4. HYDROCHEMICAL INVESTIGATIONS

4.1. LONG-TERM OBSERVATIONS (M. ZUPAN)

The main purpose of the long-term observations was to collect the data about physical and chemical properties of the springs. On the basis of the collected physical, chemical and geological data we intended to estimate the background characteristics of the springs.

In twelve springs at the food of Trnovsko Banjška plateau monthly sampling and analyzing was carried out for two years.

In the two main springs, Hubelj and Vipava (4/2), weekly samples had been taken. In the Hubelj the sampling lasts from March 1993 to May 1996 while in the Vipava from July 1993 to May 1996.

From September 1995 to February 1996 daily samples have been taken in the springs Hubelj, Vipava and Mrzlek. The aim of this investigation was to define the changes of physical and chemical parameters depending on the water quantity more detail.

In November 1995 the water pulse of the Vipava spring 4/2 was observed to estimate the changes during discharge increasing.

In the spring Hubelj continuous measuring of temperature, pH value and conductivity was performed during entire investigation period. In the springs Vipava more extensive measurements of mentioned parameters last from September 1995 till February 1996. The precipitation was observed on 5 sampling sites from January 1993 to December 1995.

4.1.1. Monthly observations of water of the karst springs and selected rivers (J. KOGOVŠEK)

For two years observations, measurements and analyses were undertaken by sampling approximately once per month, the springs at the border of Trnovsko-Banjška Planota: Vipava, Hubelj, Lijak at overflow, Mrzlek, Kajža, Hotešk, and Podroteja, and also Prelesje and the rivers Soča, Bela and Belščica. Altogether 24 series of samples were taken from January 1993 to June 1995. The Vipava was sampled at first at the spring 4/5 Pod Skalco, and later at 4/3 Perhavčeva Klet. Prelesje was sampled at test-well No. 3, the Soča in front of Mrzlek, the Bela at Sanabor and the Belščica at its swallow-hole near Belsko.

In the field we measured temperature and specific electric conductivity (SEC) with the instrument WTW-LF 91 and pH with the WTW-pH 90. Other analyses were done in the laboratory of the Karst Research Institute. Carbonate, calcium and total hardnesses and also chloride levels were defined titrimetrically, nitrate levels spectrophotometrically and sulfate levels turbidimetrically according to standard methods (STANDARDS METHODS 1992). Analyses of sodium and potassium were done by HMZ.

4.1.1.1. Temperature

During the whole observation period the temperature of spring waters (Hotešk, Hubelj, Kajža, Podroteja and Vipava) varied in a narrow temperature band (Fig. 4.1). At Podroteja and Vipava seasonal variations of temperature were felt, having maximum in summer and minimum in winter; these variations were less distinct at Hotešk and but more so at Kajža, however with more intermediate variations. The temperature at Hubelj varies between 8.0 and 8.5° C (unfortunately we have only 9 measurements from February to September), at Hotešk between 8.6 and 10.3° C, at Vipava between 8.9 and 10.9° C and at Kajža from 8.7 to 11.0° C. Slightly higher variations appeared at Korentan (8.5 - 11.9° C), while at Prelesje the measured temperature was substantially higher due to seasonal fluctuations (10.3 - 16.8° C). In summer months its temperature increased proportionally to the Soča temperature, yet

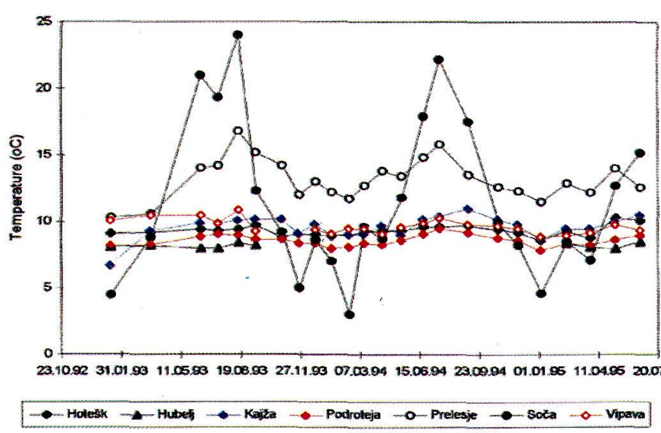

Fig. 4.1: Temperature variations of the observed karst spring waters and of the Soča river water during the observation period (monthly samples).

the amplitude is lower, probably reflecting the Soča influence. The temperature of Mrzlek, measured at the resurgence within the Soča riverbed, in face of a water-works, showed that the inflow water of Mrzlek replaces the Soča water at high water level only, while in dry periods the mixing of both waters moves deeper into the spring. The calculated Ca/Mg ratio as also the isotopic analyses of $\delta^{18}O$ (Chapter 5.2) indicate the same.

HABIČ (1981) reports on the relatively permanent temperature of Mrzlek, between 8 and 10° C. He concluded that water drainage is relatively slow and that it is retained for a long time underground. The temperature measurements in 1993 to 1995 showed rather constant values from 8.3 to 8.9° C at the spring from September to March; this probably reflects the real temperatures of Mrzlek at this time of the year. From March onwards, in the same period of year, we measured the values from 8.4 to 12.0° C in the water-works, even at the end of July 13.5° C but this probably reflects the influence of the Mrzlek and Soča mixing during pumping. The Soča rate depends each time on how much the catchment area of the Mrzlek is filled and also on the quantity of pumping.

The superficial flows such as the Soča, Bela and Belščica reflect the outer temperature and their seasonal variations are considerable. The temperature oscillations of all the sampled waters are shown in Fig. 4.1.

4.1.1.2. Calcium, magnesium and total hardness

Different levels of magnesium and calcium, or calculated ratio Ca/Mg, indicate different recharge areas (Fig. 4.2). The values of single springs vary

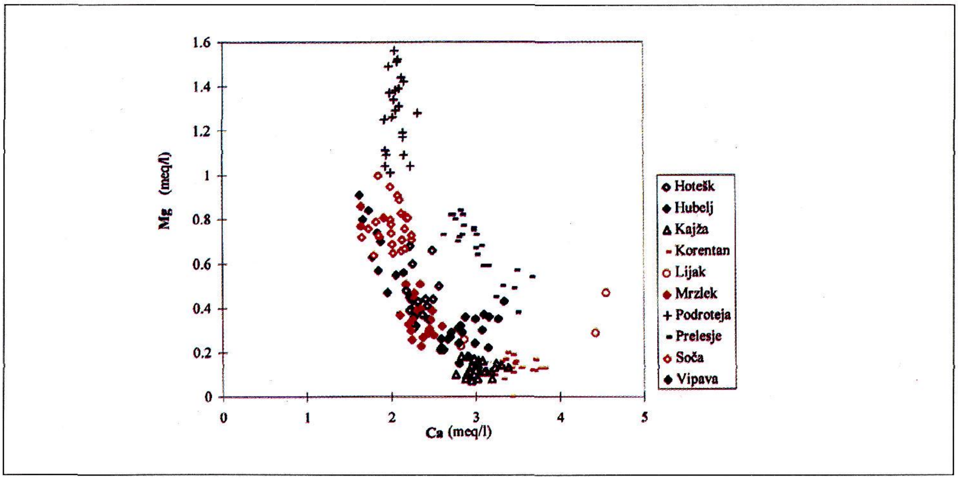

Fig. 4.2: Calcium and magnesium levels in the analysed waters (analyses of the monthly samples).

during the year by different amounts (Fig. 4.3). The lowest Ca/Mg ratio and the smallest variations during the year were recorded at Podroteja where the variations in temperature are minimal showing long water retention in its background and a strong suppression of its influence. In the Hotešk, Mrzlek, Prelesje, Bela and Vipava the Ca/Mg ratio varies more, but not over the value 10; at Vipava only we periodically recorded higher values. The Ca/Mg varia-

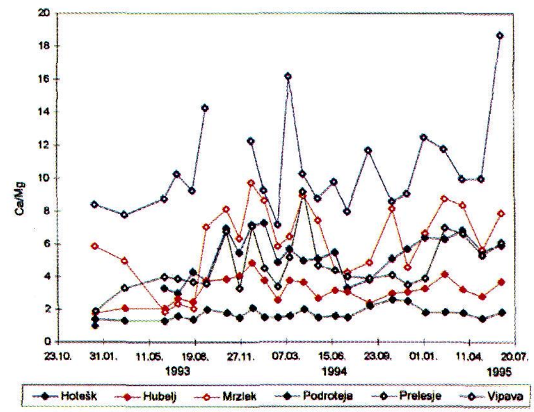

Fig. 4.3: Variations of the Ca/Mg ratios of the various karst springs during the observation period (monthly samples).

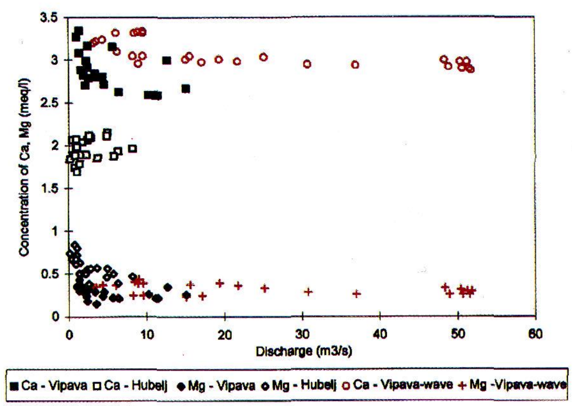

Fig. 4.4: Relationship between the spring discharge and the calcium and magnesium levels of the springs Hubelj and Vipava for the monthly measurements and for various water pulses.

tions in the Hotešk and Mrzlek (excluding the measurements when this water is mixed with the Soča water) may be compared to that of the Podroteja; the variations in the Vipava are higher, and still higher again in the Prelesje. Considerably higher values of the Vipava ratio compared to the Belščica indicate the latter's insignificant share to the Vipava springs.

The highest Ca/Mg ratio (average value 26) with greatest variations during the year was recorded in Kajža. The faults between Banjški and Avški fault are hydrogeologically very important for this spring. The spring reacts to rainfall very quickly (JANEŽ & ČAR 1990), and it explains considerable variations in Ca/Mg ratio.

At monthly sampling the comparison of Ca and Mg level related to discharge indicated that Ca level in the Vipava decreases by the increase of discharge (up to 10 m^3/s); also the analyses of water pulse, however in smaller extent, indicated the same (Fig. 4.4). But the seasonal variations in hardness are felt; the lowest hardness appears in late winter and in spring. The Ca level in Hubelj varies slightly more without an obvious trend, while the Mg level decreases slightly when discharge is increasing. In the Vipava this was not perceived, neither at monthly sampling nor in the water pulse when we have taken the samples during higher water level during monthly sampling.

The total hardness of all the springs varies from 2.4 to 4.2 meq/l. Total hardness of Hotešk, Kajža and Korentan varies seasonally while these oscillations are less prominent at other springs. A similar picture is displayed by specific electric conductivity and carbonates content. The highest value of total hardness was recorded in Prelesje, followed by Korentan, Podroteja, Kajža, Vipava and Hotešk, while Mrzlek and Hubelj had the lowest values. Total

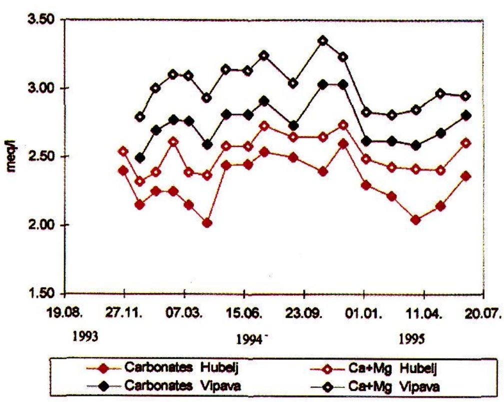

Fig. 4.5: Variations of the total hardness and the carbonate contents in the springs Hubelj and Vipava during the observation period (monthly samples).

hardness of Prelesje, Korentan and the Vipava oscillate the most, within an interval of 1 meq/l. They are followed by Podroteja, Kajža, Hotešk, Mrzlek and Hubelj, the latter oscillating the least, within an interval of 0.5 meq/l. Fig. 4.5 shows rather constant level of carbonates and total hardness in the Vipava and Hubelj.

4.1.1.3. Chloride, nitrate, sulfate, sodium and potassium

In the monthly samples the levels of chloride, nitrate, sulfate, sodium and potassium were also recorded. Over a two years period in all the springs and in the Bela and Soča the level of chloride was up to 4 mg Cl^-/l. The only deviation was recorded in the Belščica; it increased up to 8 mg Cl^-/l, and once even to 12 mg Cl^-/l, indicating the human impact on its superficial flow to the swallow-hole.

The levels of nitrate in the Hotešk, Kajža and Soča never rose beyond 5 mg NO_3^-/l. Their average value is between 3.1 in 3.6 mg NO_3^-/l. Slightly higher values were recorded in Mrzlek, Korentan, Bela and Prelesje with average values between 3.9 do 4.3 mg NO_3^-/l . The highest values were recorded in the Hubelj, Podroteja, Belščica and Vipava with average values from 5.7 to 6.5 mg NO_3^-/l. In Vipava the values varied between 4.3 and 10 mg NO_3^-/l, in Belščica between 4.4 and 7.5 mg NO_3^-/l. Actually, in the Vipava slightly higher values of nitrate levels were recorded than in the Belščica. The variations of the nitrate levels during these two years were observed, yet there is no evident mutual connection. Probably the more distinctive pollution is due to nitrates, but also chlorides and sulfates appear during the initial time of a water pulse.

The lowest sulfate level was recorded in Kajža (average value 6.8 mg SO_4^{2-}/l), followed by Podroteja, Mrzlek and Hotešk being up to 9 mg SO_4^{2-}/l; the Vipava, Korentan and Soča had up to 11 mg SO_4^{2-}/l. Higher values were recorded in the Belščica, and in particular in Prelesje and the Bela where up to 18 mg SO_4^{2-}/l were measured.

The lowest levels of Na were recorded at Hubelj, Mrzlek, Podroteja, Soča and Kajža (up to 1,7 mg/l). They are followed by Hotešk, Prelesje and Korentan with maximal values up to 2.9 mg/l and Vipava with values in an interval from 0.9 to 3.1 mg/l. The highest values were measured in the Bela and Belščica. In the Bela up to 4.8 mg/l and in the Belščica up to 7.2 mg/l.

Hubelj, Podroteja, Mrzlek, Hotešk and Kajža contain less than 0.5 mg/l of potassium. The Vipava and Soča contained up to 0.7 mg K^+/l, Korentan and Prelesje up to 1.3 or 1.6 mg/l; the highest values were measured in the Belščica (1.9 mg/l) and Bela (2.4 mg/l).