europium, which is retained in the solution, and in more diluted samples strong positive europium anomalies are observed.

Conclusions

Tertiary sediments and sedimentary rocks in the Mura basin include aquifers with thermal and mineral water. Thermal waters from the Radgona depression are dominated by sodium and bicarbonate, although some waters may be sulphate-rich. Mineral waters are abundant in the marginal area of the Radgona depression, and occur in shallow aquifers or springs. They are bicarbonate waters, dominated by calcium, or calcium and sodium.
In deeper compartments of the Ptuj-Ljutomer depression, saline waters predominate regardless of the aquifer wall-rock composition and abundance of CO_2 gas. Aquifers in the Mura formation are characterized by intergranular porosity and thermal water dominated by sodium and bicarbonate, and also, by insignificant amounts of undissolved CO_2 gas.
Overexploitation of the Sob-1 well which abstracts composite water from Termal I and the aquifers of the Lendava formation is reflected in time-dependent changes in pressure, temperature, conductance, pH, salinity and overall chemical composition. At the beginning of exploitation, concentration of total dissolved solids constantly decreased due to sufficiently high hydrodynamic pressures in Termal I, and consequently higher inflow of its waters to the well. From the beginning of exploitation, the amounts of abstracted water were to high for the aquifer – Termal I – to recover. In the first 5 years from the beginning of exploitation, the mineralization of absracted water has been constantly decreasing. After this period, an intensive change in the chemical composition occurred. The changes are related to the changing hydrodynamical pressures in the aquifer – Termal I – which

occur regularly in a 70-min or 30-min cycle. The pressure decrease in the aquifer enables more intensive incursion of the highly mineralized water from the underlying Lendava formation. The overall mineralization of abstracted composite water increases. When the pressure in the aquifer recovers, the influx of less mineralized water begins and the overall mineralization decreases. Plotted changes in chemical composition versus time form a continuous wave-like curve. We beileve the process will lead to well collapse in the near future. Exploitation of thermal water from the intergranular aquifer – Termal I – in the Mura basin should be planned carefully and the used water reinjected from the beginning of well operation.

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