

4.1.2. Monthly observations of the precipitation

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The monthly precipitation sampling started in December 1992 at the four meteorological stations Vojsko, Trnovo, Podkraj and Bilje (changed in January 1995 by Slap). In April 1993 Lokve and Postojna were added. The sampling on Trnovo was stopped in July 1994 from technical reasons. The main purpose of the precipitation sampling was to provide the samples for isotope analyses. However we wanted to get some information about the physical and chemical composition of precipitation as well.

The sampling was carried out by Bergerhoff (VDI 1972) samplers. In the precipitation samples we analyzed the same parameters than in the spring water samples. The same methods were used (chapter 2.5) and the same control criteria (chapter 4.1.2) than for spring water analysis. The data analysis showed some seasonal trends in some of the sampling points. However, we decided the meteorological data should be taken in to the consideration. Unfortunately it could not be done in the short period of time we had.

4.1.3. Weekly sampling in the springs Hubelj and Vipava

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In weekly samples we measured pH value, conductivity, calcium (Ca), magnesium (Mg), sodium (Na), potassium (K), bicarbonate, nitrate, chloride and sulfate. The methods used are described in chapter 2.5 (Water Quality).

All measured data were controlled by conductivity (measured and calculated) and ion difference. The permissible value of the coefficient between calculated and measured conductivity 0.9 - 1.1 was taken in to account (GREENBERG et al. 1992). In the Hubelj spring 90 % of analyzed samples were in this range while in the Vipava spring 87 %. The highest value of coefficient for the rest of samples was in the Vipava 1.24 and the lowest 0.85. In the Hubelj the highest coefficient was 1.19 and the lowest 0.85. The calculated ion difference (GREENBERG et al. 1992) was for the Hubelj between -3,5 % and +1.6 % and for the Vipava between -3.4 and +1.6 %.

The summary of the measured concentrations of single parameters is presented in Tab. 4.1. In both springs the most changeable parameters have been conductivity and bicarbonate. The differences between minimum and maximum values have been higher in Vipava than in Hubelj. The changes of calcium concentration have been higher in the Vipava while the changes of magnesium concentration higher in the Hubelj (Fig. 4.6).

For the establishment of seasonal changes in the investigation period of time we used AARDVARK (WRc 1995) seasonal model. In the Hubelj spring

Tab. 4.1: The summary of the weekly samples in the springs Vipava and Hubelj in the entire investigation period

THE SPRING HUBELJ						
Parameter	Number of samples	Minimum value	Maximum value	Mean value	Median value	Standard deviation
Conductivity - $\mu\text{S/cm} - 25^\circ\text{C}$	145	155	273	217	219	14.4
pH	140	7.2	8.5	8.0	8.1	0.23
Calcium	145	26.1	45.8	38.2	38.3	3.4
Magnesium	144	3.7	11.1	6.9	6.7	1.5
Sodium	145	0.4	1.3	1.0	1.0	0.16
Potassium	145	0.1	0.5	0.2	0.2	0.04
Bicarbonate	114	106.8	158.6	141.7	143.4	6.1
Nitrate	143	3.8	10.4	5.9	5.6	1.1
Sulphate	144	5.3	17.4	9.0	8.7	1.9
Chloride	144	1.2	7.7	2.0	1.8	0.75

THE SPRING VIPAVA 4/2						
Parameter	Number of samples	Minimum value	Maximum value	Mean value	Median value	Standard deviation
Conductivity - $\mu\text{S/cm} - 25^\circ\text{C}$	142	207	333	270	269	22.9
pH	140	7.3	8.4	8.0	8.1	0.19
Calcium	142	28.4	67.2	54.9	55.2	6.4
Magnesium	140	1.1	5.8	3.2	3.1	0.82
Sodium	141	0.5	3.3	1.5	1.5	0.46
Potassium	141	0.1	2.3	0.39	0.3	0.25
Bicarbonate	103	128.1	213.5	171.1	164.7	16.0
Nitrate	142	3.4	9.4	6.6	6.0	0.98
Sulphate	142	7.8	20.1	11.2	10.8	1.7
Chloride	142	1.5	3.9	2.3	2.2	0.44

we found seasonal changes for conductivity, Ca, Mg, Ca/Mg, bicarbonate and nitrate (Fig. 4.7). For other measured parameters the seasonal changes had not appeared. In the Hubelj spring the parameters characterizing the geological origin showed the seasonal changes. The conclusion from the seasonal model could be the hinterland of the Hubelj is not changing a lot in different hydrological conditions.

In the Vipava spring only conductivity, the sum Ca+Mg and bicarbonate disclosed the seasonal changes. We could presume the hinterland of the Vipava

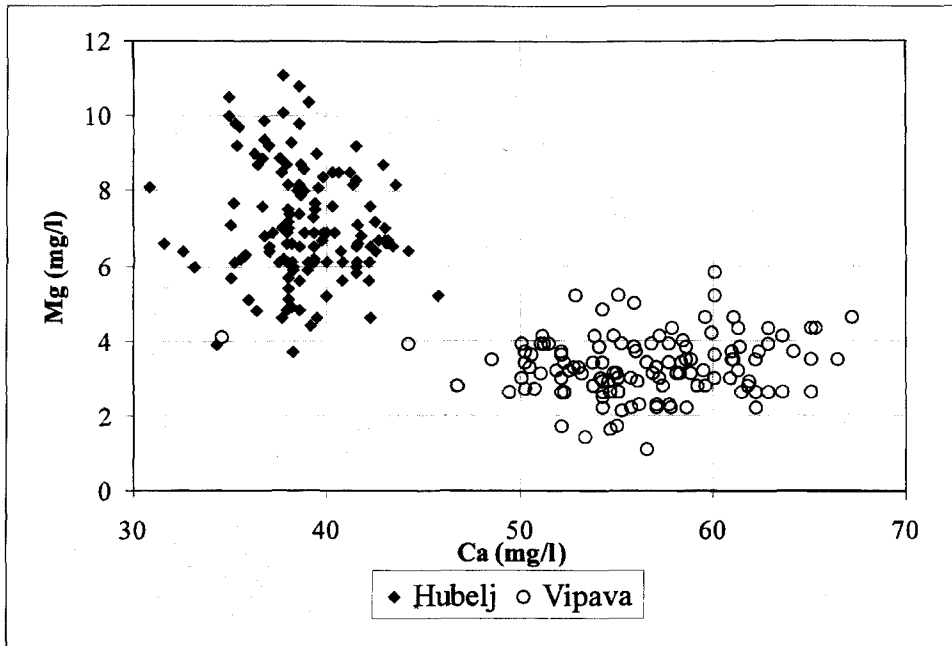


Fig. 4.6: Calcium and magnesium concentrations in the springs Hubelj and Vipava (4/2) from the analyses of all weekly samples taken during the observation period.

is changing at different hydrological conditions. Namely the concentrations of Ca and Mg are changing very irregularly (Fig. 4.8).

Very similar behavior we establish by the comparison of the ratio Ca/Mg with the flow (Fig. 4.9). In the Hubelj the ratio is very constant while in the Vipava much more variable. However, we observed the diminution of the magnesium concentration in the Hubelj up to the discharge about 5 m³/s (Fig. 4.10) while in the Vipava spring this interdependence did not occur.

Other analysed parameters (pH, sodium, potassium, sulphate, and chloride) have not shown any seasonal variation. Probably they are influenced besides geological structure from pollution sources (wastewater, fertilizers) as well.

Finally we tried to find out which time period and frequency of sampling would be enough to get satisfied statistical confidence level. The calculation of the statistical characteristics showed that the results for one year weekly sampling gave us almost the same result than three years long weekly sampling (Tab. 4.2 and Fig. 4.11). For the comparison we choose the year 1994 which was after hydrological characteristics a dry year and the year 1995 which was after hydrological characteristics an average year.

4. Hydrochemical investigations

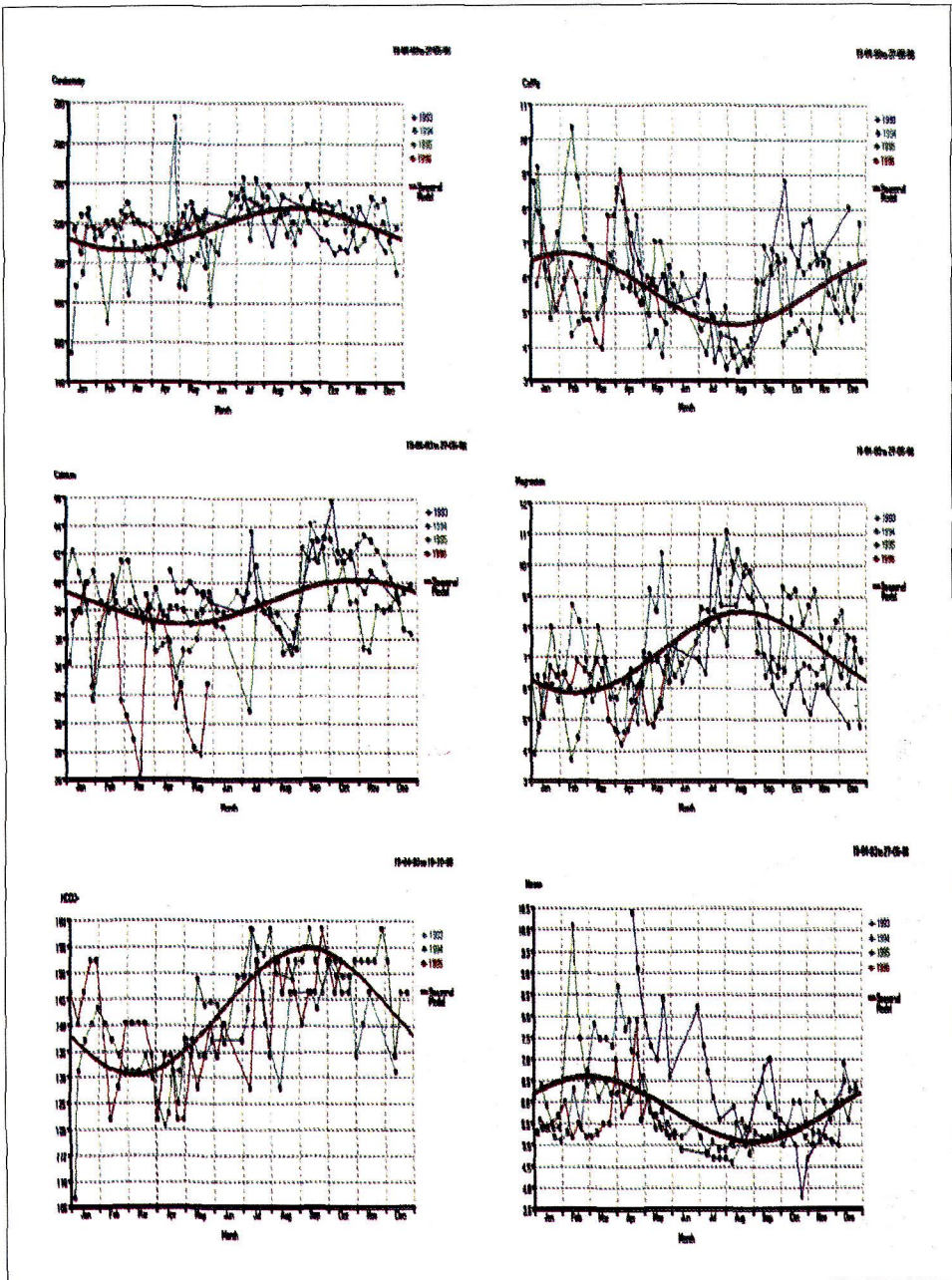


Fig. 4.7: Seasonal variation of conductivity, Ca/Mg ratio, calcium, magnesium, bicarbonate and nitrate in the Hubelj spring during the whole investigation period (weekly samples).

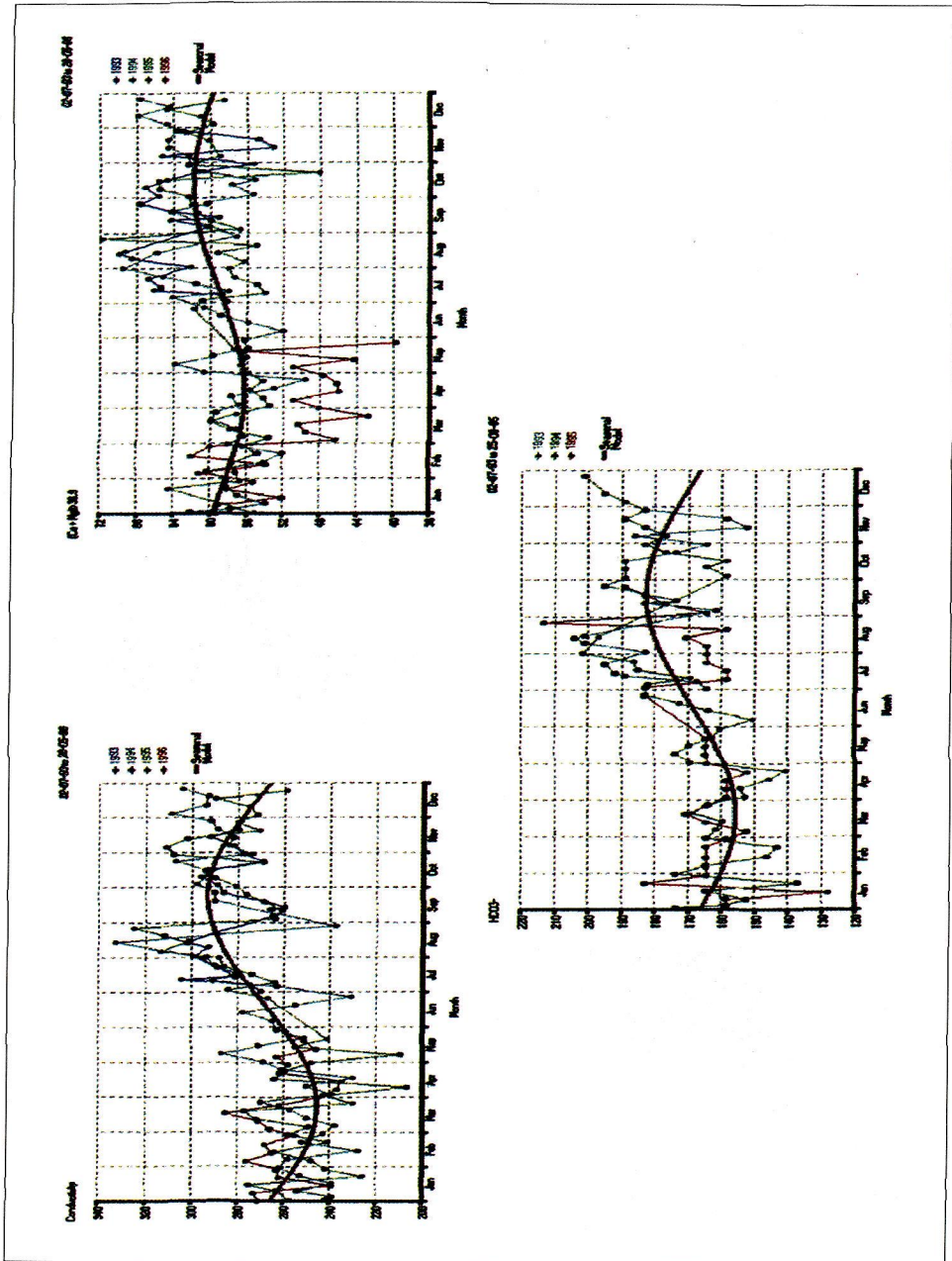


Fig. 4.8: Seasonal variation of conductivity, the sum of calcium, magnesium and bicarbonate in the Vipava spring 4/2 during the whole investigation period (weekly samples).

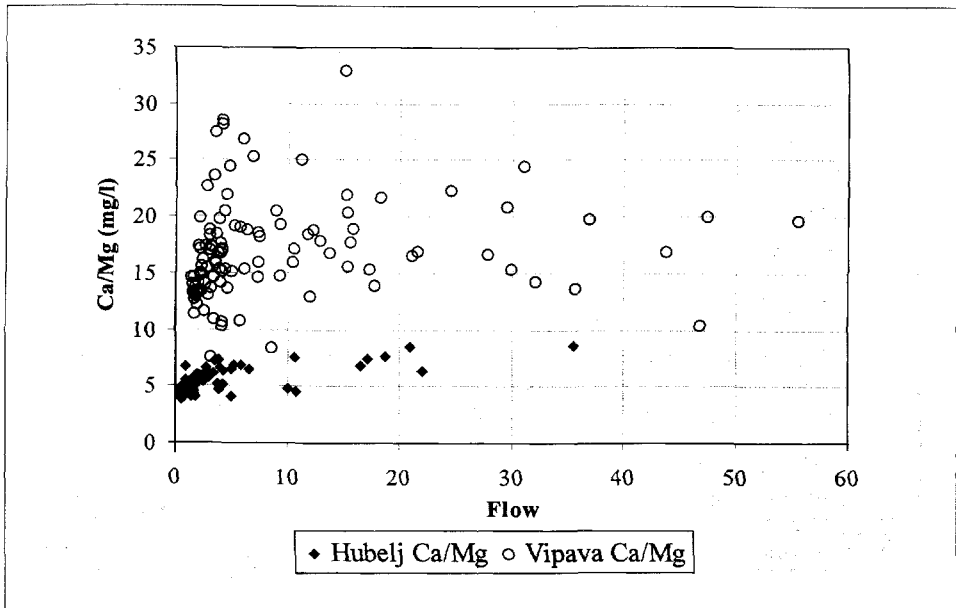


Fig. 4.9: Measured Ca/Mg-ratios versus discharge of the Hubelj and Vipava (4/2) springs for all weekly samples.

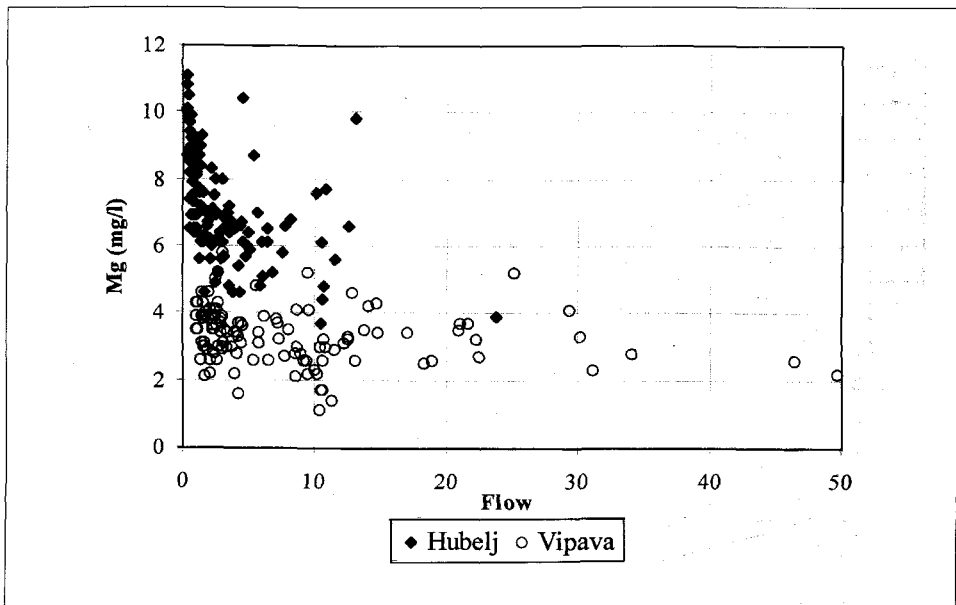


Fig. 4.10: Analysed Mg concentration versus discharge in the Hubelj and Vipava (4/2) spring for all weekly samples.

Tab. 4.2: The summary of the weekly samples in the spring Vipava and Hubelj in year 1994 and 1995.

THE SPRING HUBELJ

Parameter	Number of samples		Minimum value		Maximum value		Mean value		Standard deviation	
	1994	1995	1994	1995	1994	1995	1994	1995	1994	1995
Year	1994	1995	1994	1995	1994	1995	1994	1995	1994	1995
Conductivity - $\mu\text{S/cm} - 25^\circ\text{C}$	51	49	155	170	273	237	218	216	19.2	13.4
pH	46	49	7.2	7.2	8.3	8.5	8.0	8.0	0.27	0.21
Calcium	51	49	34.3	30.9	44.2	42.5	39.5	37.8	2.2	2.7
Magnesium	51	48	3.9	3.7	11.1	10.5	7.2	7.1	1.6	1.6
Sodium	51	49	0.9	0.8	1.2	1.2	1.0	1.0	0.08	0.14
Potassium	51	49	0.2	0.1	0.5	0.3	0.2	0.2	0.04	0.04
Bicarbonate	51	39	106.8	122.0	158.6	158.6	142.7	140.6	11.4	10.1
Nitrate	51	47	4.6	4.8	8.7	10.1	5.9	5.8	0.97	0.88
Sulphate	51	49	5.3	5.8	15.5	17.4	9.1	9.1	2.1	2.1
Chloride	51	49	1.3	1.5	3.3	2.5	2.0	1.8	0.38	0.31

THE SPRING VIPAVA 4/2

Parameter	Number of samples		Minimum value		Maximum value		Mean value		Standard deviation	
	1994	1995	1994	1995	1994	1995	1994	1995	1994	1995
Year	1994	1995	1994	1995	1994	1995	1994	1995	1994	1995
Conductivity - $\mu\text{S/cm} - 25^\circ\text{C}$	49	48	228	207	333	325	270	269	24.6	25.7
pH	47	48	7.5	7.4	8.3	8.4	8.0	8.0	0.18	0.17
Calcium	49	48	46.8	28.4	65.3	67.2	56.3	53.8	4.2	6.8
Magnesium	49	46	1.1	1.4	5.8	5.0	3.3	3.3	0.93	0.73
Sodium	49	47	1.1	0.8	2.3	3.3	1.6	1.5	0.25	0.40
Potassium	49	47	0.2	0.2	0.7	2.3	0.4	0.4	0.11	2.3
Bicarbonate	45	35	137.3	128.1	201.9	213.5	169.3	166.3	16.1	13.7
Nitrate	49	48	5.2	3.4	8.0	8.4	6.3	6.7	0.62	0.92
Sulphate	49	48	7.8	8.2	17.5	14.5	10.9	11.3	1.7	1.4
Chloride	49	48	1.5	1.6	3.9	2.9	2.3	2.2	0.46	0.34

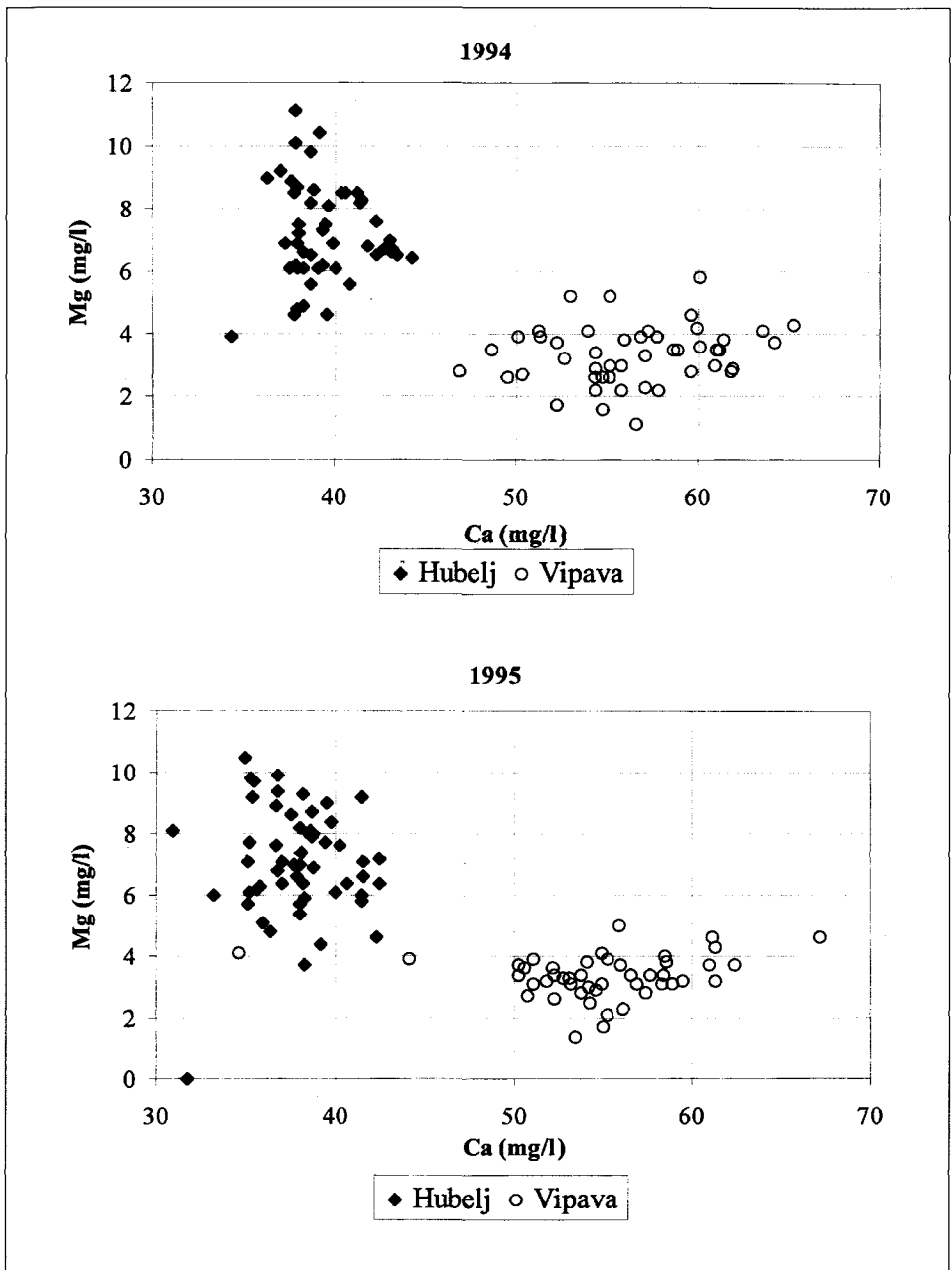


Fig. 4.11: Calcium versus magnesium concentration in the Hubelj and Vipava (4/2) spring, separately for the weekly samples in the hydrological dry year 1994 (above) and the hydrological average year 1995 (below).