

## **2.7. WATER QUALITY**

### **2.7.1. Long-term Quality Monitoring (M. ZUPAN)**

#### **2.7.1.1. Introduction**

Long-term water quality monitoring of the springs in Slovenia has been run since 1990. Already the first results of some main springs at the foot of the Trnovo plateau reminded that some pollution sources in the catchment area exist. In the frame of the present project the monitoring program in the springs was more extensive in years 1993-96.

#### **2.7.1.2. Sampling And Chemical Analyses Program**

The samples for the water quality observations in the following sampling points were taken in 1993-1996:

The Vipava spring	15 times for basic physical, chemical and bacteriological analysis and 6 times for the analysis of heavy metals and organic micropollutants in water and sediments and saprobiological analysis
The Hubelj spring	15 times for basic physical, chemical and bacteriological analysis and 6 times for the analysis of heavy metals and organic micropollutants water and sediments and saprobiological analysis
The Lijak spring	1 time for basic physical, chemical (including heavy metals and organic micropollutants in water) and bacteriological analysis in 1993; later the sampling was impossible because the borehole was stopped
The Mrzlek spring	3 times for basic physical, chemical (including heavy metals and organic micropollutants in water) and bacteriological analysis
The Podroteja spring	14 times for basic physical, chemical and bacteriological analysis and 6 times for the analysis of heavy metals and organic micropollutants in water and sediment and saprobiological analysis.
In the catchment area	two water supply captures in Čepovan (Čepovan and Čepovan Puštale) were sampled and analysed once in 1993; physical, chemical (including heavy metals and organic micropollutants in water and sediment) and bacteriological analysis

The investigation program was run conforming to the methodology recommended by international organisations.

### 2.7.1.3. Analytical Methods And Water Quality Standards

Sampling was done in various seasons of the year, preferably at low to mean low discharges. Samples for all types of analyses at one location were taken simultaneously. Samples were taken at a depth of 0.5 m and as close to the spring outlet as possible. In waters less than 1 m deep, samples were taken at mid depth.

When sampling, air and water temperature, as well pH value, conductivity, free carbon dioxide and dissolved oxygen were measured. Samples for determining nitrite, chemical oxygen demand (COD), colour, and phosphates were conserved, samples for determining detergents, phenols, mineral oils, and formaldehyde were cooled.

#### Basic physical and chemical analyses:

In unfiltered, mixed samples, suspended solids, chemical oxygen demand (COD), biochemical oxygen demand (BOD), phenols, and detergents were determined. The unfiltered, sedimented sample was used to determine ammonium and nitrite ion, real colour, mineral oils, formaldehyde and ligninsulphonates. Other analyses were performed on samples filtered in Filtrak 388.

Samples are analysed in the shortest possible time according to the following standard analysing methods for determining the basic water-pollution parameters (3, 4, 5):

determination of free carbonic acid:	titration with NaOH
determination of dissolved oxygen:	titration acc. to Winkler and measuring by an WTW probe
determination of COD:	$K_2Cr_2O_7$ and $KMnO_4$
determination of Ca and Mg ions:	titration with NaEDTA
nitrate ions:	Na - salicylate procedure
nitrite ions:	procedure with sulfanilic acid solution
iron ions:	procedure with 1,10 - phenanthroline
$SiO_2$ :	procedure with ammonium molybdate solution
aluminium:	procedure with alizarin
actual colour:	comparison with $K_2PtCl_6$ standards
anionic surfactants in detergents:	methylene-blue method
phenols:	procedure with 4-aminoantipyrine
ammonium ions:	procedure with Nessler reagent
phosphate ions:	procedure with ammonium molybdate solution

sodium and potassium:	flame AAS
sulphate ions:	titration by thorin (6)
formaldehyde:	procedure with phenylhydrazine hydrochloride (7)
mineral oils:	fluorescence measurement in hexan-extract (8)
ligninsulphonates:	fluorescence method (9)

### **Analyses of heavy metals and organic compounds**

Sampling of water, suspended solids, and sediments for analyses of metals and organic compounds (organic micropollutants) was performed according to the sampling methods as stated by DIN 38402-T15 and ISO 5667-T6. Concentrations of individual elements were measured by analytical procedures according to the standards stated in Table 2.10.

The following organic compounds were analysed in unfiltered water by the method of gas chromatography: phenols, pesticides, polycyclic aromatic hydro-

*Tab. 2.10: Analytical methods to determine the content of metals in water, suspended solids, and river sediment.*

<b>METAL</b>	<b>WATER</b>		<b>SEDIMENTS AND SUSPENDED SOLIDS</b>	
	<b>Regulation</b>	<b>Method</b>	<b>Regulation</b>	<b>Method</b>
Copper	DIN 38406-T7	F AAS	DIN 38406-T7	F AAS
Chromium	DIN 38406-T10	ET AAS	DIN 38406-T10	F AAS
Nickel	DIN 38406-T21	F AAS	DIN 38406-T21	F AAS
Zinc	DIN 38406-T21	F AAS	DIN 38406-T21	F AAS
Lead	DIN 38406-T21	ET AAS	DIN 38406 T21	F AAS
Cadmium	DIN 38406-T19	ET AAS	DIN 38406 T19	F AAS
Mercury	DIN 38406-T12	CV AAS	DIN 38406 T12	CV AAS

Notes: F AAS Atomic absorption spectrophotometric analysis, flame AAS, instrument PE 1100B

ET AAS Atomic absorption spectrophotometric analysis, electrothermal AAS, instrument Zeeman 3030

CV AAS Atomic absorptional spectrophotometrical analysis, cold vapour AAS, instrument PE 2380 MHS 20

*Tab. 2.11: Analytical methods to determine the content of organic compounds in water.*

	<b>Regulation</b>	<b>Method</b>
Pesticides	EPA 608, 1982 and DIN 38407-T6 and T14	GC/MS/SIM
Phenols	EPA 604 and ref. 21	GC/MS/SIM
PAO	EPA 610	GC/MS/SIM
PCB	EPA 608, modified	GC/ECD
AOX	DIN 38409 - T14	Stroehlein Coulomet 702 CL
EOX	DIN 38414 - T17	Stroehlein Coulomet 702 CL

## 2. Natural background

carbons, (PAH) and polychlorinated biphenyles (PCB). Also the adsorbed organohalogen compounds (AOX) were analysed and GC/MS screening was performed (identification of untargeted organic compounds). Analytical methods for determining concentrations of organic compounds in water are given in Table 2.11.

PCB was determined in the untreated sample of the sediment too. A GC/MS screening was made from the extract of the sediment to identify untargeted organic compounds. As well halogenated extracted organic compounds (EOX) were analysed.

### Saprobiological and bacteriological analyses

For the evaluation of the quality of surface waters from the biological point of view we used the saprobic system (10 - 15) and the calculation of the value of the saprobic index of a biocoenosis (16, 17). The value of the saprobic index (SI) increases with the deterioration of the living conditions from 1 to 4. Samples were taken biannually, in the cold and in the warm season of the year at lower discharges. The biological material was sampled in the littoral of the effluent down to a depth of ca. 0.5 m, where the sampling was not hampered by either water depth or speed. Semiquantitative and qualitative samples of periphyton and macrozoobenthos were taken. Macrozoobenthos was collected in the gravel to a depth of down to 15 cm in the ground semiquantitatively by means of a standard manual net (ISO 7828(E), 1985) with 0.5 x 0.5 mm mesh.

With regard to the value of the saprobic index, the river is at a particular sampling point ranged into the corresponding quality class according to the values stated in Table 2.12.

The bacteriological conditions of surface waters are subject to change due to the nature of the rivers, therefore the results of bacteriological analyses reflect the current state, i.e. pollution. Samples for bacteriological analyses were taken simultaneously with the samples for physicochemical analyses to be analysed according to the standard methods (4). The most probable number of

Tab. 2.12: *Quality classes according to the value of saprobic index.*

Trophic degree	SI value	Quality class	Description of the quality of the water body
oligosaprobic	1.0 - 1.5	1	uncharged to very little charged
oligo to beta	1.51 - 1.8	1 - 2	little charged
betamezosaprobic	1.81 - 2.3	2	moderately charged
beta to alfa	2.31 - 2.7	2 - 3	critically charged
alfamezosaprobic	2.71 - 3.2	3	heavily polluted
alfa to poly	3.21 - 3.5	3 - 4	very heavily polluted
polysaprobic	3.51 - 4.0	4	excessively polluted

bacteria (MPN/l) was determined and the following more important groups of bacteria were qualitatively determined as well:

faecal coliforms, faecal streptococci, *Proteus* sp., *Pseudomonas aeruginosa*, sulphite-reducing clostridia and total number of aerobic mesophilic bacteria.

### Standards and guidelines for water quality assessment

In general the Slovenian regulation classifies running waters with regard to their potential utilisation into four quality classes:

- **1<sup>st</sup> class:** waters which in their natural state or following disinfection may be used as drinking-water, in food-processing industry, as well as in breeding high-class fish species (Salmonidae);
- **2<sup>nd</sup> class:** waters which in their natural state may be used for bathing, water sports, breeding other species of fish (Ciprinidae), or following normal treatment (coagulation, filtration and disinfection), may be used as drinking-water or in food-processing industry;
- **3<sup>rd</sup> class:** waters which may be used in irrigation, or, following normal treatment, in industry, except in food-processing industry;
- **4<sup>th</sup> class:** waters which may be used for any purpose only following an adequate treatment.

The criteria used in ranging spring water courses into quality classes according to the contents of metals in water and suspended solids are shown in Table 2.13. Concentrations in bold type in the table make up the division between 1<sup>st</sup>-2<sup>nd</sup> and 3<sup>rd</sup>-4<sup>th</sup> quality class.

Table 2.13. lists criteria for categorising watercourses into quality classes according to the content of metals in sediments. The criteria are based on natural contents of metals in carbonate sediment rocks (18, 19), amended with the results of investigation of certain surface waters in Slovenia at their springs or in polluted sections. Values in bold indicate the division between natural

*Tab. 2.13: Standards and guide-lines for classification of watercourses into quality classes according to the contents of metals in water and suspended solids.*

Metal µg/l	Classification into quality classes			
	1.	2.	3.	4.
Cooper	< 30	100	140	> 140
Chromium	< 45	150	800	> 800
Nickel	< 15	50	140	> 140
Zinc	< 50	200	1400	> 1400
Lead	< 15	50	140	> 140
Cadmium	< 1.5	5	15	> 15
Mercury	< 0.5	1	1.4	> 1.4

Tab. 2.14: Standards and guide-lines for classification of watercourses into quality classes according to the contents of metals in river sediment

Metal µg/l	Classification into quality classes			
	1.	2.	3.	4.
Copper	< 50	50 - 100	100 - 340	> 340
Chromium	< 75	75 - 150	150 - 540	> 540
Nickel	< 50	50 - 100	100 - 360	> 360
Zinc	< 650	650 - 1300	1300 - 4600	> 4600
Lead	< 80	80 - 120	120 - 1000	> 1000
Cadmium	< 6	6 - 12	12 - 40	> 40
Mercury	< 0.1	0.1 - 0.2	0.2 - 1	> 1

values and pollution.

Table 2.14 lists criteria for categorising into 1.-2. quality class according to the content of organic micropollutants considering EC (20,21) and WHO (22) recommendations. The AOX and EOX are used as group criteria for monitoring the pollution with chlorinated organic compounds. The value of 0.5 - 2.5 µg EOX/kg air dried sample represents the natural background, a concentration from 30 - 700 µg EOX/kg might cause the extermination of some benthos organisms (23).

The identification of organic compounds in the GC/MS screening of samples of waters and sediments shows which organic compounds are present in watercourses and makes it possible to determine the pollution caused by man. In performing and evaluating the analyses less stress is laid on the quantity. Based on GC/MS screening, watercourses were evaluated according to the following criteria (Tab. 2.15):

Tab. 2.15: Considered standards for classification of watercourses into the first(1.) and the second (2.) quality class according to the contents of organic micropollutants.

ORGANIC COMPOUND	1.-2. QUALITY CLASS
AOX - µg Cl/l	< 5
Mineral oils - mg/l	0.01
Polychlorinated biphenyles - µg/l	0.1
Phenols - µg/l	0.001
Polycyclic aromatic hydrocarbons - µg/l	0.2
Pesticides - individual - µg/l.	< 0.1
Pesticides - total - µg/l	< 0.5

- 1<sup>st</sup> quality class:** the water shows presence of compounds of natural origin only
- 2<sup>nd</sup> quality class:** the water shows presence of compounds which are biodegradable and may be removed from the water with simple methods used in preparation of drinking water
- 3<sup>rd</sup> quality class:** the water shows presence of not easily destructible compounds, which when infiltrating into the groundwater remain almost unchanged or are transformed into stable metabolites
- 4<sup>th</sup> quality class:** the water shows presence of chlorinated compounds which are typical man-caused pollutants, compounds which tend to accumulate in living beings and compounds with carcinogenic and/or mutagenic potential.

#### 2.7.1.4. Results and water quality assessment

The pollution of the water springs, in particular of the water, was relatively slight. The chemical parameters in most water samples did not exceed the normative for drinking water. On the other hand relatively high concentrations of mercury, cadmium, lead and copper in sediment samples were measured, which means that the pollution was nevertheless present in the investigated springs (Fig. 2.27.). The phenolic compounds and polycyclic aromatic hydrocarbons (PAH) were very often present in water samples of the Vipava, Hubelj and Podroteja springs (Fig. 2.28). The number of present PAHs determined in GC/MS screening was very high in water and sediments extracts. In the all investigated springs numerous compounds which originate from different human activities, were determined in GC/MS screening of water and sediment as well.

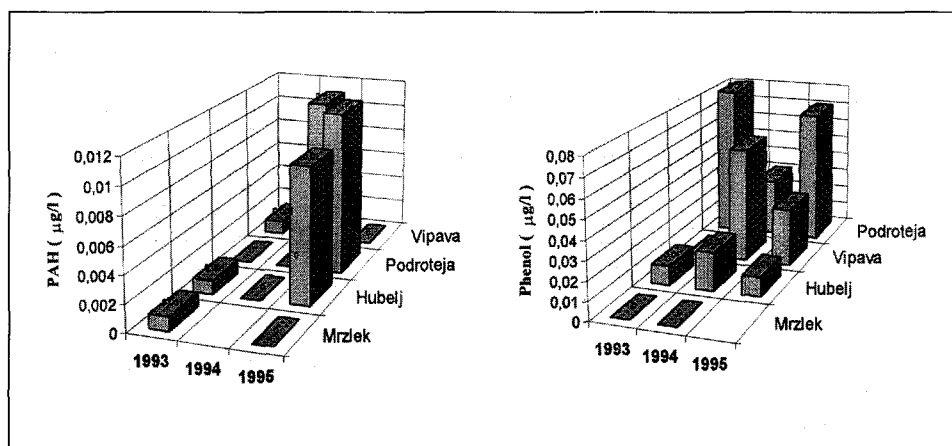


Fig. 2.28: Polycyclic aromatic hydrocarbons and phenolic compounds in the water samples of the investigated springs (maximal values).

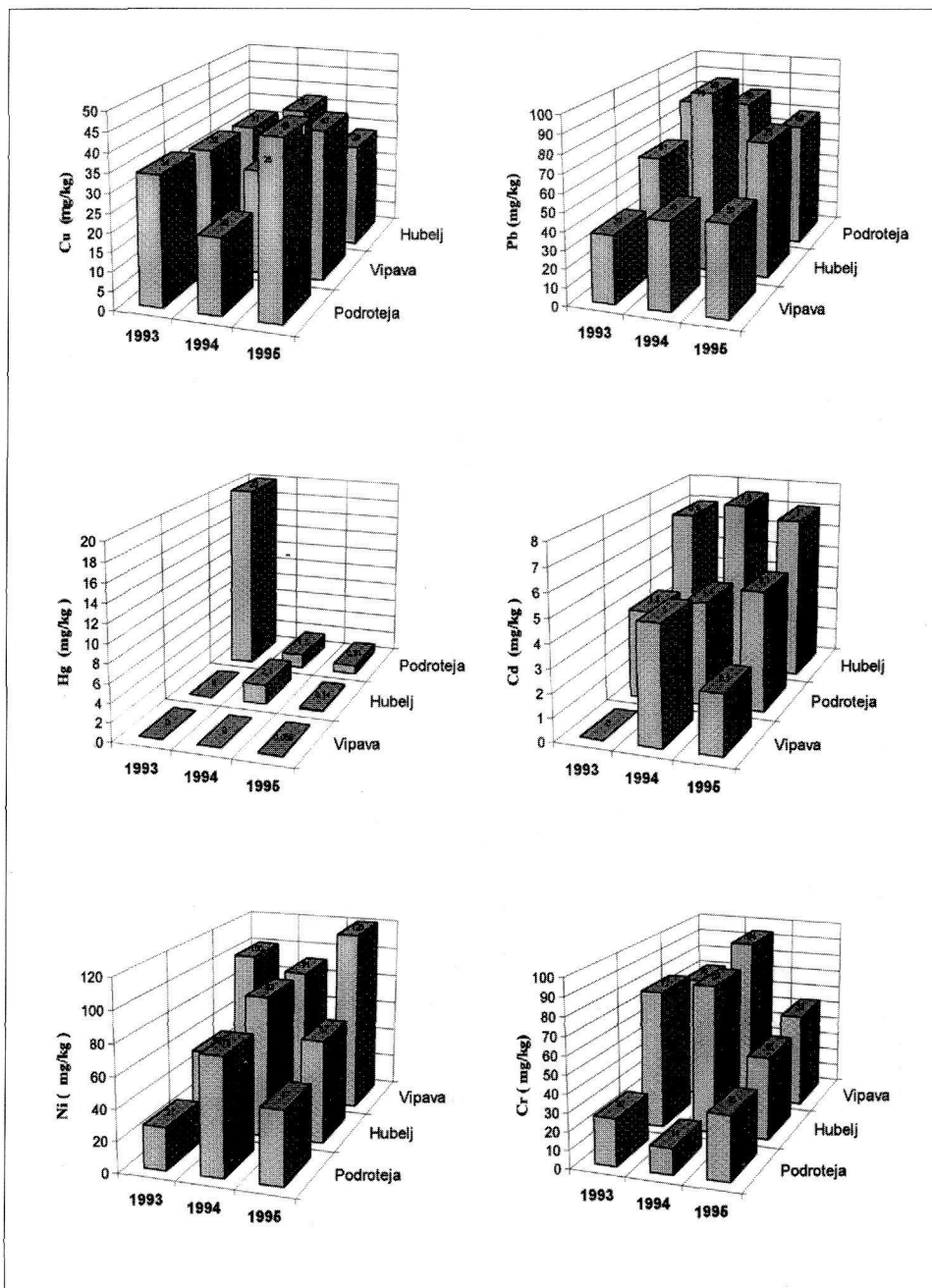


Fig. 2.27: Heavy metal levels (maximal values) in the sediment samples of the investigated springs.



Tab. 2.16: Content of heavy metals in the sediments of the two water springs in Čepovan.

Water spring	Copper mg/kg	Zinc mg/kg	Cadmium mg/kg	Chromium mg/kg	Nickel mg/kg	Lead mg/kg	Mercury mg/kg
Čepovan	58	583	4.4	81	61	<10	<0.05
Čepovan — Pultale	56	1600	6.5	37	43	228	<0.05

Tab. 2.17: Content of phthalic acid esters (sum) in the investigated springs.

	Sum of phthalic acid esters - µg/l		
	1993	1994	1995
Čepovan	0.065	-	-
Vipava	0.120	0.115	0.520
Hubelj	0.126	0.200	0.360
Mrzlek	0.175	0.234	0.420
Lijak	0.145	-	-
Podroteja	0.260	0.615	1.110

In the catchment area we analysed two springs in Čepovan, which were polluted by polycyclic aromatic hydrocarbons in water ( $0.009 \mu\text{g/l}$ ) and sediment. The concentrations of single PAH-s were not high but they were present in great number, thirteen in each Čepovan spring. We determined high contents of heavy metals in the sediment as well (Tab. 2.16). Phthalic acid esters were determined once a year and were found in all analysed water samples. Besides we establish a trend of increasing concentration (Table 2.17).

The presence of heavy metals and many different organic compounds in water and sediment samples is pointing to a constant pollution from the hinterlands.

For the estimation of the water quality in the investigated springs all in the chapter 2.7.1.2 mentioned criteria have been taken into account and the results are shown in the Table 2.18.

WATER-COURSE	SAMPLING POINT	DATE	QUALITY EVALUATION						FINAL EVALUATION	
			PHYSICO-CHEMICAL ANALYSES			BIOLOGICAL ANALYSES				
			Basic	Metals*	Organic compounds**	Saprobio-logical	Bacteriological			
							MPN/l	Bacteria of faecal origin***		
KRAŠKI IZVIR	Podroteja	09.06.93	2	1/3 -Hg	1/1,1-2,1,1-2/2 1-2	1	1	2	++	2
		19.11.93	1					1	0	0
		14.2.93	1 - (2)					1	0	0
		15.03.94	2	1/1				1	0	0
		23.06.94	(1) - 2					1	0	0
		05.07.94	(1) - 2		1/1,1,1,1,1-2 1	1	1	1	0	1 - 2
		13.09.94	(1) - 2					1	+	
		04.04.95	2	1/2 -Hg	1/1,1,1,1,2-3/1-(2) 2	2	1	1	0	2
		11.07.95	2 - (3)					1	0	0
		03.08.95	2					1	0	0
VIPAVA	Vipava	03.10.95	2					1	0	
		18.03.93	2		1/1,1,1,1,2-3/2 2-1	1	1	1	0	
		09.06.93	2	1/1				1	+	2
		29.07.93	2					2	0	
		18.11.93	1 - (2)	1/1				1	0	2
		16.03.94	2		1/1,1,1,1,1-2/1-2	1	1	2	+	
		23.06.94	2					1	+	
		06.07.94	2					1	0	2
		14.09.94	- 2		1/1,1,1,1,2-3/2-3 2	2	1	1	0	
		04.04.95	2	1/1				1	0	
HUBELJ	spring	11.07.95	2					1	0	
		02.08.95	2	2/l Zn,Ni/-				1	0	
		03.10.95	2	1/1	1/1,1,1,1,1/1	1	1	1	++	
		09.06.93	1 - 2					1	0	1 - 2
		29.07.93	1 - 2					1	0	
		18.11.93	1 - 2					1	0	
		14.12.93	1					1	0	
		16.03.94	1 - 2	1/2 -Zn,Hg,Cd				1	0	2
		23.06.94	1 - 2		1/1,1,1,1,1/3 2-1	1	1	1	0	
		06.07.94	1 - 2					1	0	
		14.09.94	1 - 2					1	0	
		04.04.95	1 - 2					1	0	
		11.07.95	2 - (3)	1/2 -Hg	1/4,1,1,1,(2)-3/2-3 3	1	1	1	0	2/3*
		02.08.95	1 - 2					1	0	
		03.10.95	1 - (2)					1	0	

Notes:

- \* evaluation of metals - in water / in sediment; metals present in higher concentration in water / in sediment
- \*\* sequence of evaluations of organic compounds: PCB (water/sediment), phenols, pesticides, polycyclic aromatic hydrocarbons, GC/MS (water/sediment); final evaluation with regard to the present organic compounds; PCB in evaluation mark means that only polychlorinated biphenyls in water / in sediment have been analysed; EOX - extracted organohalogen compounds; AOX - adsorbed organohalogen compounds
- \*\*\* each + sign denotes one species of qualitatively determined bacteria of faecal origin
- water quality after GC/MS screening of organic micropollutants.

Notes:

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- \*\*\* each + sign denotes one species of qualitatively determined bacteria of faecal origin
- water quality after GC/MS screening of organic micropollutants.

Tab. 2.18: Evaluation of the quality of the investigated karstic springs in 1993-1995.

### **2.7.1.5. Contour diagrams of fluorescence intensity**

We used the excitation-emission matrix (EEM) method as pattern recognition technique and as semi-quantitative technique to follow the transport of natural and anthropogenic pollution in hydrologic system (WOLFBEISS 1993).

We scanned the 3D spectra in all background samples. Emission spectra (300 nm to 550 nm, 5 nm intervals) were scanned over the range of excitation wavelengths (300 nm to 500 nm, 5 nm intervals) on the Hitachi-4500 fluorescence spectrophotometer. Slit widths for both excitation and emission monochromators were set at 10 nm.

The comparison with the unchlorinated tap water shows that in all measured samples different organic compounds of unknown origin are present. Namely, we did not have the standards for this compounds and the determination of present compounds will be task for some investigation in the future.

### **2.7.1.6. Conclusions**

The chemical analyses of sediment in the Hubelj, Vipava and Podroteja springs have shown that pollution from the hinterlands is present and that water quality may suffer an abrupt deterioration. The results of microbiological analyses have been shown periodical pollution in the Podroteja, Hubelj and Vipava springs as well.

Investigations of water quality should be followed by appropriate actions. Actions to protect water quality wherever it is still satisfactory and rehabilitation actions where appropriate.

## **2.7.2. Agricultural threats to pollution of water of Trnovsko-Banjška Planota (B. MATIČIČ)**

### **2.7.2.1. Introduction**

The objective has been to determine the relationship between the soil water balance and mineral balance in the Karst region of Trnovsko-Banjška Planota in western part of Slovenia above Vipava valley and to find out if the possible excessive use of fertiliser and/or high intensity of animal husbandry in upland catchment area on Trnovsko-Banjška Planota could affect the quality of drinking water down in Vipava valley.

The altitude of Trnovsko-Banjška Planota is about 800 m. In this region mainly shallow soil types (with depth of 10-50 cm) on limestone are found with low water holding capacity (22-142 mm) and high rate of infiltration.

The amount of precipitation in Trnovsko-Banjška Planota is very high. The average annual value (1951-1980) in meteorological station Otlica was 2457