UNDP/GEF Danube Regional Project
Strengthening the Implementation Capacities for Nutrient Reduction and Transboundary Cooperation in the Danube River Basin

Five-years Report on Water Quality in the Danube River Basin Based on Trans-National Monitoring Network

1996-2000

Project Component 2.2: Development of operational tools for monitoring, laboratory and information management with particular attention to nutrients and toxic substances

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Executive summary

The objective of this report was to assess water quality in Danube River basin, including classification and identification of spatial and temporal changes. The basis for assessment is data on physico-chemical and biological determinands collected in the frame of TNMN in five-years period 1996 – 2000. The main assessment objectives were as follows:

- Checking of compliance with water quality target values expressed by joint classification prepared for Danube River Basin;
- Identification of water quality changes along the Danube River;
- Detection of trends in water quality;
- Assessment of dangerous substances content in water in accordance to EQS established or proposed for use in EU.

In general, following facts concerning classification and trend evaluation of the processed TNMN data should be highlighted:

Nutrients

Ammonium-N and nitrite-N concentrations increase from upper to lower Danube. In the Danube River, 53.3 % of ammonium-N and 37.2 % nitrite-N values were found to be above the target limits for these determinands. A special concern should be paid to the ammonium-N content recorded on the Arges river, where all five yearly values of C90 in time period 1996-2000 were above the limit for Class V; these extremely high values, correlated with BOD5 values, show the impact of untreated or insufficiently treated waste waters from municipalities. In the Danube River, occurrence of ammonium-N shows a decreasing tendency from 1996 to 2000 in the upper part and in the middle section in Slovak monitoring sites.

The spatial distribution of nitrate-N concentrations shows a decrease from upper/middle to lower Danube. Tributaries with the highest content of nitrate-N are Morava, Dyje, Sio in the upper/middle part, and Iskar, Russenski Lom, Arges and Prut in the lower part of river basin. For nitrate-N concentrations the fluctuations in time profile are low for the Danube River, but rather high for the tributaries.

Orthophosphate-P shows a spatial pattern similar to that of total phosphorous characterized by a slight increasing profile from upper to lower Danube. In the upper/middle part of the Danube a decreasing tendency in P concentration is seen in the section from Danube-Bratislava (km 1869) down to Danube-Szob (km 1708) with an exception at Danube-Medvedov/Medve (km 1806). In general, the time variance of total P concentrations is much higher than that of ortho-phosphates.

Heavy metals

Except of manganese, for which a maximum of the spatial profile is present in the middle Danube reach, for most of the discussed heavy metals the general pattern is an increase from the upper and middle to the lower Danube. Furthermore, the heavy metals content in some tributaries – mainly those located in the lower Danube - is higher than the content in the Danube River itself.

The contamination of the Danube River by lead and copper was found rather high. A slightly better was the situation for cadmium and mercury with 47.4% of values exceeding cadmium target level and 36.6% of values exceeding mercury target level. In general, relatively high fluctuations of heavy metal concentrations were observed along the Danube. Despite these uncertainties the development of heavy metal content in some tributaries was found positive – a decrease is indicated in Drava river (cadmium, chromium, copper, lead, nickel and zinc), in Arges (cadmium, chromium, copper, lead), Prut (cadmium, chromium, lead) and in Siret (chromium, copper, lead).

In general, five years trends of heavy metal pollution can hardly been evaluated because a relatively high deviation of results occurred. High values of heavy metals often result from high loads of suspended solids caused by flood events. The statistical parameter used in this report (90% percentile)

– was certainly influenced by such hydrological processes. For this five-years evaluation report the data on total concentration of heavy metals in water samples had been used because data related to dissolved fraction was not available in sufficient amount. Therefore, it must be stressed that such a rather scattered pattern of the heavy metal pollution data for the water matrix clearly supports future orientation of TNMN activities on the solid phase, i.e., in TNMN planning activities the analysis of suspended solids and sediments should be preferred.

Oxygen regime

Dissolved oxygen concentrations show positive results, with only 7.4% of values being below the quality target in the Danube River and 8.6% being below the quality target in monitored tributaries. Oxygen concentration decreases from upper to lower part of the Danube River, lowest values being in the section from Danube-Bazias to Danube-Novo Selo/Pristol. As for the tributaries, rather low oxygen content was identified in those located in the lower part of the river basin.

As for BOD values 13.3% of them are above the target value in the Danube River (mainly in the middle and in the lower sections) and 35.9% exceed the target value in tributaries. Organic pollution expressed by BOD increases along the Danube, reaching its maximum in the secion from Danube-Dunafoldvar (rkm 1560, H04) to Danube-Pristol/Novo Selo (rkm 834, RO02). The tributaries most polluted by degradable organic matter are Morava, Dyje and Sio in the upper/middle part of the Danube mainstream and Russenski Lom and Arges in the lower part.

For CODCr, 22.4% of all values for the Danube mainstream and 39.7% for tributaries were found above the quality target; the situation is more positive in case of CODMn - no value above this limit for the Danube River and 18.2% for tributaries. In principle, the results obtained for CODCr and CODMn show the highest values in the lower part of the Danube River.

Organic micropollutants

The organochlorine compounds (Lindan and p,p'-DDT) showed similar spatial profile, with an increasing pattern from upper/middle to lower Danube. The polar pesticide Atrazine was undetectable at most of the monitoring sites along the Danube River, only 12.5% of the data were found above the target limit. In tributaries, 30% of Atrazine values were above the quality target, the maximum values were found in rivers Sio and the Sajo.

For the volatile organic compounds, data is available for upper and middle Danube only. Chloroform and tetrachloroethylene show values above the target limits in a following pattern: 29.0% of the Danube samples and 39.5% of the samples taken from tributaries exceeded the target values for chloroform, for tetrachloroethylene the respective numbers were 13.6% for the Danube and 7% for tributaries. The situation was found to be better for tetrachloromethane and trichloroethylene - in the Danube River mainstream no value was detected above the target limit for these compounds, while in tributaries only a small percentage of all data (2.3%) was above the target limits for both these determinands.

Biological determinands

Evaluation of saprobic index of macrozoobenthos using Austrian standard ÖNORM M6232 showed that the Danube River and most of its tributaries correspond to classes II – II-III. Only Sava River was characterized by a worse quality class (III – III-IV), however, within the years the situation improved.

In 1996 – 2000 the microbiological water quality corresponded to classes I – IV in the Danube River mainstream. Some tributaries, as e.g., Vah, Tisza and Siret can be characterized as extensively polluted, however, data from many other relevant tributaries is missing. It was observed that sedimentation had positive effects to number of total coliforms below Gabčíkovo Reservoir, Iron Gates and in Danube Delta as well.

For biological determinands a slightly positive time trend appeared in case of saprobic index of macrozoobenthos, but no significant trend in microbiological determinands was observed.

1. Introduction

The Danube River flows through ten countries, and its large river basin of 817 000 km^2 is shared between 17 countries. The waters in Danube River Basin serve people for many purposes – drinking water preparation, use for industrial and agricultural activities, recreation, hydropower generation, and navigation. Very important function of the rivers in Danube River Basin is ecological function, to which attention is growing also due to the latest development of EU legislation. On the other hand human activities result in discharging of waste waters, release of pollutants from diffuse sources, change of natural habitats for aquatic biota and risk of accidental pollution. To protect waters in the Danube River Basin and to ensure their functions and sustainable human uses, cooperation of Danubian states is inevitable.

The Danube River Protection Convention (DRPC), signed in 1994 and entering into force in 1998, creates the basis for such cooperation. Its main objective is to achieve sustainable and equitable water management, including conservation, improvement and the rational use of surface and ground waters. Danubian countries shall take all appropriate legal, administrative and technical measures to at least maintain and improve environmental and water quality conditions of the Danube River and of waters in its catchment area.

To be able to assess the progress in improvement of environmental conditions of waters in Danube River basin, and to assess effectiveness of measures set up, the role of information from water quality monitoring is crucial. The Danube River Protection Convention says that the Contracting Parties shall cooperate in the field of monitoring and assessment. For this aim they shall harmonise or make comparable their monitoring and assessment methods and shall periodically assess the quality conditions of Danube River and the progress made by taken measures.

As one of the tools for implementation of DRPC, Joint Action Programme for the Danube River Basin (JAP) had been prepared defining the integrated measures for improvement of the environment related to the waters in the Danube River Basin. Danubian States and Permanent Secretariat of ICPDR had developed JAP for period of years 2001-2005. In relation to basin-wide cooperation in the field of monitoring JAP stresses necessity to prepare the data in such a way that allows using them in comparative way and serving as a reliable basis for making decisions throughout the Basin.

Presented report would like to contribute to fulfil the above-mentioned requirements on information related to the quality of waters in Danube River Basin. It contains assessment of the data, collected by Danubian countries in the period of years 1996-2000 in the frame of joint Trans-national monitoring network (TNMN).

2. Objectives of the report

The process of assessing of water quality in this report is an evaluation of the physico-chemical and biological status of waters based on the results collected in the frame of TNMN in five-years period 1996 – 2000, with the following main assessment objectives:

- checking of compliance with water quality target values expressed by joint classification prepared for Danube River Basin;
- identification of water quality changes along the Danube River;
- detection of trends in water quality;
- assessment of dangerous substances content in water in accordance to EQS established or proposed for use in EU.

Load assessment generally belongs to main assessment objectives and is of concern also in Danube River Basin. As the load assessment programme started in year 2000, it is not included in the 5-years summarising report.

This is the first time, when complete data sets from 5-years operation of TNMN will be processed. For the first time these data will be used for classification of water quality in accordance to joint classification system prepared for the Danube river basin; and for assessment of temporal and spatial changes in water.

The results of this activity should have not been seen as a self-standing activity, but should be seen in a broader context to recognise the needs for TNMN improvements. On one hand, in the report TNMN data from the first phase of its operation are evaluated, which can be used in identification of possible weak points in the monitoring programme and the following suggestions for future TNMN improvement. On the other hand it has to be mentioned that improvement of TNMN has to be strongly connected to continuous implementation of Water Framework Directive, which entered in force in EU in 2000 and Danube countries agreed on its joint implementation in the river basin.

3. History of TNMN

The first steps towards joint water quality monitoring network in Danube River basin were taken when governments of the Danube countries signed the Bucharest Declaration. The monitoring network used for the purposes of the Declaration consisted of eleven monitoring locations and were located on the Danube River itself where the river formed or crossed the border between the countries.

In 1991 the Danubian countries started preparation of the Convention on cooperation for the protection and sustainable use of the Danube River (DRPC), which was signed in 1994.
The Environmental Programme for the Danube River Basin, lead by a Task Force, also started in 1991 with the main objective to strengthen the operational basis for environmental management in the Danube River Basin and to support the Danubian countries to implement the DRPC.

In 1992, the Task Force agreed a three-year Work Plan (1992-95) with monitoring, laboratories and information management having between the main Programme actions. In 1992 the Monitoring, Laboratory and Information Management Sub-Group (MLIM-SG) was established to deal with this topic.
The main outcome of the three-year Work Plan was the Strategic Action Plan (SAP). Its approval marked the end of the first phase of the EPDRB (1992-95) and implementation was scheduled to start in the next phase (1996-2000).

The TNMN was originally designed in 1993 during the project “Monitoring, Laboratory Analysis and Information Management for the Danube River Basin”, conducted by the WTV Consortium in close cooperation with MLIM-SG.
The responsibility for TNMN was assigned to MLIM-SG, which consisted of three Working Groups – Monitoring WG, Laboratory Management WG and Information Management Working Group. MLIM-SG should address the development of water quality monitoring network in Danube River Basin; introduce harmonised sampling procedures and enhanced laboratory analysis capabilities; and form the core of a Danube information system on the status of in-stream water quality. The 1996 and 1997 budgets of Phare Multi-Country Environmental Programme allocated substantial funds to EPDRB projects to support further development of the monitoring and assessment programme and the launch of TNMN into operation.

After entry of the DRPC into force in October 1998, MLIM-Expert Group was incorporated in the organisational structure of International Commission for the Protection of the Danube River (ICPDR) and has been working on the basis of TORs agreed by the ICPDR Plenary Meeting. In accordance with the TORs, the overall objective of the MLIM-EG is to create a strengthened and more strategic approach to monitoring, laboratory and information management for surface waters. The key role of the Group is to address the organisational and operational aspects related to the monitoring of water riverine conditions in the Danube River Basin and to provide basic data as an input to the ICPDR information system.

4. Description of TNMN

4.1. Objectives of TNMN

TNMN has been designed with purpose to meet the main objectives defined for monitoring network in Danube River basin by the Work Plan of EPDRB. The Work Plan states that the monitoring network shall:

- strengthen the existing network set up by the Bucharest Declaration;
- be capable of supporting reliable and consistent trend analysis for concentrations and loads for priority pollutants;
- support the assessment of water quality for water use;
- assist in the identification of major pollution sources;
- include sediment monitoring and bioindicators;
- include quality control.

Furthermore, the Work Plan provides that:

- the monitoring network shall provide outputs compatible with those in other major international river basins in Europe;
- the monitoring network shall in future comply with standards used in the western part of Europe;
- the monitoring network shall be designed in a way to reflect immediate and long-term needs - starting with practical and routine functions already performed.

As was already mentioned, the TNMN was originally designed in 1993 during the project conducted by WTV Consortium. The implementation was agreed by MLIM-SG, but the design was further simplified for operation in the first phase, starting in 1996. The first phase is seen as a period with:

- the operation of a limited number of stations with defined objectives already included in national monitoring networks according to defined objectives;
- a determinand list reflecting the Bucharest Declaration and EU-Directives;
- an information management based on a simple data exchange file format between the countries.

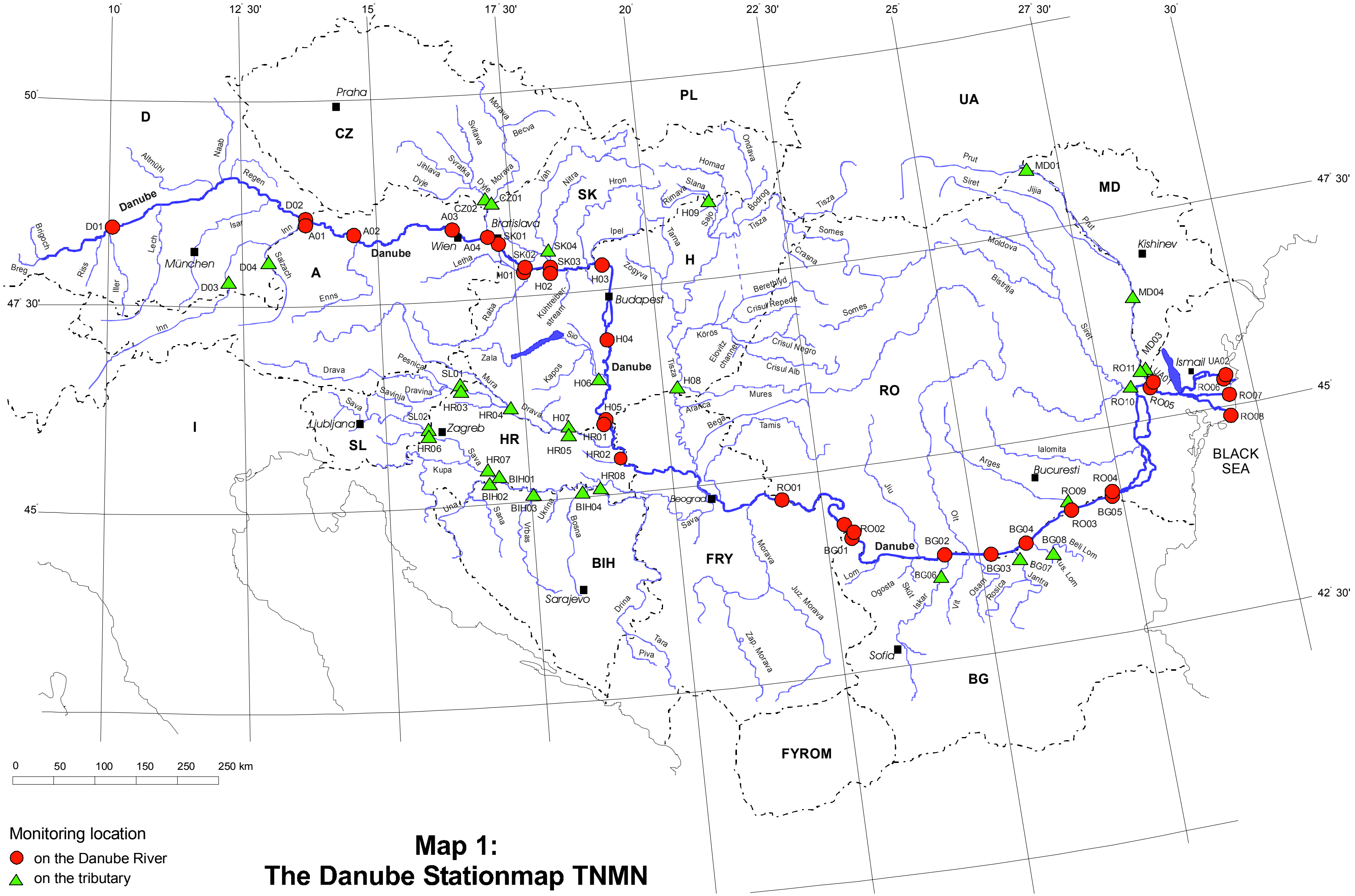
4.2. Network of monitoring locations

The monitoring network in the frame of TNMN builds on national surface water monitoring networks. To select monitoring locations for the purposes of international network in Danube River Basin, respecting also the above-mentioned TNMN objectives, the following concrete selection criteria had been set up:

- located just upstream/downstream of an international border
- located upstream of confluences between Danube and main tributaries or main tributaries and larger sub-tributaries (mass balances)
- located downstream of the biggest point sources
- located according to control of water use for drinking water supply

Monitoring location included in TNMN should meet at least one of the selection criteria.

The selection procedure has lead to preparation of a final list of 61 monitoring locations. These are given in Map.1. and Table 4.2.1 with basic information characterising the location. The monitoring locations in the Table 4.2.1 are grouped in accordance to countries and not as they are ordered along the Danube River.



Map 1:
The Danube Stationmap TNMN

Monitoring location
● on the Danube River
▲ on the tributary

Each monitoring location can have up to three sampling points, located on the left side, right side or in the middle of a river. More than one sampling point was proposed for selected monitoring locations in the middle and lower part of the Danube River and for large tributaries like Tisza and Prut Rivers are. In spite of the fact, that monitoring locations from Bosnia and Herzegovina create a part of the network, no data had been provided from them in evaluated period 1996-2000.

Table 4.2.1: List of monitoring sites.

Country Code	River Name	Town/Location Name	Latitude d. m. s.	Longitude d. m. s.	Distance [Km]	Altitude [m]	Catchment [km^2]	DEFF Code	Loc.in profile
D01	Danube	Neu-Ulm	48 25 31	10 1 39	2581	460	8107	L2140	L
D02	Danube	Jochenstein	48 31 16	13 42 14	2204	290	77086	L2130	M
D03	/Inn	Kirchdorf	47 46 58	12 7 39	195	452	9905	L2150	M
D04	/Inn/Salzach	Laufen	47 56 26	12 56 4	47	390	6113	L2160	L
A01	Danube	Jochenstein	48 31 16	13 42 14	2204	290	77086	L2220	M
A02	Danube	Abwinden-Asten	48 15 21	14 25 19	2120	251	83992	L2200	R
A03	Danube	Wien-Nussdorf	48 15 45	16 22 15	1935	159	101700	L2180	R
A04	Danube	Wolfsthal	48 8 30	17 3 13	1874	140	131411	L2170	R
CZ01	/Morava	Lanzhot	48 41 12	16 59 20	79	150	9725	L2100	R
CZ02	/Morava/Dyje	Pohansko	48 48 12	16 51 20	17	155	12540	L2120	R
SK01	Danube	Bratislava	48 8 10	17 7 40	1869	128	131329	L1840	M
SK02	Danube	Medvedov/Medve	47 47 31	17 39 6	1806	108	132168	L1860	M
SK03	Danube	Komarno/Komarom	47 45 17	18 7 40	1768	103	151961	L1870	M
SK04	/Váh	Komarno	47 46 41	18 8 20	1	106	19661	L1960	M
H01	Danube	Medve/Medvedov	47 47 31	17 39 6	1806	108	131605	L1470	M
H02	Danube	Komarom/Komarno	47 45 17	18 7 40	1768	101	150820	L1475	M
H03	Danube	Szob	47 48 44	18 51 42	1708	100	183350	L1490	LMR
H04	Danube	Dunafoldvar	46 48 34	18 56 2	1560	89	188700	L1520	LMR
H05	Danube	Hercegszanto	45 55 14	18 47 45	1435	79	211503	L1540	LMR
H06	/Sio	Szekszard-Palank	46 22 42	18 43 19	13	85	14693	L1604	M
H07	/Drava	Dravaszabolcs	45 47 00	18 12 22	78	92	35764	L1610	M
H08	/Tisza	Tiszasziget	46 9 51	20 5 4	163	74	138498	L1700	LMR
H09	/Tisza/Sajo	Sajopuspoki	48 16 55	20 20 27	124	148	3224	L1770	M
SI01	/Drava	Ormoz	46 24 12	16 9 36	300	192	15356	L1390	L
SI02	/Sava	Jesenice	45 51 41	15 41 47	729	135	10878	L1330	R
HR01	Danube	Batina	45 52 27	18 50 03	1429	86	210250	L1315	M
HR02	Danube	Borovo	45 22 51	18 58 22	1337	89	243147	L1320	R
HR03	/Drava	Varazdin	46 19 21	16 21 46	288	169	15616	L1290	M
HR04	/Drava	Botovo	46 14 27	16 56 37	227	123	31038	L1240	M
HR05	/Drava	D.Miholjac	45 46 58	18 12 20	78	92	37142	L1250	R
HR06	/Sava	Jesenice	45 51 40	15 41 48	729	135	10834	L1220	R
HR07	/Sava	us. Una Jasenovac	45 16 02	16 54 52	525	87	30953	L1150	L
HR08	/Sava	ds. Zupanja	45 02 17	18 42 29	254	85	62890	L1060	MR
BIH01	/Sava	Jasenovac	45 16 0	16 54 36	500	87	38953	L2280	M
BIH02	/Sava/Una	Kozarska Dubica	45 11 6	16 48 42	16	94	9130	L2290	M
BIH03	/Sava/Vrbas	Razboj	45 3 36	17 27 30	12	100	6023	L2300	M
BIH04	/Sava/Bosna	Modrica	44 58 17	18 17 40	24	99	10308	L2310	M
RO01	Danube	Bazias	44 47 55,57,58	21 23 24,40,54	1071	70	570896	L0020	LMR
RO02	Danube	Pristol/Novo Selo Harbour	44 11 18,23,29	22 45 57,64,69	834	31	580100	L0090	LMR
RO03	Danube	us. Arges	44 4 25	26 36 35	432	16	676150	L0240	LMR
RO04	Danube	Chiciu/Silistra	44 7 18	27 14 38	375	13	698600	L0280	LMR
RO05	Danube	Reni-Chilia/Kilia arm	45 28 50	28 13 34	132	4	805700	L0430	LMR
RO06	Danube	Vilkova-Chilia arm/Kilia arm	45 24 42	29 36 31	18	1	817000	L0450	LMR
RO07	Danube	Sulina - Sulina arm	45 9 41	29 40 25	0	1	817000	L0480	LMR
RO08	Danube	Sf.Gheorghe-Ghorghe arm	44 53 10	29 37 5	0	1	817000	L0490	LMR
RO09	/Arges	Conf. Danube	44 4 35	26 37 4	0	14	12550	L0250	M
RO10	/Siret	Conf. Danube Sendreni	45 24 10	28 1 32	0	4	42890	L0380	M
RO11	/Prut	Conf.Danube Giurgiulesti	45 28 10	28 12 36	0	5	27480	L0420	M
BG01	Danube	Novo Selo Harbour/Pristol	44 09 50,58,66	22 47 36,47,58	834	35	580100	L0730	LMR
BG02	Danube	us. Iskar - Bajkal	43 42 58	24 24 45	641	20	608820	L0780	R
BG03	Danube	Downstream Svishtov	43 37 50	25 21 11	554	16	650340	L0810	MR
BG04	Danube	us. Russe	43 48 06	25 54 45	503	12	669900	L0820	MR
BG05	Danube	Silistra/Chiciu	44 7 02	27 15 45	375	7	698600	L0850	LMR
BG06	/Iskar	Orechovitza	43 35 57	24 21 56	28	31	8370	L0930	M
BG07	/Jantra	Karantzi	43 22 42	25 40 08	12	32	6860	L0990	M
BG08	/Russ.Lom	Basarbovo	43 46 13	25 57 34	13	22	2800	L1010	M
MD01	/Prut	Lipcani	48 16 0	26 50 0	658	100	8750	L2230	L

Country Code	River Name	Town/Location Name	Latitude d. m. s.	Longitude d. m. s.	Distance [Km]	Altitude [m]	Catch-ment [km^2]	DEFF Code	Loc.in profile
MD02	/Prut	Leuseni	46 48 0	28 9 0	292	19	21890	L2250	M
MD03	/Prut	Conf. Danube-Giurgiulesti	45 28 10	28 12 36	0	5	27480	L2270	LMR
UA01	Danube	Reni - Kilia arm/Chilia arm	45 28 50	28 13 34	132	4	805700	L0630	M
UA02	Danube	Vilkova-Kilia arm/Chilia arm	45 24 42	29 36 31	18	1	817000	L0690	M

Distance:	The distance in km from the mouth of the mentioned river	Sampling location in profile:
Altitude:	The mean surface water level in meters above sea level	L: Left bank
Catchment:	The area in square km, from which water drains through the station	M: Middle of river
ds.	Downstream of	R: Right bank
us.	Upstream of	
Conf.	Confluence tributary/main River	
/	Indicates tributary to river in front of the slash. No name in front of the slash means Danube.	

4.3. Determinands

To be able to fulfil TNMN objectives listed in chapter 4.1, determinands to be measured in monitoring network of Danube River basin should be indicative to human uses, functions of the rivers and problems identified in the river basin. On the other hand, the scope of determinands was limited by available and affordable methods of measurements.

The original determinand list for the first phase of TNMN prepared to reflect also existing EU directives and the riparian countries´ own demands had to be reduced after discussions held in MLIM-SG. The resulting list is given in Tables 5.2.1.1 and 5.2.1.2 for water and sediment phase, respectively. The agreed frequency of measurements for determinands in water was 12 per year and 2 per year for biomonitoring and determinands analysed in sediments.
Sampling and analysis were carried out on the national level, respecting agreed quality system, which is described in more details in the chapter 5.

4.4. TNMN data management

The primary purpose of data management is to transform raw data to needed information, coming from monitoring objective. The basic assumption for this process is to have got standard procedure for collection, validation, merging, storage, and processing of the data.

The importance of TNMN data management was recognised in very early stage of TNMN operation and well-defined structure for data storage had been prepared. The data are organised in a system of joined tables, containing information related to monitoring locations, determinands, methods of sampling, methods of analysis, remarks and information on taken samples and results of analysis. From 1996, several parts of the database had been modified to adjust the system to the new needs, or to increase efficiency of the system.

The procedure of TNMN data collection starts on a national level of each country. Nominated National Information Managers (NIMs) are responsible for collection of the data from National Reference Laboratories and other national laboratories involved in TNMN, where the data from sampling and analysis are generated. In the next step the NIMs are responsible for data checking, preparation in agreed data exchange file format (DEFF) and sending to the Central Point. Here the data are checked again and suspicious data are consulted with NIMs. After the consultation process the data from TNMN are merged and stored in one relational database for further use.

Collection of TNMN data started in 1996, TNMN data have been regularly collected from Germany, Austria, the Czech Republic, Slovakia, Hungary, Slovenia, Croatia, Bulgaria and Romania. Data from Ukraine and Moldova have been available since 1998.
Basic processing and presentation of the TNMN data is done on a yearly basis in the form of Danube Yearbook, first of which was prepared from 1996 data.

5. Quality System

5.1. Introduction

Before 1985, water quality monitoring in the Danube river basin had been carried out independently in the different countries, in several cases as part of bilateral agreements. In 1985, the Bucharest Declaration was the first sign of a basin-wide international cooperation. The gaps in existing knowledge and the problems of the comparability of the monitoring results have been recognized. The Environmental Programme for the Danube River Basin (EPDRB), started in 1991, provided a framework to extend and upgrade the monitoring program. One of the major tasks of the EPDRB was to establish the Trans-National Monitoring Network (TNMN) using accepted methodologies and appropriate quality control. The mission of the established Monitoring, Laboratory and Information Management Expert Group (MLIM-EG), and particularly of its Laboratory Management Working Group (LMWG), included the harmonization of the sampling and analytical methods for use in the TNMN and establishment of an appropriate, effective quality assurance system. In the late 90s, after ratification of the International Convention for the Protection of the Danube River Basin (ICPDR) the water quality/pollution monitoring became one of the important activities, and the monitoring and laboratory experts further improved the operational elements of the TNMN.

The most difficult issue in the monitoring of international rivers is to obtain reliable information, comparable data on the different pollutants. Therefore, implementation of monitoring programmes in international river basins requires harmonization and coordination. Harmonization should be first of all during the design period when target determinands and matrices for monitoring are identified, sampling locations and frequencies, sampling and analytical methodologies, the quality control measures particularly for the analytical quality control (AQC) are selected and agreed.

Evaluation of the quality of the river system, the realistic description of the concentrations and trends of pollution the analytical results should be of the same high quality, irrespective of the laboratory that provided the results. The appropriate operation of the TNMN was an important part of the monitoring strategy ensured throughout harmonization sampling and analytical methodologies, establishment of quality targets and appropriate quality assurance scheme. This was a prerequisite to the proper operation of the monitoring network which includes selected monitoring sites along the Danube and its tributaries. In each country, a National Reference Laboratory (NRL) was nominated and additional national laboratories were involved in the implementation of the TNMN. The LMWG took the responsibility to harmonize the monitoring methodologies and coordinate the AQC among the 11 NRLs and the additional 18 national laboratories.

In addition to the preparation of Standard Operational Procedures (SOPs) to be followed during sample collection and analysis, the quality assurance program in the Danube river basin laboratories included: (a) recommendations for similar laboratory facilities, (b) provision of necessary analytical instrumentation in the laboratories, (c) implementation of integrated training programs, and (d) proficiency testing carried out in interlaboratory comparison studies.

The implementation plan for the TNMN was prepared and agreed. This included provision of sampling equipment and analytical instruments for the eligible countries from the EU PHARE programme. As far as the laboratory work is concerned, harmonization of the related activities, coordinated by the LMWG of MLIM-EG, included:

- Selection of determinands and matrices for the TNMN in the Danube river basin;
- Selection of appropriate sampling and sample handling procedures for water, sediment and biota;
- Selection of reference and optional analytical methods for determination of the identified physical, chemical, radiochemical, biological and microbiological determinands;
- Establishment of the AQC, performance testing system;
- Regular revision of the methodologies;

- Harmonization of laboratory facilities, instrumentation;
- Identification of training needs and implementation; and
- Co-ordination of the laboratory work through regular meetings of the National Reference Laboratories.

During 1998-2000, in the frame of the EU supported projects on “Water Quality Enhancement in the Danube River Basin” and “Strengthening Capabilities in the Danube River Basin” significant efforts were devoted to the development of the quality assurance elements of the Danube TNMN. In the second project, the Volume 2 of the Guidance Notes dealt with all quality assurance issues pertaining to the sampling, sample preparation and analysis of TNMN determinands.

5.2. Quality Assurance in Water Quality Data Collection

The measurement cycle for the implementation of the monitoring starts with the collection of samples and closes with reporting the analytical results and the reliability of the results depends on the effectiveness of the quality assurance as shown in Fig. 5.2.1.

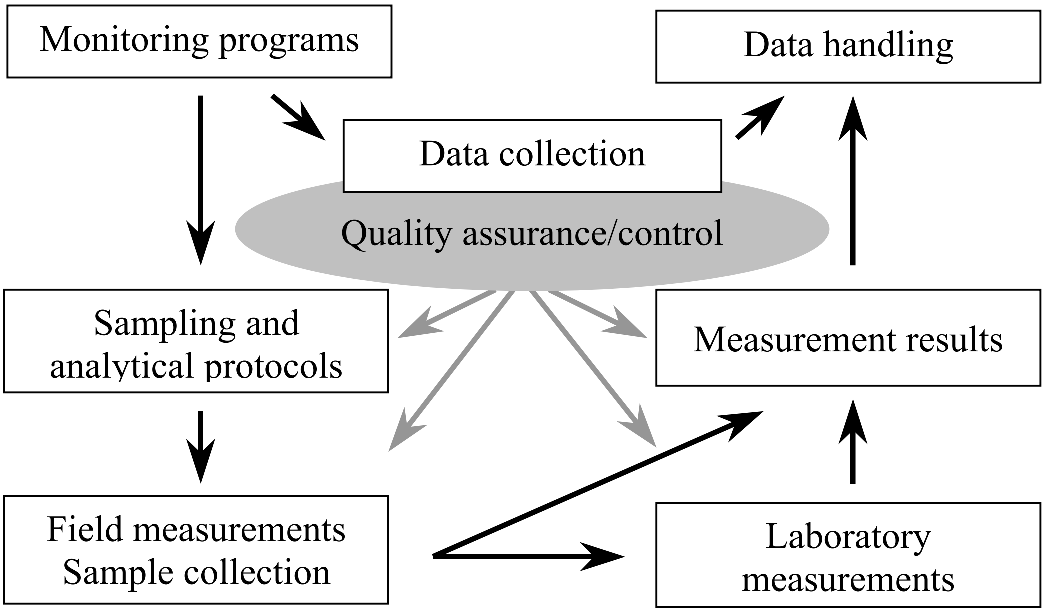


Fig. 5.2.1. Quality assurance/control in the data collection/measurement cycle

Quality assurance/control in monitoring programme design as well as in the data handling is considered in the relevant chapters of this review report. Here, major emphasise is given to the laboratory work, particularly to the analytical quality control.

5.2.1. Quality and Accuracy Targets

Water/sediment quality targets, objectives and standards are set to evaluate the quality of the water resources, both surface and subsurface water bodies, to characterise chemical and ecological status (for surface waters) and to establish satisfactory condition for intended uses of the aquifer. The laboratory data define whether that condition is being met, and whether the water is at acceptable quality to fit for the purpose. If the laboratory results indicate a violation of the standard, action is required by the pollution control authorities. The analyst must be aware that his professional competence, the procedures he has used, and the reported values are reliable and may be used with confidence.

The approach adopted in proposing the analytical accuracy targets for monitoring the quality of water (Table 5.2.1.1) and sediment (Table 5.2.1.2) in the Danube river basin is summarized as follows:

- Two key concentration levels have been defined for each determinand. These are: (i) the lowest level likely to be encountered in the waters / sediments of interest (**the minimum level of interest**); and (ii) the concentration which represents the likely level at which most monitoring (for example, for the assessment of trends or compliance with water quality standards) will be carried out (**the principal level of interest**). These levels define the aims of the program; they can be used to establish the performance needed from analytical systems used in the laboratories.
- It is then assumed that the aims of the program will be satisfied provided: (i) that relatively few results are reported as "less than" the minimum level and (ii) that the accuracy achieved at the principal level is not worse than ± 20% of the principal level. This assumption has been tested in a wide range of environmental monitoring laboratories. Experience suggests that it is usually appropriate to set a required limit of detection which is at least one tenth of the principal level of interest. A subsidiary aim is that the limit of detection should be at least one third of the minimum level of interest.
- Any practical approach to monitoring must take into account the current capabilities of analytical science. This means that if some targets are recognized as very difficult to achieve, it may be necessary to set more relaxed, interim targets and to review performance and data use in the course of the monitoring program.

5.2.2. Analytical Methodologies

The analytical methodologies for the determinands applied in TNMN are based on a list containing reference and optional analytical methods. The National Reference Laboratories (NRLs) have been provided with a set of ISO standards (reference methods) reflecting the determinand lists, but taking into account the current practice in environmental analytical methodology in the EU. It has been decided not to require each laboratory to use the same method, providing the laboratory would be able to demonstrate that the method in use (optional method) meets the required performance criteria. Therefore, the minimum concentrations expected and the tolerance required of actual measurements have been defined for each determinand (as reported in Tables 5.2.1.1 and 5.2.2.2), in order to enable laboratories to determine whether the analytical methods currently in use are acceptable.

Table 5.2.1.1: Accuracy targets of water quality variables selected for the TNMN

DETERMINANDS in Water	**Level of Interest**		**Analytical Accuracy Targets**	
	Minimum likely (Note 1)	**Principal (Note 2)**	**Limit of Detection (Note 3)**	**Tolerance (Note 4)**
Physical, Chemical Parameters				
Temperature, °C	-	0-25	-	0.1 °C
Suspended Solids, mg/l	1	10	*1*	*1mg/l or 20%*
Dissolved Oxygen, mg/l	0.5	5	0.2	0.2 or 10%
pH	-	7.5	-	0.1
Conductivity µS/cm, @ 20°C	30	300	5	5 or 10%
Alkalinity, mmol/l	1	10	0.1	0.1
Chloride, mg/l	5	50	1	1 or 10%
Sulphate, as SO_4 mg/l	5	50	5	5 or 20%
Nutrients				
Ammonium (NH_4) as N mg/l	0.05	0.5	0.02	0.02 or 20%
Nitrite (NO_2) as N mg/l	0.005	0.02	*0.005*	*0.005 or 20%*
Nitrate (NO_3) as N mg/l	0.2	1	0.1	0.1 or 20%
Organic Nitrogen as N mg/l	0.2	2	0.1	0.1 or 20%
Total - Nitrogen as N mg/l	0.2	2	0.5	0.5

DETERMINANDS in Water	**Level of Interest**		**Analytical Accuracy Targets**	
	Minimum likely (Note 1)	**Principal (Note 2)**	**Limit of Detection (Note 3)**	**Tolerance (Note 4)**
Orthophosphates (PO_4) as P mg/l	0.02	0.2	0.005	0.005 or 20%
Total Phosphorus as P mg/l	0.05	0.5	0.01	0.01 or 20%
Elements (Metals)				
Sodium mg/l	1	10	0.1	0.1 or 10%
Potassium mg/l	0.5	5	0.1	0.1 or 10%
Calcium mg/l	2	20	0.2	0.1 or 10%
Magnesium mg/l	0.5	5	0.1	0.2 or 10%
Iron mg/l	0.05	0.5	0.02	0.02 or 20%
Manganese mg/l	0.05	0.5	0.01	0.01 or 20%
Zinc mg/l	0.01	0.1	0.003	0.003 or 20%
Copper mg/l	0.01	0.1	0.003	0.003 or 20%
Chromium mg/l	0.01	0.1	0.003	0.003 or 20%
Lead mg/l	0.01	0.1	0.003	0.003 or 20%
Cadmium mg/l	0.001	0.01	*0.0005*	*0.0005 or 20%*
Mercury mg/l	0.001	0.01	0.0003	0.0003 or 20%
Nickel mg/l	0.01	0.1	0.003	0.003 or 20%
Arsenic mg/l	0.01	0.1	0.003	0.003 or 20%
Aluminium mg/l	0.01	0.1	*0.01*	*0.01 or 20%*
Organic Components				
BOD_5 , mg/l	0.5	5	*0.5*	*0.5 or 20%*
COD_{Cr} , mg/l	10	50	*10*	*10 or 20%*
COD_{Mn} , mg/l	1	10	0.3	0.3 or 20%
DOC, mg/l	0.3	3	*0.3*	*0.3 or 20%*
Phenol index, mg/l	0.005	0.05	*0.005*	*0.005 or 20%*
Anionic surfactants, mg/l	0.1	1	0.03	0.03 or 20%
Petroleum hydrocarbons, mg/l	0.02	0.2	*0.05*	*0.05 or 20%*
AOX, μg/l	10	100	10	10 or 20%
Lindane, μg/l	0.05	0.5	0.01	0.01 or30%
pp'DDT, μg/l	0.05	0.5	0.01	0.01 or30%
Atrazine, μg/l	0.1	1	0.02	0.02 or30%
Chloroform, μg/l	0.1	1	0.02	0.02 or30%
Carbontetrachloride, μg/l	0.1	1	0.02	0.02 or30%
Trichloroethylene, μg/l	0.1	1	0.02	0.02 or30%
Tetrachloroethylene, μg/l	0.1	1	0.02	0.02 or30%

Table 5.2.1.2. Accuracy targets of sediment quality variables selected for the TNMN

DETERMINANDS in Sediment	**Level of Interest**		**Analytical Accuracy Targets** (for <63 µm size fraction)	
	Minimum likely (Note 1)	**Principal (Note 2)**	**Limit of Detection (Note 3)**	**Tolerance (Note 4)**
Elements				
Organic Nitrogen, mg/kg	50	500	10	10 or 20%
Total Phosphorus, mg/kg	50	500	10	10 or 20%
Calcium, mg/kg	1000	10000	300	300 or 20%
Magnesium, mg/kg	1000	10000	300	300 or 20%
Iron, mg/kg	50	500	20	20 or 20%
Manganese, mg/kg	50	500	20	20 or 20%
Zinc, mg/kg	250	500	50	50 or 20%
Copper, mg/kg	2	20	*1*	*1 or 20%*
Chromium, mg/kg	2	20	*1*	*1 or 20 %*
Lead, mg/kg	2	20	*1*	*1 or 20 %*
Cadmium, mg/kg	0.05	0.5	*0.05*	*0.05 or 20%*
Mercury, mg/kg	0.05	0.5	0.01	0.01 or 20%
Nickel, mg/kg	2	20	*1*	*1 or 20 %*
Arsenic, mg/kg	2	20	*1*	*1 or 20 %*
Aluminium, mg/kg	50	500	*50*	*50 or 20%*
Organic pollutants				
TOC, mg/kg	50000	500000	10000	10000 or 20%
Petroleum Hydrocarbons, mg/kg	10	100	1	1 or 20 %
Total Extractable Matter, mg/kg	100	1000	10	10 or 20 %
PAH - 6 (each), mg/kg	0.01	0.1	0.003	0.003 or 30%
Lindane, mg/kg	0.01	0.1	0.003	0.003 or 30%
pp' DDT, mg/kg	0.01	0.1	0.003	0.003 or 30%
PCBs - 7 (each), mg/kg	0.01	0.1	0.003	0.003 or 30%

Note 1 - The minimum likely level of interest is the lowest concentration considered likely to be encountered or important in the Danube monitoring program.
Note 2 - The principal level of interest is the concentration at which it is anticipated that most monitoring will be carried out.
Note 3 - The required limit of detection is the target limit of detection (LD) which laboratories are asked to achieve. This has been set, wherever practicable, at one third of the minimum level of interest. This is intended to ensure that the best possible precision is achieved at the principal level of interest and that relatively few less than results will be reported for samples at or near the lowest level of interest. (N.B. Where the performance of current analyses is not likely to meet the criterion of a LD of one third if the lowest level of interest, the LD has been revised to reflect best practice. In these cases, the targets have been entered in italics).
Note 4 - The tolerance indicates the largest allowable analytical error which is consistent with the correct interpretation of the data and with current analytical practice. The target is expressed as "x concentration units or P%". The larger of the two values applies for any given concentration. For example, if the target is 5 mg/l or 20% - at a concentration of 20 mg/l the maximum tolerable error is 5 mg/l (20% is 4 mg/l); at a concentration of 100 mg/l, the tolerable error is 20 mg/l (i.e. 20%) because this value exceeds the fixed target of 5 mg/l.

5.3. Performance testing in the Danubian laboratories

As part of the AQC, a performance testing scheme under the name of *QualcoDanube* has been established and implemented as the primary inter-laboratory quality control program in the Danube basin, started in 1993 with the participation of the laboratories involved in the Danube water quality monitoring in the framework of the Bucharest Declaration. In 1995, it was extended, in the frame of the TNMN, to the 11 National Reference Laboratories and in 1996 to another 19 national laboratories within the Danube river basin implementing the TNMN. Since 1996, the *QualcoDanube* performance testing intercalibration results demonstrate significant improvement.

5.3.1. Perspectives of Proficiency Testing

One of the most important parts of the sustainable AQC is the design of an organisational structure for proficiency testing that can ensure continuity of analytical quality control in the Danube TNMN and the following points had to be considered: (a) the determinands of interest and type of matrix, (b) the level of concentration of determinands, (c) sample preparation, (d) analysis and reporting, and (e) evaluation of the results.

The key agreed requirements for the performance testing scheme are as follows:

- The sample should be considered to be adequately representative of a real test material. Determinands and matrix depend on parameters and sample type analysed routinely by the laboratories of Danube River Basin. Care needs to be taken to ensure that no sample is lost during shipment and that the sample is well homogenised.
- Concentration level of determinands depends on parameters and sample type analysed routinely by the laboratories in the Danube river basin. In the case of real surface water, sediment samples or biota, concentration range is limited. In other cases (e.g., synthetic sample) concentrations vary depending on the target level of contamination.
- The number of samples should be sufficient to distribute sample-pairs according to the Youden-technique, to each of the 29 TNMN implementing laboratories. As it is anticipated that other laboratories in Danubian countries should have the opportunity to take advantage of the respective performance testing exercises, an additional sample set should be prepared per material.
- Sampling should ideally be at a frequency of four-times per year according to the distribution schedule. Samples should be accompanied with clear instructions on the procedures for the PT analysis and the reporting procedure.
- The results reported back from the analytical laboratories should be evaluated and fed back to the laboratories within two weeks. Laboratories are identified by code numbers.

The sample preparation, distribution and evaluation schemes of the performance testing is demonstrated in Fig. 5.3.1.1. Laboratories receive selected well homogenized environmental samples for analysis. The reported analytical results are compared with the assigned reference values.

The test materials to be distributed in the scheme must be similar to the materials that are routinely analysed (in respect of composition of the matrix and the concentration range or quality of the determinand) including the type of samples as follows:

- synthetic water samples as concentrate-pairs (according to the Youden-technique),
- real-world water and sediment samples and their spikes ensuring sample-pairs again according to the Youden-technique,

reference materials (water and sediment). Sediment references materials shall be prepared from samples collected at different representative sites in the Danube river basin in a relatively large quantity allowing to use these samples for internal quality control as in-house RM.

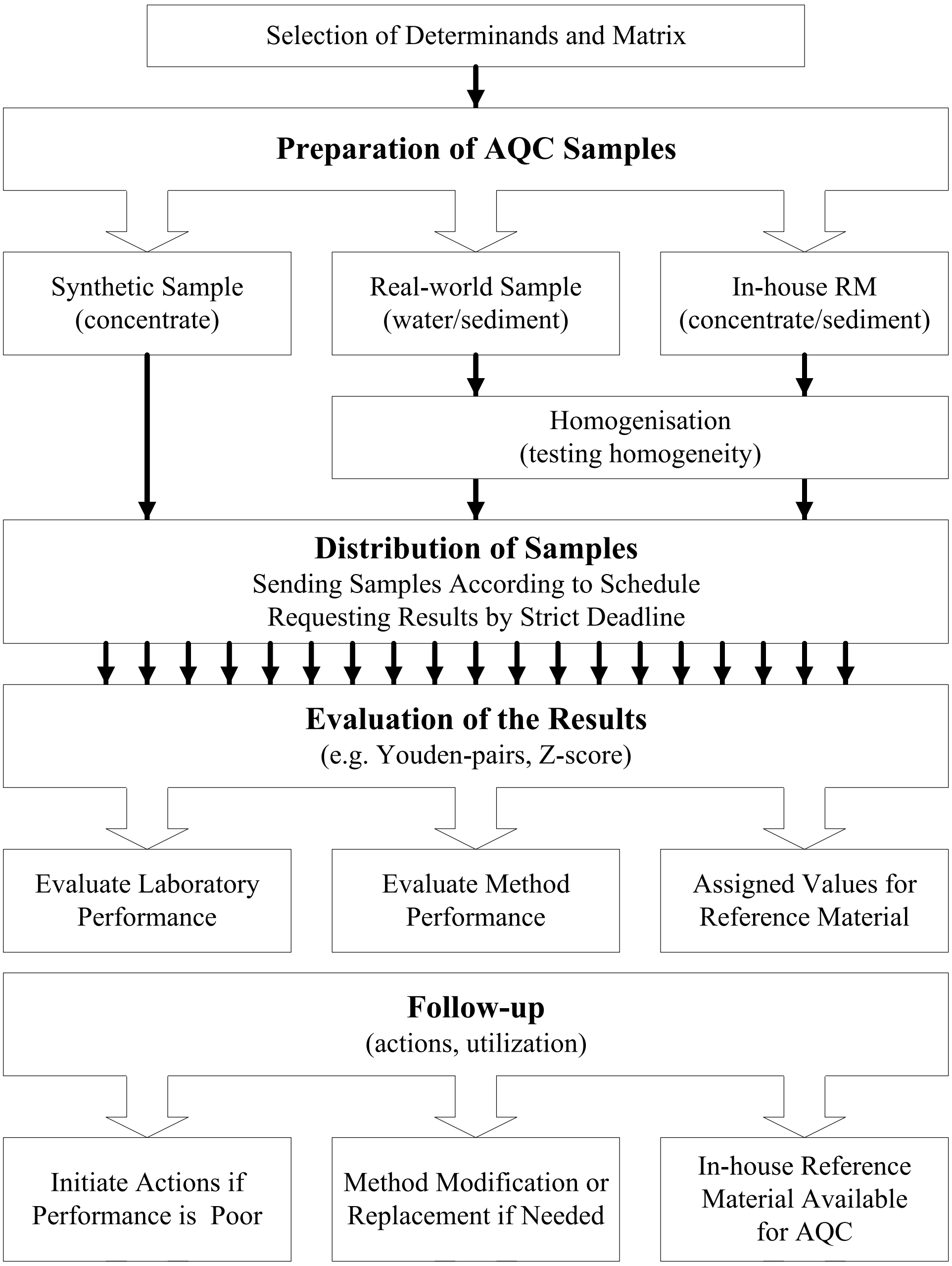


Figure 5.3.1.1: Sample preparation and evaluation scheme for AQC in the Danube river basin

5.3.2. QualcoDanube, AQC in Water Labs in the Danube River Basin

The organisation of interlaboratory comparison in the Bucharest Declaration Danube monitoring was agreed in 1992. The Institute for Water Pollution Control of VITUKI, Budapest, Hungary, offered and took the responsibility for organising the first study under the name of QualcoDanube. The first distribution in 1993 included samples for the analysis of three determinands: pH, conductivity and total hardness. By the end of 1995, four more distributions had been made for the analysis of the following determinands: chlorides, COD, nutrients (ammonium, nitrate, Kjeldahl-nitrogen, orthophosphate and total-P) as well as different metals, including Fe, Mn, Ca, Mg, Cd, Cu, Hg, Pb, Ni, Zn.

In 1996 the QualcoDanube proficiency testing scheme was extended to the National Reference Laboratories (NRL) in the Trans-National Monitoring Network (TNMN) and the 1996/2 distribution already included all Danubian laboratories - 11 NRLs and 18 national laboratories - implementing the

TNMN. This distribution was further extended to 6 Black Sea laboratories responsible for pollution monitoring in their area.

Since 1996 QualcoDanube check samples are distributed quarterly in each year.

5.3.3. Other Proficiency Testing Schemes

In addition to the QualcoDanube, another interlaboratory comparison, the AQUACHECK performance testing scheme, organized by WRc (UK), was conducted for the NRLs, mainly aiming at the analysis of specific micropollutants.

5.4. Main achievements

The described approach supports the work of harmonising the analytical activities within the Danube Basin related to the TNMN as well as the implementation and operation of an Analytical Quality Control (AQC) programme. Therefore, it has been used in development of the training needs required to improve the laboratory performance of the National Reference Laboratories as well as the other laboratories involved in the implementation of the TNMN. The result is that managers and personnel of the involved laboratories have been provided with practical training for analytical instrumentation and on-site sampling as well as with theoretical aspects of AQC.

Interlaboratory studies - organized regularly - help to improve analytical performances because the participants can review their own performance concerning the accuracy of the analytical results and where necessary, investigate the sources of error and take corrective actions.

5.4.1. Lessons learnd from the 5 year QA/QC Activies

The four QualcoDanube distributions in each year provided information on the analytical performance of the participating laboratories implementing the TNMN in the Danube river basin. The overall output of the results is the demonstration of the comparability of the analytical data on the studied determinands as well as the possible methodological problems during the analysis.

Since the start of the QualcoDanube AQC programme nutrients were included in several distributions and therefore it was possible to assess the quality improvement in the analytical work by comparing the performance during the different distributions.

The results in **1996** showed the quality improvement in most of the determinands. Although the number of laboratories during the first distributions was almost one third of the other distributions the performance significantly improved during the study period, particularly in the case of Nitrate-N. Variation in the Orthophosphate-P and the Total-P was significant, therefore, improvement is needed before the monitoring data of these determinands could be considered reliable in the entire Danube basin. The results of the heavy metal analysis were promising because with very few exceptions they were within an acceptable range.

It was expected that the performance of the Danube basin laboratories as well as of the additional laboratories from the Black Sea region would further improve which would ensure the comparability of the water quality monitoring results in the river basin and related marine regions.

Most of the data provided by the laboratories during the **1997** QualcoDanube intercalibration study were satisfactory, when comparing to error thresholds.

While the results in 1996 showed the quality improvement in most of the determinands, further improvement could not be observed in 1997. The performance for the general parameters was satisfactory. Some problems arose due to stability of the samples (e.g. MBAS, PO_4-P) and a relatively long analysis time which can influence the variation between results. In the case of metals different digestion methods were used and there were some problems for less commonly measured metals (e.g. Hg, As) and at low concentration level (e.g. Cd, Ni, Pb).

In **1998**, the analytical results of synthetic samples were better than results of real water samples. In the latter case, due to matrix effect, results were influenced by both systematic and random errors, while systematic error characterized mainly the results of the synthetic samples. Among the nutrients Kjeldahl-N (1998/2) and among the organic pollutants the Chemical Oxygen Demand with dichromate method (1998/1) were analysed. In general, the results of the metals were satisfactory, especially of zinc, and only the results of mercury were scattered. Similarly to the real water samples, the results of the sediment samples were also influenced by both random and systematic errors.

In addition to regularly analysed determinands, distributions in **1999** included specific trace organic determinands in waters for quantitative determinations as being involved in the TNMN for the River Danube, (e.g. lindane, DDT). The results of these determinands were poor, unsatisfactory together with the results of petroleum hydrocarbons in both water and sediment. In the case of water samples solvent extracts were distributed so the discrepancies in the results most likely originated from incorrect analyses and/or unsuitable analytical methods.

In **2000**, the analytical results of synthetic samples were again better than results obtained from real water samples. Results of general determinands, nutrients in synthetic samples and metals were relatively good, but results of nutrients in real water samples were influenced by significant systematic error and slight random error. Analysis of organic compounds proved to be a field requiring improvement, especially of micropollutants, in case of which the performance was not sufficient.

In summary, there was significant quality improvement in most of the determinands during the five years. For further improvement more attention should be paid particularly to:

- the distributed samples were preserved (regularly by acid and/or by sterilization depending on determinands), so before analyses pH checking and adjustment should have been done. This simple but important step might have been left out of consideration, e.g., at NO_3^--N determination. The results of some laboratories could be out of range due to this reason.
- In the case of determination of metals, particularly in sediment, the reason for discrepancies could be the different way of mineralization, or systematic errors during analyses.
- Most of the measurements were influenced by systematic error which is calling for more attention in the sample preparation and calibrations.
- There were some laboratories which regularly reported outlying results for certain determinands. They should pay attention to the whole process of analysis of these determinands (analytical method, standard materials, etc.).

5.4.2. Need for continuation of interlaboratory comparison studies

Intercalibration studies organised regularly present an important part of QA/QC system. They help to improve analytical performances because the participants can review their own performance concerning the accuracy of the analytical results and, where necessary, investigate the sources of error and take corrective actions.

It is expected that performance of laboratories analysing samples in the frame of TNMN will further improve and the comparability of the water quality monitoring results in the river basin and related regions will be ensured. To achieve this goal regular performance testing and the continuation of the interlaboratory comparison studies are of paramount importance.

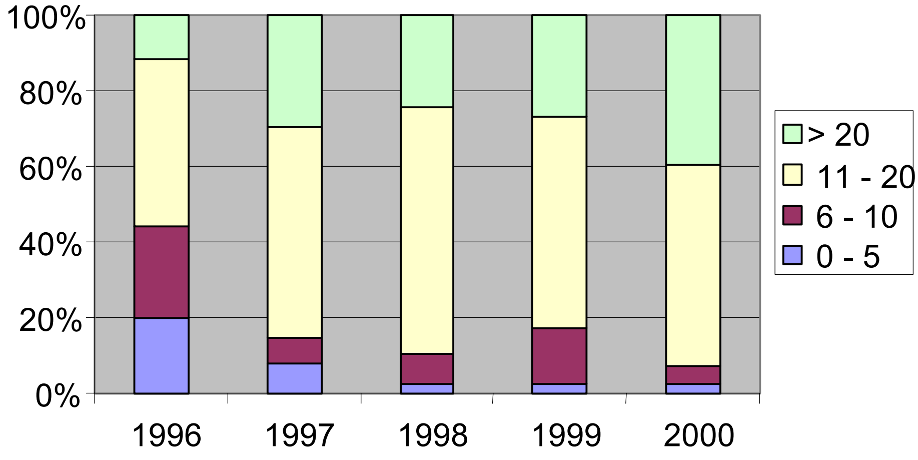
6. Five Years of Monitoring – a Statistical Overview

Over the five years period the number of sampling sites where data have been provided has increased from 75 (1996) to 81 (2000). Most of the sites have been maintained – only a few sites were shifted from one river side to another: BG03 from middle to right, HR08 from right to middle, HR06 from right to left.

The amount of investigations differs, not all determinands were analysed at all monitoring sites. Table 6.1 gives an overview on the number of monitoring sites where data of a specific determinand is available. Comparing the years an upward trend can be stated. At the same time the number of samples per year increased. As an example, in Fig. 6.1 the percentage of sites with the number of nitrate measurements in 1996-2000 is shown.

However, there are big differences regarding the determinands. As to basic descripters, currently many samples are taken but for specific organic pollutants the number of samples is still very low. Seasonal fluctuations and particular situations like flood events or algae blooms can not be detected and for this reason data processing and data interpretation is rather limited for several determinands.

Fig.6.1: Nitrate – percentage of sites with number of measurements per year.



Concerning analytical methods changes over time have been reported for every data delivery. Frequently these changes have been affected the detection limit. This has to be beared in mind when processing the data of determinands, which usually occur in low concentrations. For the five-years period table 6.2 shows the overall range of detection limits reported by countries, which are stored in the TNMN database.

Table 6.1: Number of monitoring sites where data are available

Determinand	**Number of monitoring sites**				
	1996	**1997**	**1998**	**1999**	**2000**
Basic Descriptors					
Water temperature					
Dissolved oxygen *	74	75	77	81	71
Conductivity	72	74	71	75	77
Suspended solids	66	74	74	81	81
pH	74	75	77	81	81
Alkalinity	62	67	71	75	80
Nutrient regime					
Ammonium-N	70	75	77	81	81
Nitrite-N	71	76	76	79	79
Nitrate-N	75	75	77	81	81
Organic N	29	24	22	33	34
Total-N					4
Ortho-phosphate-P	72	74	75	76	69
Total-P	65	66	67	79	78
Chlorophyll-a					
Pollution indicators					
BOD_5	73	71	77	81	82
COD_{Mn}	72	74	74	78	78
COD_{Cr}	64	70	73	77	79
AOX	8	8	23	22	14
Heavy Metals (total)					
Zinc	70	70	73	73	77
Copper	70	70	73	73	77
Chromium (Cr-III+VI)	64	65	68	68	68
Lead	66	69	68	68	74
Cadmium	65	66	66	68	74
Mercury	52	34	33	29	35
Nickel	69	42	42	63	74
Arsenic	29	30	31	31	39
Manganese	67	71	71	75	68
Iron	68	73	74	80	70
Toxic substances					
Lindane	28	51	56	66	69
p,p´-DDT	28	47	59	66	69
Atrazine	37	27	28	36	62
Trichloromethane	9	15	23	28	29
Tetrachloromethane	9	15	23	28	29
Trichloroethene	9	15	23	28	27
Tetrachloroethene	9	15	23	28	27
PAL A	29	53	73	73	77
NES	28	37	44	48	51

Table 6.2: Range of detection limits in 1996-2000, reported by countries.

Determinands	**Range of detection limits 1996-2000 (all monitoring sites)**	**Units**
Basic Descriptors		
Suspended solids	0,2 - 10	mg.l^{-1}
Alkalinity	0,01 - 0,4	mmol.l^{-1}
Ca	0,003 - 10	mg.l^{-1}
Mg	0,0005 – 5	mg.l^{-1}
Na	0,005 – 1,0	mg.l^{-1}
K	0,005 – 1,0	mg.l^{-1}
Nutrient regime		
Ammonium-N	0,008 - 0,05	mg.l^{-1}
Nitrite-N	0,001 - 0,02	mg.l^{-1}
Nitrate-N	0,002 - 1	mg.l^{-1}
Organic N	0,05 - 1	mg.l^{-1}
Total-N	0,2	mg.l^{-1}
Ortho-phosphate-P	0,003 - 0,05	mg.l^{-1}
Total-P	0,005 - 0,05	mg.l^{-1}
Pollution indicators		
BOD$_5$	0,01 - 1	mg.l^{-1}
COD$_{Mn}$	0,01 - 0,8	mg.l^{-1}
COD$_{Cr}$	0,01 - 15	mg.l^{-1}
AOX	0,01 - 10	µg.l^{-1}
Heavy Metals (total)		
Zinc	0,003 - 20	µg.l^{-1}
Copper	0,003 - 3	µg.l^{-1}
Chromium (Cr-III+VI)	0,03 - 10	µg.l^{-1}
Lead	0,003 - 2	µg.l^{-1}
Cadmium	0,01 - 5	µg.l^{-1}
Mercury	0,01 - 3	µg.l^{-1}
Nickel	0,003 - 2,5	µg.l^{-1}
Arsenic	0,02 - 2	µg.l^{-1}
Manganese	0,00001 - 0,5	mg.l^{-1}
Iron	0,00002 - 0,2	mg.l^{-1}
Toxic substances		
Lindane	0,001 - 0,1	µg.l^{-1}
p,p´-DDT	0,001 - 0,05	µg.l^{-1}
Atrazine	0,001 - 1	µg.l^{-1}
Trichloromethane	0,01 - 1	µg.l^{-1}
Tetrachloromethane	0,01 - 1	µg.l^{-1}
Trichloroethene	0,01 - 1	µg.l^{-1}
Tetrachloroethene	0,01 - 1	µg.l^{-1}
PAL A	0,005 - 0,1	mg.l^{-1}
NES	0,005 - 0,2	mg.l^{-1}

7. Description of Methodology of Assessment in the Report

Reffering to objectives of the report, there is a need to obtain information on water quality in the Danube River and its main tributaries based on data from five-years joint monitoring of Danubian states. The questions regarding the water quality, its compliance with set up target values, spatial changes along the river and questions whether and where the water quality is improving or deteriorating, are of concern for not only decision makers, but also for public.

Assessment in the report consists of several parts:

- classification of surface water quality in accordance to classification system developed for TNMN, methodology of which is described in chapter 7.1.;
- assessment of spatial changes and trend assessment of physico-chemical determinands, approach for which is described in chapter 7.2 and 7.3, respectively;
- assessment of biological determinands measured in TNMN, for which methodology described in chapter 7.4.;
- assessment of dangerous substances content in waters in accordance to Environmental Quality Standards established or proposed for use in EU, methodology of which is described in chapter 7.5.

7.1. Water Quality Classification

The first attempt to come up with proposal of joint water quality classification for Danube river basin had been done in 1997 by PHARE Applied Research Project EU/AR/203/91 "Water Quality Targets and Objectives for Surface Waters in the Danube basin" (WRRC, Vituki, Plc., 1997).
The proposed classification has not been applied for evaluation of results from TNMN, it was only partly used by means of using its limit values for illustration of BOD_5, PO_4^{3-}-P and NO_3^--N concentrations on the maps in the TNMN-Yearbooks 1996-2000.

In 1999 the EU PHARE Programme contributed to the EPDRB by initiating the project "Danube River Basin Water Quality Enhancement". One of its objectives was to make a proposal for a unified water quality classification for the entire Danube River basin region based on

- review of existing water quality and sediment quality classification methods in Danubian countries
- review of EU legislation
- experience within the different countries

The activity was realised by IWACO BV Consultants for water and environment in Rotterdam. Although the attention was given to Water Famework Directive (WFD) (at that time still under preparation), it was concluded that to come to ecologically based and regionally differentiated water quality criteria according to WFD in Danube River Basin will take considerable effort and time. In the meantime interim water quality classification scheme had been proposed. This proposal was further discussed and adjusted by Monitoring, Laboratory and Information Management Sub-Group and approved finally in 2001.

The classification scheme as presented in Table 7.1.1 is meant to serve international purposes for the presentation of current status and improvements of water quality in Danube river and its main tributaries and is not to be a tool for implementation of a national water policy.
Five classes are used for assessment, with target value being the limit value of class II. The class I should represent reference conditions or background concentrations. For number of determinands it was not possible to establish real reference values due to existence of many types of water bodies in Danube river basin differing in its physico-chemical characteristics naturally. For synthetic substances the detection limit or minimal likely level of interest was chosen as limit value for class I.

The classes III – V are on the “non-complying“ side of the classification scheme and their limit values are usually 2-5-times the target values. They should indicate the seriousness of the exceedance of the target value and help to recognise the positive tendency in water quality development.
For compliance testing 90-perentile value of at least 11 measurements in a particular year is used.

Table 7.1.1: Water Quality Classification used for for TNMN purposes.

Determinand	**Unit**	**Class**				
		I	**II** **TV**	**III**	**IV**	**V**
		Class limit values				
Oxygen/Nutrient regime						
Dissolved oxygen *	mg.l^{-1}	7	6	5	4	< 4
BOD$_5$	mg.l^{-1}	3	5	10	25	> 25
COD$_{Mn}$	mg.l^{-1}	5	10	20	50	> 50
COD$_{Cr}$	mg.l^{-1}	10	25	50	125	> 125
pH	-		> 6.5* and < 8.5			
Ammonium-N	mg.l^{-1}	0.2	0.3	0.6	1.5	> 1.5
Nitrite-N	mg.l^{-1}	0.01	0.06	0.12	0.3	> 0.3
Nitrate-N	mg.l^{-1}	1	3	6	15	> 15
Total-N	mg.l^{-1}	1.5	4	8	20	> 20
Ortho-phosphate-P	mg.l^{-1}	0.05	0.1	0.2	0.5	> 0.5
Total-P	mg.l^{-1}	0.1	0.2	0.4	1	> 1
Chlorophyll-a	µg.l^{-1}	25	50	100	250	> 250
Metals (dissolved) **						
Zinc	µg.l^{-1}	-	5	-	-	-
Copper	µg.l^{-1}	-	2	-	-	-
Chromium (Cr-III+VI)	µg.l^{-1}	-	2	-	-	-
Lead	µg.l^{-1}	-	1	-	-	-
Cadmium	µg.l^{-1}	-	0.1	-	-	-
Mercury	µg.l^{-1}	-	0.1	-	-	-
Nickel	µg.l^{-1}	-	1	-	-	-
Arsenic	µg.l^{-1}	-	1	-	-	-
Metals (total)						
Zinc	µg.l^{-1}	bg	100	200	500	> 500
Copper	µg.l^{-1}	bg	20	40	100	> 100
Chromium (Cr-III+VI)	µg.l^{-1}	bg	50	100	250	> 250
Lead	µg.l^{-1}	bg	5	10	25	> 25
Cadmium	µg.l^{-1}	bg	1	2	5	> 5
Mercury	µg.l^{-1}	bg	0.1	0.2	0.5	> 0.5
Nickel	µg.l^{-1}	bg	50	100	250	> 250
Arsenic	µg.l^{-1}	bg	5	10	25	> 25
Toxic substances						
AOX	µg.l^{-1}	10	50	100	250	> 250
Lindane	µg.l^{-1}	0.05	0.1	0.2	0.5	> 0.5
p,p´-DDT	µg.l^{-1}	0.001	0.01	0.02	0.05	> 0.05
Atrazine	µg.l^{-1}	0.02	0.1	0.2	0.5	> 0.5
Trichloromethane	µg.l^{-1}	0.02	0.6	1.2	1.8	> 1.8
Tetrachloromethane	µg.l^{-1}	0.02	1	2	5	> 5
Trichloroethene	µg.l^{-1}	0.02	1	2	5	> 5
Tetrachloroethene	µg.l^{-1}	0.02	1	2	5	> 5
Biology						
Saprobic index - macrozoobenthos	-	≤ 1.8	1.81 – 2.3	2.31 – 2.7	2.71 – 3.2	> 3.2

* values concern 10-percentile value

** for dissolved metals only guideline values are indicated

bg background values

TV target value

For the purpose of classification, the data 1996-2000 had been processed and are presented in tables of Annex 1. The classification scheme originally covers 37 determinands, out of which 29 are presented in the report. The tables showing results of each determinand are sequenced in the Annex in the same order as determinands in the classification scheme, given in Table 7.1.1. The group of metals in dissolved phase is missing because number of available data in evaluated period 1996-2000 is not sufficient to provide representative picture along the Danube River. Similarly in case of some other determinands, like are AOX and volatile hydrocarbons there are parts of Danube River basin covered rather sparsely.

The results of classification are given in tables prepared separately for each water quality determinand. The rows of tables present sampling points, ordered in a way as they occur in a reality from the most upper sampling point in Germany down to the mouth to Black Sea. *Italic letters* used for name of river and location indicate tributaries.

Results characterising each year in a period from 1996-2000 are given in columns of tables. Both calculated mean annual value and so-called "testing value" are given in a cell for each sampling site in a year. Testing value was equal to 90 %-ile (10 %-ile for dissolved oxygen and lower limit of pH value), if number of measurements in a year was at least eleven. If number of measurements in a year was lower than eleven, the testing value was represented by maximum value from a data set (a minimum value for dissolved oxygen and a lower limit of pH value).
Water quality classes in sampling points for each year were expressed by using the following colours:

blue colour	class I
green colour	class II
yellow colour	class III
orange colour	class IV
red colour	class V

It happened in some cases (Cd, Hg, p,p′ DDT, atrazine, trichloromethane) that limit of detection used by country was higher than limit value for class II, representing the target value. In these cases only statistics was calculated and presented in a table, but classification has not been done.

An agreed frequency of measurements has not always been kept in monitoring programme. Using blue colour for figures presenting the statistical haracteristics in tables of Annex 1 expresses those results of classification, which are based on very few (less than three) measurements and therefore are not sufficiently reliable. An exception is saprobic index of macrozoobenthos, in case of which agreed frequency of measurements is two times per year.

7.2. Assessment of spatial changes of physico-chemical determinands

In each profile of the river the water quality reflects the effects of both natural and antropogenic origin. In accordance to the type and extent of these processes water is differently affected in particular sections along the river. To indicate the changes between locations or sections of the river, visualisation by using the charts for each evaluated determinand is provided in the report. Where it is relevant, the charts are also accomplished by target value indication for respective determinands, providing also visualisation of the distance of real situation from this value.

In assessment ofspatial changes in water quality 57 monitoring stations are included, out of which 31 sites are located on the main course of the Danube River and 26 on the first and second tributaries. They are illustrated in Table 7.2.1. in the order of their occurrence along the Danube River. This order was also used in graphical presentations illustrating situation along the river.

Table 7.2.1: List of Monitoring Sites located on the Danube River and its tributaries.

Country Code	River	Town/Location	Distance (km)	River km	Location in Profile	Section
D01	Danube	Neu-Ulm	2581	2581	L	UPPER
D03	/ Inn	Kirchdorf	195	/ 2225	M	
D04	/ Inn / Salzach	Laufen	47	-	M	
D02	Danube	Jochenstein	2204	2204	M	
A01	Danube	Jochenstein	2204	2204	M	
A02	Danube	Abwinden-Asten	2120	2120	R	
A03	Danube	Wien-Nussdorf	1935	1935	R	
CZ01	/ Morava	Lanzhot	79	/ 1880	R	
CZ02	/ Morava / Dyje	Breclav	17	-	R	
A04	Danube	Wolfsthal	1874	1874	R	
SK01	Danube	Bratislava	1869	1869	M	MIDDLE
SK02	Danube	Medvedov/Medve	1806	1806	M	
H01	Danube	Medve/Medvedov	1806	1806	M	
SK03	Danube	Komarno/Komarom	1768	1768	M	
H02	Danube	Komarom/Komarno	1768	1768	M	
SK04	/ Vah	Komarno	1	/ 1766	M	
H03	Danube	Szob	1708	1708	LMR	
H04	Danube	Dunafoldvar	1560	1560	LMR	
H06	/ Sio	Szekszard - Palank	13	/ 1497	M	
H05	Danube	Hercegszanto	1435	1435	LMR	
HR01	Danube	Batina	1429	1429	M	
SL01	/ Drava	Ormoz	300	-	L	
HR03	/ Drava	Varazdin	288	-	M	
HR04	/ Drava	Botovo	227	-	M	
HR05	/ Drava	D. Miholjac	78	/ 1379	R	
H07	/ Drava	Dravaszabolcs	78	/ 1379	M	
HR02	Danube	Borovo	1337	1337	R	
H08	/ Tisza	Tiszasziget	163	/ 1215	LMR	
H09	/ Tisza/ Sajo	Sajopuspoki	124	-	M	
SL02	/ Sava	Jesenice	729	-	R	
HR06	/ Sava	Jesenice	729	-	R	
HR07	/ Sava	Us. Una Jasenovac	525	-	L	
HR08	/ Sava	Ds. Zupanja	254	/ 1170	M	
RO01	Danube	Bazias	1071	1071	LMR	LOWER
RO02	Danube	Pristol/Novo Selo	834	834	LMR	
BG01	Danube	Novo Selo/Pristol	834	834	LMR	
BG02	Danube	Us. Iskar - Bajkal	641	641	M	
BG06	/ Iskar	Orechovitza	28	637	M	
BG03	Danube	Ds. Svishtov	554	554	MR	
BG07	/ Jantra	Karantzi	12	537	M	
BG04	Danube	Us. Russe	503	503	MR	
BG08	/ Russenski Lom	Basarbovo	13	498	M	
RO03	Danube	Us. Arges	432	432	LMR	
RO04	Danube	Chiciu/Silistra	375	375	LMR	
RO09	/ Arges	Conf. Danube	0	/ 432	M	
BG05		Silistra/Chiciu		375	LMR	
RO10	/ Siret	Conf. Danube - Sendreni	0	/ 154	M	
MD01	/ Prut	Lipcani	658	-	L	
MD02	/ Prut	Leuseni	292	-	M	
MD03	/ Prut	Conf. Danube - Giurgiulesti	0	/ 135	M	

Country Code	River	Town/Location	Distance (km)	River km	Location in Profile	Section
RO11	/ Prut	Conf. Danube - Giurgiulesti	0	/ 135	M	
RO05	Danube	Reni-Chilia/KiliaArm	132	132	LMR	
UA01	Danube	Reni-Kilia Arm/Chilia Arm	132	132	M	
RO06	Danube	Vilkov-Chilia Arm/Kilia Arm	18	18	LMR	
UA02	Danube	Vilkov-Kilia Arm/Chilia Arm	18	18	M	
RO07	Danube	Sulina – Sulina Arm	0	0	LMR	
RO08	Danube	Sf. Gheorghe – Sf. Gheorghe Arm	0	0	LMR	

Legend for Table 7.2.1:
- River: The water course where the sampling site is located
- Distance: The distance (km) from the mouth of the considered river
- River km (rkm): The Danube River km (from confluence with the Black Sea) where the sampling site is located
- / Tributary
- Us. – Upstream of
- Ds. – Downstream of
- Conf.: Confluence tributary / main river
- Location in profile:
  - L – left bank of the river
  - M – middle of the river
  - R – right bank of the river
- Section:
  - Upper Danube
  - Middle Danube
  - Lower Danube

According to a previous approach (*Joint Danube Survey – Technical Report, 2002*) and to a regional agreement among the Danube countries, the Danube Basin was divided into three main sections for the purpose of assessmen (Fig. 7.2.1):
- Upper Section: from Danube-Neu Ulm (km 2581, D01) to Danube-Wolfsthal (km 1874, A04), comprising of 6 monitoring sites;
- Middle Section: from Danube-Bratislava (km 1869, SK01) to Danube-Borovo (km 1337, HR02), comprising of 10 monitoring sites;
- Lower Section: from Danube-Bazias (km 1071, RO01) to Danube-Sf. Gheorghe/Sf. Gheorghe arm (km 0, RO08) comprises 15 monitoring sites. In order to make the charts more clear and due to the fact that entire lower section has more than 1000 km length, this section was further divided into two parts. Second part of the lower section starts in Danube-Us. Arges (km 432, RO03).

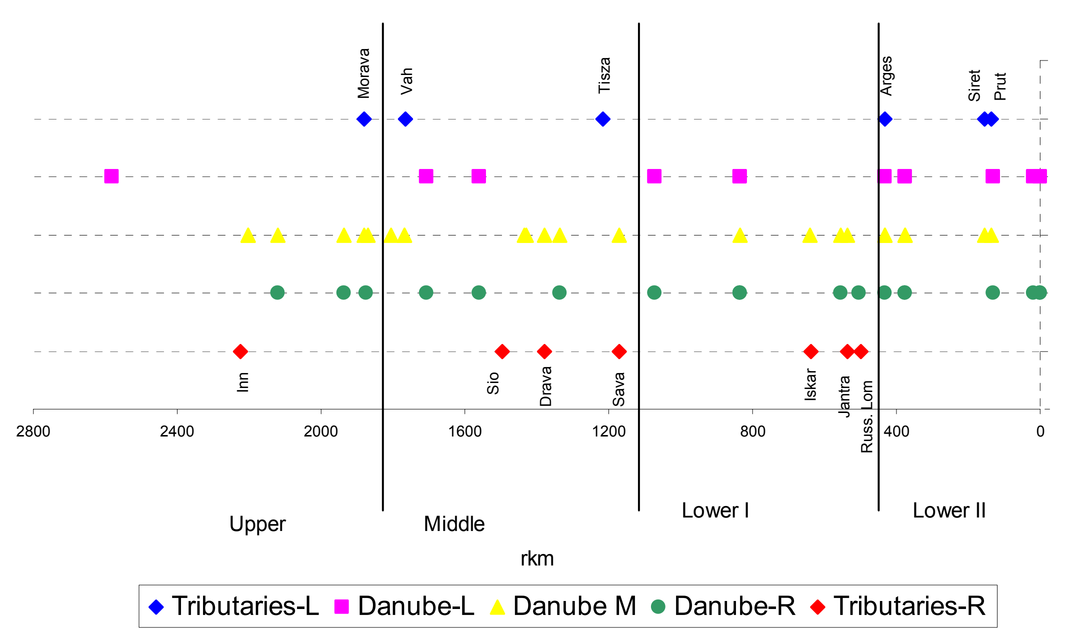


Fig. 7.2.1: Selected monitoring sites

Legend for Fig. 7.2.1:

- Danube-L: the left bank of the Danube River
- Danube-R: the right bank of the Danube River
- Tributary-L: tributary for which the confluence is located on the left side of the Danube River
- Tributary-R: tributary for which the confluence is located on the right side of the Danube River

Physico-chemical determinands selected for the assessment have been divided to five groups in accordance to Table 7.2.2.

Table 7.2.2.: List of selected physico-chemical determinands for water quality assessment

Group of determinands	Determinand	Unit
General characteristics	Suspended Solids (SS)	mg/l
	pH	-
	Conductivity	µS/cm
	Alkalinity	mmol/l
Nutrients	Ammonium-N (N-NH_4^+)	mg/l
	Nitrite-N (N-NO_2^-)	mg/l
	Nitrate-N (N-NO_3^-)	mg/l
	Ortho-phosphate-P (P-PO_4^{3-})	mg/l
	Total Phosphorous	mg/l
Oxygen regime	Dissolved oxygen (concentration)	mg/l
	Biochemical Oxygen Demand (BOD_5)	mg/l
	Chemical Oxygen Demand by $K_2Cr_2O_7$ (COD_{Cr})	mg/l
	Chemical oxygen demand by $KMnO_4$ (COD_{Mn})	mg/l
Heavy Metals	Iron (Fe)	mg/l
	Manganese (Mn)	mg/l
	Zinc (Zn)	µg/l
	Copper (Cu)	µg/l
	Chromium – total (Cr)	µg/l
	Lead (Pb)	µg/l
	Cadmium (Cd)	µg/l
	Mercury (Hg)	µg/l

Group of determinands	Determinand	Unit
	Nickel (Ni)	µg/l
	Arsenic (As)	µg/l
Organic micropollutants	Lindan	µg/l
	pp'-DDT	µg/l
	Atrazine	µg/l
	Chloroform	µg/l
	Carbon tetrachloride	µg/l
	Trichloroethylene	µg/l
	Tetrachloroethylene	µg/l

The basis for the evaluation was 90 %-ile (c90) for each considered determinand (90 percentile method has the advantage that extreme values caused by exceptional conditions or measuring errors are not taken into account, but still represents "unfavourable" situation that occurred in monitoring site in a year). For dissolved oxygen content 10%-ile data were considered, but maximum and minimum values were also taken into account.

Here is necessary to stress that whilst for assessment of spatial and temporal changes c90 was used, in classification c90 value was used in all those cases when frequency of measurements of determinand in a year was at least 11. In case of lower frequency, testing value as a basis for classification was maximum value from a data set, as was explained in a chapter 7.1. Therefore, c90 value in charts presented in evaluation part of the report can differ from numerical value given in classification tables at a place of "testing value".

There are two main types of the charts used for illustration of determinands. The first type is a bar chart presenting 90 %-iles calculated for each year in all monitoring sites measured in TNMN (it means that in case of measurements made on right side, left side and in the middle of a profile the data from all three sites are presented). The distance between monitoring sites is proportional on the x-axis. This type of chart is made separately for Danube River and for tributaries.

The second type is x/y chart with river kilometres on x-axis. The chart is prepared separately for Danube River itself and for tributaries again. In case of presenting tributaries concentrations are plotted at the river km of the confluence of the tributary with the Danube. Therefore, in the Table 7.2.1. also river km of confluence with Danube is given for tributaries. In this type of chart a lne is added displaying the target value equal to class II limit value. By comparing the real values against the distance from target value can be seen.

7.3. Trend Analysis

After five years of monitoring the question rises whether water quality in the Danube River Basin improves, remains stable or get worse. Many changes took place regarding the economic situation in the countries, industrial production, agricultural methods, land use and protection of environment. The human impact on rivers might differ now from that of 1996. In the meantime the physical, chemical and biological characteristics of the Danube and its tributaries have also varied because they are dependent on hydrological conditions and climate. There are the natural trends in water quality that reflect either short-term or long-term changes and cyclic repetitions like daily, seasonal or longer periodicity. Taking this in consideration five years are not very much for trend analysis.

Several methods for trend analysis are described in literature. Nearly every software used for calculation or data base has a tool for adding trend line to time-series plots. However without having any information on the behaviour of the determinands no serious evaluation can be done. To calculate trend lines as a precondition periodic cycles have to be substracted from the time-series. Afterwards the quality of the so called trend model has to be proved e.g. by checking the distribution frequency of the square deviations from the line. To apply these procedures for time-series analysis sufficient data of high quality is needed and much information on the processes, which steer the environmental turnover of a substance, should be available. Within the TNMN network about 60 samples should be stored for every determinand, but actually there are much less particularly for specific pollutants. For some determinands few samples may be sufficient if there is no seasonal periodicity and if fluctuations of values are either random or very strong dependent on a known predicting variable. While only few determinands fulfil these preconditions it was decided to firstly use a very simple approach for trend analysis comparing to the models mentioned above.

The simple approach for trend assessment is based on the comparison of statistical parameters of yearly data sets. According to the parameter different situations can be evaluated, the choice is dependent on the target of the analysis. Critical situations can be expressed best by the 90percentile (or 10percentile for pH and dissolved oxygen) of a yearly data set. As they occur naturally or as a result of human impacts it often appears difficult to interpret the year-on-year variations. To calculate 90percentiles mathematically reliable a sufficient number of samples per year are required, too. Although all data sets, which consist of more than five samples, were considered, valid statements can only be given for some determinands where more samples are available.

The trend assessment was carried out for all monitoring sites of the TNMN. At sites where samples are taken from left, middle and right only the middle was used. In general the different riversides fit quite well together. For the year 1996 the differences are often higher than for other years and for some nutrients (ammonia, ortho-phosphate phosphorus and total phosphorus) and heavy metals greater deviations have to be observed, too. A systematic difference is monitored for Kilia-arm at Reni: values of COD_{Cr} of the left side exceed that of the right side.

7.4. Evaluation of biological determinands

An integral part of TNMN are biological determinands and MLIM-EG exerted a big effort to harmonise methodologies of their measurements and evaluation to assure their comparability throughout the River basin and to utilise their potential of being good indicators of water quality. In TNMN Phase I chlorophyll-a, macrozoobenthos and microbiological determinands had been measured.

Phytoplankton biomass – concentration of the chlorophyll-*a*

Chlorophyll-a is the essential photosynthetic pigment present in all green plants. The chlorophyll content in surface water is an indicator of its trophic state. The determination of the chlorophyll-a concentration provides information concerning the quantity and potential photosynthetic activity of the algae in the water column. The ratio of chlorophyll to phaeopigments (important metabolites of chlorophylls) is indicative of the physiological state of the algae.

Phytoplankton together with phytobenthos and water macrophytes reflect the primary production in the watercourses. Therefore it is important community to investigate it. Increase of the phytoplankton biomass is one of the characteristics of the eutrophication in the rivers. Eutrophication of the large rivers is caused by input of the nutrients in excess in combination with other factors like suitable light, temperature, transparency. High level of eutrophication lead to negative consequences for the river itself and reservoirs in particular (Wetzel, 1983).

Development of the phytoplankton biomass can be measured also as a concentration of the chlorophyll-a. For this purpose the method of ISO 10260 (1992) was recommended. Method consists of four steps (collection of algae from water by filtration; extraction of algal pigments from the filter residue into hot ethanol; spectrometric determination of chlorophyll-a concentration in the extract and evaluation of the chlorophyll-a and phaeopigment from the difference in absorbance prior to and after acidification of the extract).

Based on the TNMN database from the period 1996-2000 the statistical processing of selected characteristic values was used for individual year. In case of less than 3 measurements existing in a year, no value was used. Up to 10 measurements a maximum was used as a characteristic value. If more data were available 90 percentile was calculated. If the chlorophyll-a was measured at cross section of the river (left, middle and right), the mean value of three sites was taken into account. Characteristic values categorized individual TNMN stations according to the classification scheme (tab. 7.4.1).

Tab.7.4.1: Classification scale of the quality class for the chlorophyll-a concentration.

CLASSIFICATION SCALE	I.	II.	III.	IV.	V.
	High status	Good status	Moderate status	Bad status	Very bad status
µg/l of the chlorophyll-a	≤25	≤50	≤100	≤250	>250

Saprobic index of macrozoobenthos

Macroscopic organisms – macroinvertebrates create the important part of the aquatic community. In accordance with specific autecological demands for life in the aquatic environment, individual species react in different ways to variations in its physical and chemical state like diffuse and point sources pollution, light, temperature, flow velocity, oxygen condition and the structure of the river bed.

Macrozoobenthos taxa are space and/or food competitors with different feeding habitats and they are capable to self-regulate their population size. They also depend on other biological compartments, in particular on micro-organisms, whose metabolic activity can lead to negative effect on the oxygen budget of the water body and its fauna during decomposition of great amounts of organic substances (saprobity).

Within the TNMN the standard operational procedure have been proposed to monitor macrozoobenthos in the Danube river and its tributaries. The SOP covered macroinvertebrates only and was focused on the numerical evaluation for the system of saprobity by means of the Saprobic Index. The macroinvertebrates sampling and biological assessment was a first step in the development of a more comprehensive ecological assessment of the river water quality. There were a few sampling methods, level of taxa identification and numerical evaluation suggested. For TNMN it was recommended to use the Pantle & Buck formula, modified by Zelinka & Marvan:

$$SI = \frac{\sum h_i * s_i * I_i}{\sum h_i * I_i}$$

with: h_i = quantity of species i in sample
I_i = weight of species i in sample.
s_i = saprobic index of species i.

The quantity (h) in the formula can be expressed as an estimation of the number of individuals in the sample based on 5 class scale. The Saprobic Index ranges from 1 to 4 and is in current practice divided into 4 or 7 classes covering the range from xenosaprobic to polysaprobic. SOP proposed five class scale to evaluate biological results for TNMN (see table 7.4.2).

Tab. 7.4.2: Proposal for classification of Saprobic Index in the natural rivers in Danube basin.

Class	**I**	**II**	**III**	**IV**	**V**
Saprobic Index	< 1.8	1.81-2.3	2.31-2.7	2.71-3.2	>3.2

Whilst the results of saprobic index classification in accordance to TNMN classification scheme are presented in Annex 1, in the special chapter dedicated to biological determinands (chapter 8.2) the seven-class scale was used based on the Saprobic Index in accordance to Austrian standard ÖNORM M6232. The reason is that this scale is more detailed, mainly in the range of the first three classes (see table 7.4.3).

Tab. 7.4.3: Classification scale based on the Saprobic Index (in accordance to Austrian standard ÖNORM M6232).

	I.	I.-II.	II.	II.-III.	III.	III.-IV.	IV.
CLASSIFICATION SCALE	unpolluted	low polluted	moderately polluted	criticaly polluted	strongly polluted	very high polluted	extensively polluted
	≤1,25	≤1,75	≤2,25	≤2,75	≤3,25	≤3,75	>3,75

Based on the TNMN database from the period 1997-2000 the statistical processing of selected characteristic values was used for individual year. Usually 3-4 measurements were done by the individual countries. Characteristic values (maximum for individual year) categorized individual TNMN stations according to the above mentioned classification scale.

Microbiological determinands

Heterotrophic bacteria play a decisive role in river ecosystem in degrading organic matter. Their contribution to self purification processes of rivers is of great interest within a scope of water quality assessment. Bacteria are ideal sensors because of their fast response to changing environmental conditions (Kavka, 2002).

Bacterial indicators such as total coliforms, faecal coliforms (thermotolerant coliforms), E.coli, faecal streptococci (enterococci) and colony counts are widely applied to the assessment of water quality. On one hand, because of their mainly allochthonous origin, these standard parameters are used as indicators of change in the natural stage of rivers. On the other hand, they indicate anthropogenic impact such as faecal pollution in the water. E.coli and faecal coliform bacteria are the best indicators for assessment of faecal pollution, mainly caused by raw and treated sewage and e.g. diffuse impact from farmlands and pastures. Faecal indicators are excreted by humans and warm-blooded animals treated to a large extent in sewage treatment plants and ultimately found in aquatic environment where they survive for a relatively long time. E.coli and faecal coliforms also indicate the potential presence of pathogenic bacteria, viruses and parasites (Kavka, 2002).

For the TNMN database Total Coliforms, Faecal Coliforms, Faecal Streptococci (enterococci) and *Salmonella* sp. were proposed for monitoring. However data on Faecal Streptococci and *Salmonella* sp. are for evaluated period (1996-2000) insufficient. Therefore only Total Coliforms and Faecal Coliforms were processed for the purpose of this report.

Total Coliforms usually contained typical coliform bacteria (*Escherichia coli*, Klebsiella sp., Citrobacter sp., Enterobacter sp.). For TNMN the proposed method was according to the ISO 9308-1:1990. Method is based on membrane filtration, cultivation (mEndo-Agar LES, Difco) and incubation of 24 hours at 37ºC.

For the Faecal Coliforms (thermotolerant coliform bacteria) the method of ISO 9308-1:1990 was recommended. Method is based on membrane filtration, cultivation (mFC medium, Difco) and incubation of 24 hours at 44ºC.

Base on the TNMN database from the period 1996-2000 the statistical processing of selected characteristic values was used for individual year. In case of less than 3 measurements exist in a year, no value was used. Up to 10 measurements a maximum was used as a characteristic value. If more data were available 90 percentile was calculated. If the analyses of bacteria were provided at cross section of the river (left, middle and right), the mean value of three sites was taken into acount.

TNMN classification does not contain limit values for microbiological deterinands. Therefore, the classification scale given in table 7.4.4 was used to categorize water quality from the point of view of microbiological pollution in TNMN stations.

Table 7.4.4: Classification system of Kohl (1975), the EU-Bathing Water Quality Directive 76/160 EEC and new EU expert proposals (verbal information) were taken into account.

CLASSIFICATION SCALE	**I.**	**II.**	**III.**	**IV.**	**V.**
POLLUTION	**Low**	**Moderate**	**Critical**	**Strong**	**Extensive**
Total Coliforms (CFU/100 ml)	≤500	≤10000	≤100000	≤1000000	>1000000
Faecal Coliforms (CFU/100 ml)	≤100	≤1000	≤10000	≤100 000	>100000

7.5. Comparison of TNMN results 1996-2000 with Environmental Quality Standards of EU legislation

7.5.1. Introduction

With the publication of the Water Framework Directive (EC 2000) in December 2000 a new legal basis for the protection of ground and surface waters within the European Union has been put into force. One of the objectives of the Water Framework Directive (WFD) is to achieve a "good surface water status" for all surface waters irrespective of their size until 2015. Regarding dangerous substances this means that all environmental quality standards (EQS) "established

- in Annex IX
- and under Article 16(7) of the WFD
- and under other relevant Community legislation setting EQS at Community level" have to be met.

Annex IX of the WFD lists the daughter directives of the Dangerous Substances Directive (EEC 1976, EEC 1982, EEC 1983, EEC 1984/1, EEC 1984/2, EEC 1986). This legislation stipulates the EQS for the seventeen so called List 1 substances (see Table 7.5.1.1).

Table 7.5.1.1 Environmental Quality Standards for List 1 substances according to the daughter directives of Council Directive 76/464/EEC (Dangerous Substances Directive, EEC 1976)

List 1 Substance	**CAS number**	**Directive**	**EQS water µg/l**	**EQS sediment**	**EQS biota**
Cadmium	7440-43-9	83/514	1 a), b)	Standstill e)	Standstill c)
DDT total		86/280	0,025 d)	Standstill e)	Standstill f)
1,2-Dichloroethane	107-06-2	86/280	10		
Drins		86/280	0,01 g)	Standstill e)	Standstill f)
Hexachlorobenzene	118-74-1	86/280	0,03	Standstill e)	Standstill f)
Hexachlorobutadiene	87-68-3	86/280	0,1		
Hexachlorocyclohexane	608-73-1	84/491	0,05 h)	Standstill e)	Standstill f)
Pentachlorophenol	87-86-5	86/280	2	Standstill e)	Standstill f)

List 1 Substance	CAS number	Directive	EQS water µg/l	EQS sediment	EQS biota
Mercury	7439-97-6	82/176, 84/156	1 b)	Standstill e)	0.3 mg/kg i) Standstill j)
Tetrachloroethene	127-18-4	86/280	10		
Tetrachloromethane	56-23-5	86/280	12		
Trichlorobenzene	120-82-1	86/280	0,4 k)	Standstill e)	Standstill f)
Trichloroethene	79-01-6	86/280	10		
Trichloromethane	127-18-4	86/280	12		

a) Without direct impact of a discharge, otherwise 5 µg/l
b) Total metal concentration
c) Mollusks and shellfish (if possible, mytilus edulis)
d) p,p'-DDT 0,01 µg/l, DDT total comprises p,p'-DDT, o,p'-DDT, p,p'-DDE and p,p'-DDD
e) optional to standstill in biota
f) Standstill in Fish and/or mollusks and/or shellfish
g) Endrin and Isodrin 0,005 µg/l
h) Without direct impact of a discharge, otherwise 0,1 µg/l. The directive does not specify to which isomer the limit value relates
i) For Fish, wet weight
j) Mollusks and shellfish (optional to sediments)
k) Related to the sum of three isomers

Article 16 of the WFD summarizes the strategies against pollution of water. In 16(2) the European Commission is obliged to submit a list of priority substances "which present a significant risk to or via the aquatic environment". With Decision 2455/2001/EEC (EC 2001) this obligation was fullfilled and a first list of priority substances published. For the time being no binding EQS have been set for these compounds but on behalf of the European Commission the Fraunhofer-Institute (FHI) for Molecular Biology and Applied Ecology (Schmallenberg, Germany) carried out a study which aimed to derive EQS for the priority substances based on ecotoxicological data according to the procedure laid down in Annex V, 1.2.6 of the WFD (FHI 2002). This proposal is available now and the EQS will be put into force with minor modifications in 2003/2004. The priority substances and the proposed quality objectives are given in Table 7.5.1.2.

Table 7.5.1.2: List of Priority Substances according to Decision 2455/2001/EC and Overall Environmental Quality Standards for Inland and Transitional Waters proposed by FHI

Priority Substance	CAS number	EQS FHI [µg/l]
Alachlor	15972-60-8	0,035
Anthracene	120-12-7	0,063
Atrazine	1912-24-9	0,34
Benzene	71-43-2	16 a)
Brominated diphenylethers	32534-81-9	0,0005 b)
Cadmium and its compounds	7440-43-9	0,08 c)
C_{10-13}-chloroalkanes	85535-84-8	0,41
Chlorfenvinphos	470-90-6	0,01
Chlorpyrifos	2921-88-2	0,00046
1,2-Dichloroethane	107-06-2	10 d)
Dichloromethane	75-09-2	8,2
Di(2-ethylhexyl)phthalate (DEHP)	117-81-7	0,33

Priority Substance	**CAS number**	**EQS FHI [µg/l]**
Diuron	330-54-1	0,046
Endosulfan alpha-Endosulfan	115-29-7 959-98-8	0,004
Fluoranthene	206-44-0	0,12
Hexachlorobenzene	118-74-1	e)
Hexachlorobutadiene	87-68-3	0,003
Hexachlorocyclohexane (gamma-isomer, Lindane)	608-73-1 58-89-9	0,042 0,02
Isoproturon	34123-59-6	0,32
Lead and its compounds	7439-92-1	1 c)
Mercury and its compounds	7439-97-6	0,036 c), f)
Naphthalene	91-20-3	2,4
Nickel and its compounds	7440-02-0	0,6 c)
Nonylphenols (4-(para)-nonylphenol) (4-nonylphenol, branched)	25154-52-3 104-40-5 84852-15-3	0,33
Octylphenols (para-tert-octylphenol)	1806-26-4 140-66-9	0,1
Pentachlorobenzene	608-93-5	0,05
Pentachlorophenol	87-86-5	0,1
Polyaromatic hydrocarbons (Benzo(a)pyren) (Benzo(b)fluoroanthene) (Benzo(g,h,i)perylene) (Benzo(k)fluoroanthene) (Indeno(1,2,3-cd)pyrene)	 50-32-8 205-99-2 191-24-2 207-08-9 193-39-5	e)
Simazine	122-34-9	1
Tributyltin compounds (Tributyltin-cation)	688-73-3 36643-28-4	0,0001
Trichlorobenzenes (1,2,3-Trichlorobenzene) (1,2,4-Trichlorobenzene) (1,3,5-Trichlorobenzene)	12002-48-1 87-61-6 120-82-1 108-70-3	1,8
Trichloromethane (Chloroform)	67-66-3	3,85
Trifluralin	1582-09-8	0,03

a) No proposal for an overall QS was made in the FHI study. Specific QS derived for the protection of aquatic life is given.

b) Individual substances are very different regarding their physico-chemical properties and toxic potential. QS for the most harmful individual compound Pentabromo diphenylether is given.

c) Maximum permissible addition (MPA) according to the "Added Risk" approach for the QS derivation of metals, for details see text.

d) No proposal for an overall QS was made in the FHI study. EQS of CD 86/280/EEC currently in force is given (see also Table 1)

e) No proposal for an overall QS was made in the FHI study.

f) No proposal for an overall MPA was made in the FHI study.

The other, above-mentioned "Community legislation setting EQS at Community level" comprises application-oriented directives containing EQS for specific water uses, which are of regional and not of general significance. These EQS are not further considered within this report.

In 1996-2000 a number of List 1 and Priority Substances were analysed within TNMN in Danube River and tributaries (see Table 7.5.1.3).

Table 7.5.1.3: List 1 and Priority Substances observed within TNMN in the time period 1996- 2000 and TNMN substance code

Substance	List 1 Substance	Priority Substance	TNMN Code
Atrazine		X	4.75
Cadmium (total)	X		3.65
Cadmium (dissolved)		X	3.66
p,p'-DDT	X		4.65
Lead (dissolved)		X	3.61
Lindane (gamma-Hexachlorcyclohexane)	X	X	4.60
Mercury (total)	X		3.70
Mercury (dissolved)		X	3.71
Nickel (dissolved)		X	3.76
Tetrachloroethene	X		4.95
Tetrachloromethane (Carbon tetrachloride)	X		4.85
Trichloroethene	X		4.90
Trichloromethane (Chloroform)	X		4.80

With respect to the fact that two riparian countries of the Danube River are member states of the European Union and another four will join the community in near future and therefore are obliged to implement the WFD it seems very interesting to compare these results with already valid and future EQS.

Motivation for such an assessment is

- identification of possible problems with exceeding substance concentrations
- identification of data gaps
- recommendations for the analysis of List 1 substances and PS in future based on experiences in compliance checking of this report

7.5.2. Testing for compliance

Choice of statistical quantity

In Annex V, 1.2.6 of the WFD dealing with the derivation procedure for EQS is stated that quality objectives should be laid down by "setting of a maximum annual average concentration". No further guidance is given for compliance checking. For List 1 substances this is specified in more detail in the daughter directives of CD 76/464/EEC: the arithmetic annual mean of analytical results shall be used to check the compliance with EQS. On EC level the Expert Advisory Forum Priority Substances (EAF - an expert advisory panel supporting the European Commission in implementing the WFD) has agreed to use the arithmetic mean at least for the discussion of the proposal of EQS for Priority Substances. There are still other statistical quantities in discussion for compliance checking, namely a combination of mean and a maximum allowable concentration (MAC) and the 90 percentile, but for the time being the annual arithmetic mean is the preferred statistical quantity. For this reason the *mean* was selected too to compare TNMN data with EQS for the purpose of this report. (Note: Due to the fact that for comparison of TNMN data with EQS of EU legislation the the mean was used, the values presented in chapter 8.1.6 are different than those presented by charts in chapters 8.1.3 and 8.1.5, where c90 was used).

Dealing with "less than" values

For the time being no information can be found in EC legislation or guidance documents how to handle data below the detection limit when calculating the mean. This is a very important detail because in certain cases (EQS close to the limit of detection of the analytical method, many less than values) the chosen convention resp. method can influence the results of the compliance check dramatically. It is common practice to use simple substitution methods for taking into account less than values. The problem associated with this methods is that they have no theoretical basis and are defined by convention. The mean is biased and deviates more or less from the real location (HELSEL 2002). In TNMN yearbooks the mean is calculated by substituting the less than values with the limit of detection (LOD) of the specific analytical method. Although this is a very pesimistic approach because the mean is definitely shifted to higher concentrations in comparison with its true location this method was used for the purpose of this report to keep comparability with the yearly evaluations (this convention is named "LOD-method"). For some substances an additional evaluation using the most optimistic approach for calculation of the mean by setting the less then values to zero has been included to show the influence of the averaging method (called "Zero-method" in the following text).

Dealing with EQS lower than LOD

Derivation of EQS on a ecotoxicological basis sometimes results in a very low concentration as limit value which is out of range of the available analytical methodologies. Although this problem is evident for a number of Priority Substances it hasn't been tackled on EU level. One proposal to be discussed is to use the LOD as substitute for the actual EQS value. Of course this approach needs a harmonisation of methods or at a least the definition of minimum requirements regarding the LOD to avoid different limit values in the respective states. Whether a data set including some less than values gives compliance or non-compliance again depends on the convention used for calculating the mean. The "LOD-method" results in a non-compliance with only one figure above LOD (see also related text in an evaluation part of the report).

8. Assessment of Water Quality

The assessment of water quality in Danube River basin in the report is divided into two basic parts – assessment on the basis of physico-chemical determinands and assessment of biological determinands. Chapter 8 is dedicated to assessment on the basis of physico-chemical determinands. It is structured in a way, that for each evaluated determinand information on results of classification are given (on the basis of tables with results of classification in the Annex 1), followed by information on spatial changes and trend assessment in Danube River itself and tributaries. This chapter is supplemented by sub-chapter 8.1.6 dealing with comparison of available TNMN data on hazardous substances with Environmental Quality Standards of European Union legislation and with proposed EQS for priority substances.
Results of water quality assessment based on biological determinands are given in chapter 8.2.

8.1. Assessment of water quality based on physico-chemical determinands

8.1.1. General Characteristics

Suspended solids

Suspended matter comprises the quantity of insoluble substances in water that can be separated by filtration, centrifugal action and sedimentation. Insoluble substances, composed by organic and inorganic particles, can be both rough dispersions (particles size above 0.1 mm) and fine dispersions (particle size between 0.1 mm and 0.1 μm). Depending on size and specific gravity these particles are settling, remaining in suspended form or floating on the water surface.
In assessment of river water quality, strong correlation of suspended solids content with the flow discharge conditions must be taken into account. Several determinands measured in frame of TNMN are highly dependent on suspended solids content in waters, like total P, heavy metals (if sample is not filtered before analysis) and specific organic micropollutants with affinity to solid particles.

For the Danube River itself, the spatial pattern of suspended solids variation is shown in **Fig. 8.1.1.1a** and **Fig. 8.1.1.1b**.

As it can be seen, in the upper section of the Danube River, excepting the first monitoring station, Danube-Neu Ulm (km 2581, D01), where the concentration values are below 35 mg/l, all the other values show a relative uniform profile of spatial pattern. Still, an increasing spatial line is noticeable along this stretch.

For the middle section, suspended solids concentrations decrease from Danube-Bratislava (km 1869, SK01) down to Danube-Medvedov/Medve (km 1806, SK02) due to sedimentation process in Gabcikovo dam. For the following part of this stretch, the spatial pattern remains constant down to Danube-Hercegszanto (km 1435, H05). Slight higher concentrations, exceeding 100 mg/l in 2000, are present at Danube-Batina (km1429, HR01) and Danube-Borovo (km 1337, HR02), in conditions of discharge of 4305 m^3/s and 4464 m^3/s, respectively.

In the first part of lower section, most of the suspended solids concentration values are higher than in the middle section, but a decreasing tendency from Danube-Bazias (km 1071, RO01) down to Danube-us. Russe (km 503, BG04) can be noticed.

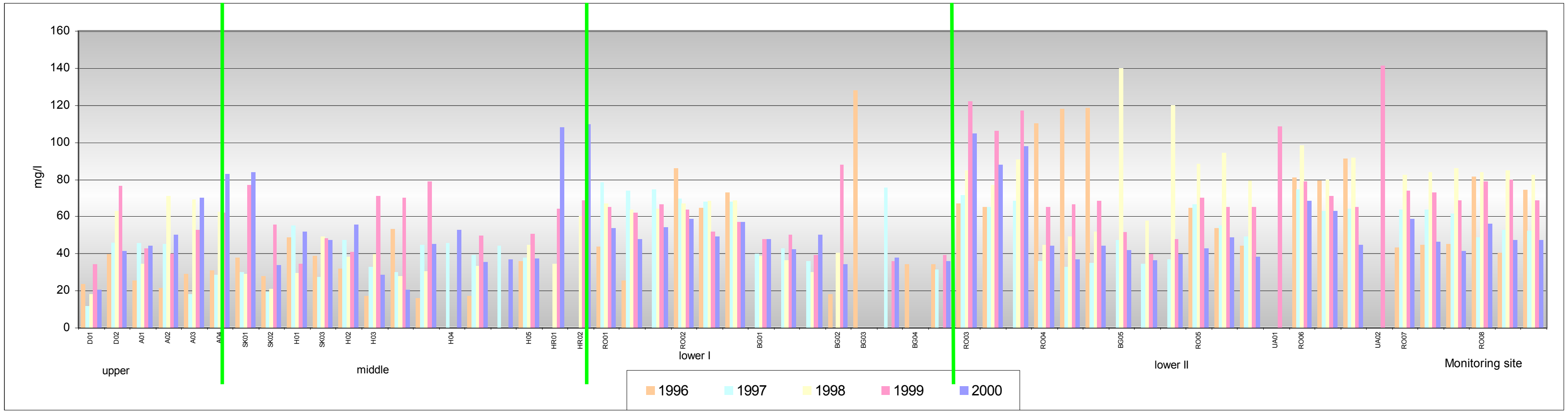


Fig. 8.1.1.1a: Spatial variation of Suspended Solids content – Danube River

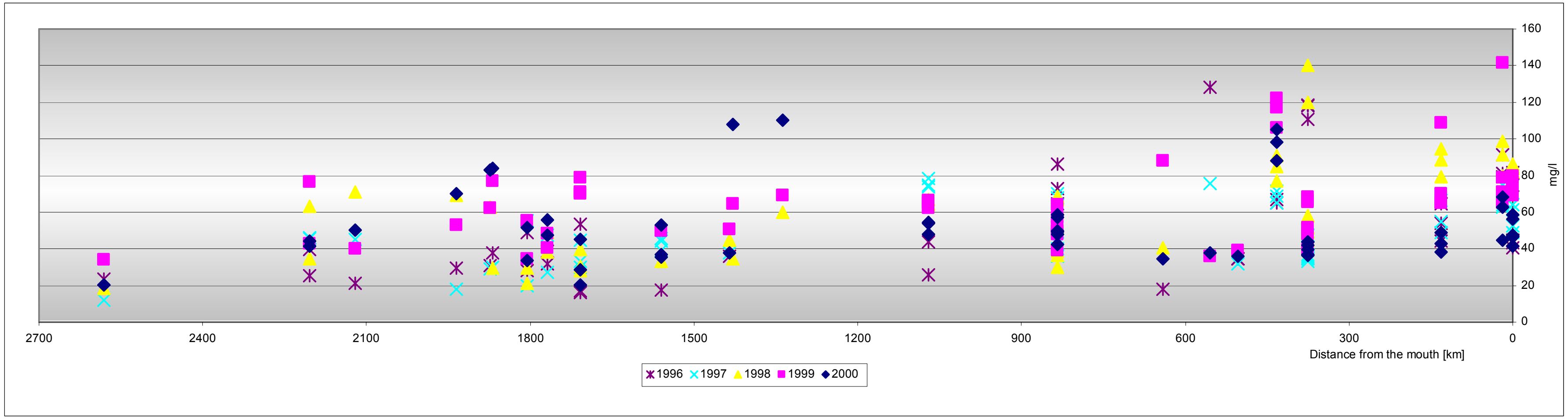


Fig. 8.1.1.1b: Spatial variation of Suspended Solids content – Danube River

The second part of the lower Danube section shows a relative constancy, but the suspended solids level is higher than in the previous part: here many values exceed 80 mg/l, while just a few of them are above this value in the first part. A few higher values are recorded at Danube-us. Arges (km 432, RO03) and at Danube-Chiciu/Silistra (km 375, RO04), but these concentration values are not very well in correlation with those reported for the same location but different site - Danube-Silistra/Chiciu (km 375, BG05).

The maximum values from this stretch belong to Danube-Silistra/Chiciu (km 375, BG05) and to Danube-Vilkov-Kilia arm/Chilia arm (km 18, UA02): 140.0 and 141.4 mg/l, respectively.

Selected tributaries generally present a higher suspended solids content than the Danube itself – **Fig. 8.1.1.2a, 8.1.1.2b and 8.1.1.3**:

- in the upper section, the Inn-Kirchdorf (D03) - 315 mg/l in 2000 and 158.4 mg/l in 1996 and the Morava-Lanzhot (CZ01) - 154.8 in 1996 versus 83.1 mg/l, represent the maximum value in the Danube River in this section;
- in the middle section, the Sio-Szekszard-Palank (H06) shows 140.8 mg/l in 1999 and 116.0 mg/l in 1998 versus approx. 50.0 mg/l for the upstream/downstream monitoring sites, Danube-Dunafoldvar (H04) and Danube-Hercegszanto (H05); but the maximum values for tributaries located in this stretch belong to the Tisza-Tiszasziget (H08) – 336.6 mg/l (L), 372.9 mg/l (M) and 414.0 mg/l (R) in 1998. The values above 100 mg/l appear also on the Sava-Jesenice (HR06) and Sava-us. Una Jasenovac (HR07), in 1998;
- from tributaries the highest suspended solids content belongs to those from the lower section, where the Russenski Lom-Basarbovo (BG08) is characterized by values ranging between 252.6 mg/l and 569.8 mg/l. Also the Siret-Conf. Danube-Sendreni (RO10) and Prut-Conf. Danube Giurgiulesti present rather high concentrations – 308.3 mg/l in 1998 and 278.0 mg/l respectively, in 2000.

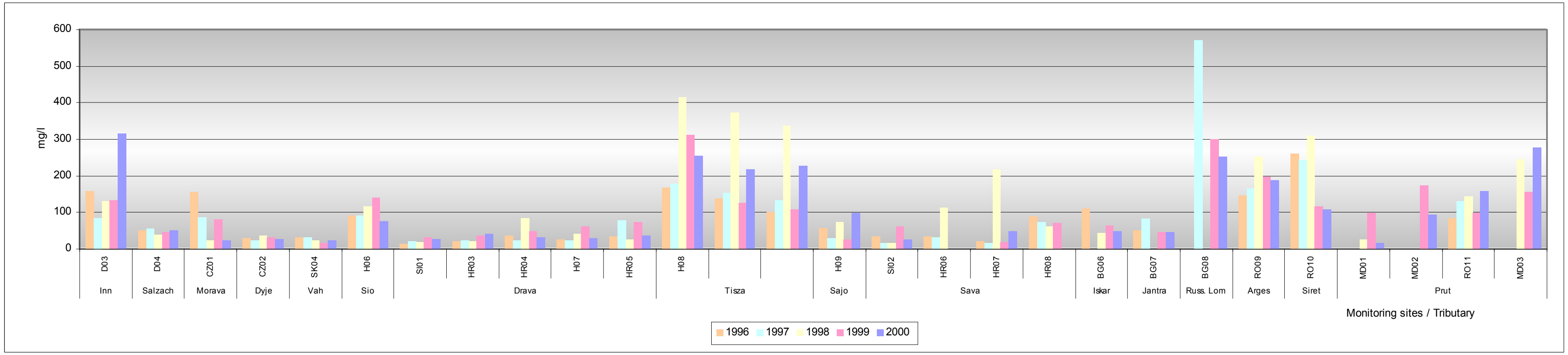


Fig. 8.1.1.2a: Spatial variation of Suspended Solids content – Tributaries

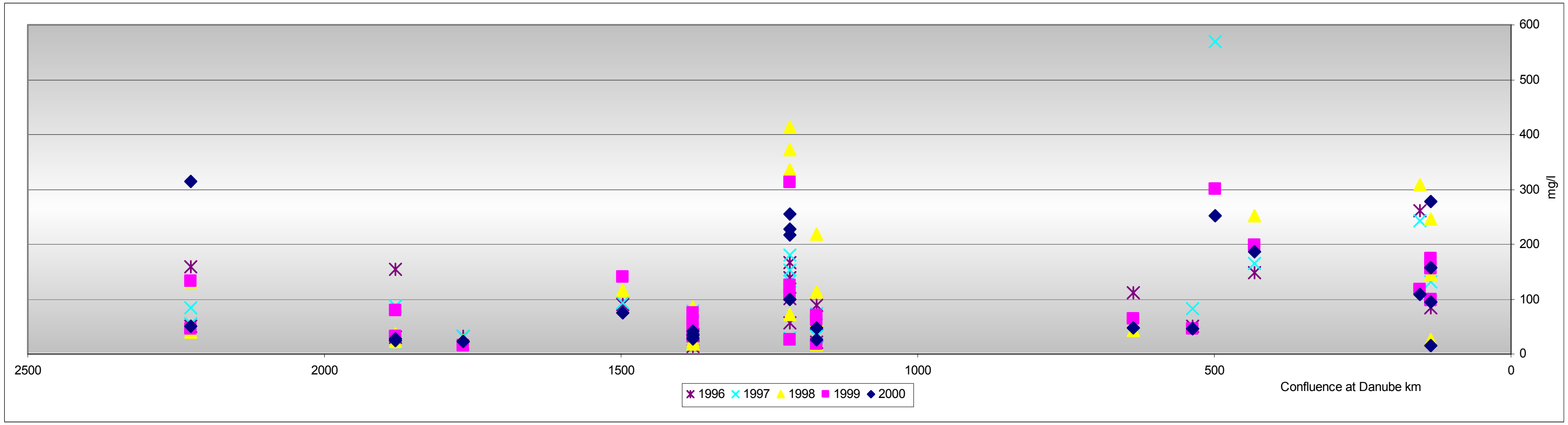


Fig. 8.1.1.2b: Spatial variation of Suspended Solids content – Tributaries

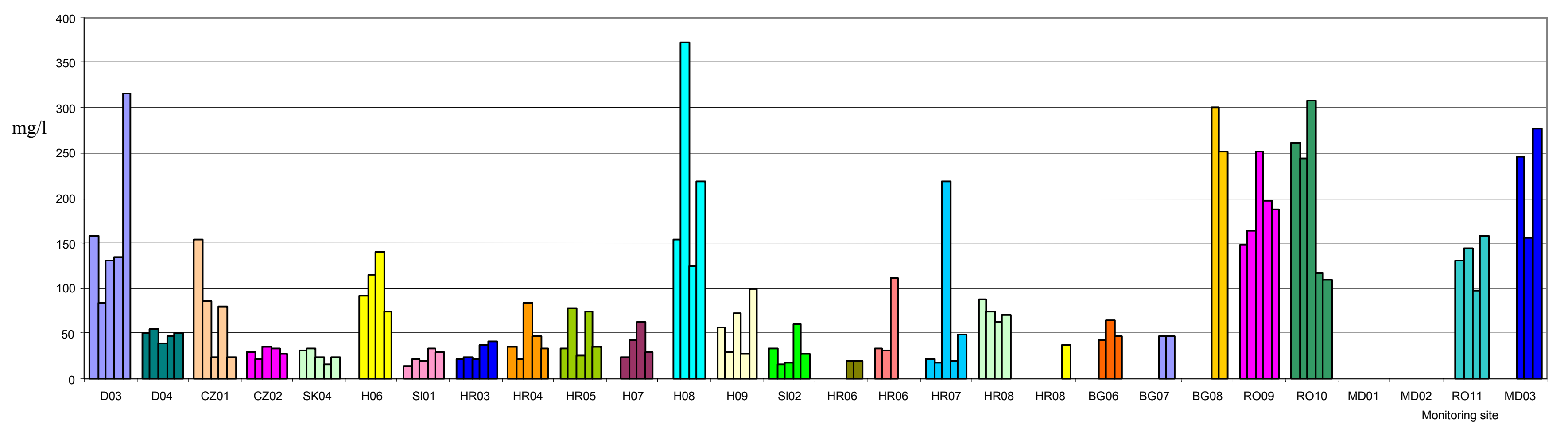


Fig. 8.1.1.3: Temporal trends of Suspended Solids content – Tributaries

pH

Hydrogen ion concentration, expressed in the form of pH value, is an important property of natural waters influenced by the substances dissolved in the water and influencing chemical reactions and the ability of water to bring other substances into solution. Beside, it represents an important factor that determines the water reactivity, its aggressiveness and its capacity of supporting life and growth of different organisms. Between the pH value and alkalinity or acidity value, no identity can be emphasized: increasing in either alkalinity or acidity is not visible in increasing or decreasing of pH value, due to the buffer capacity of natural waters, particularly. The main buffer system of natural water is composed by acid carbonates/carbonates, for a pH range of 6.50 – 8.50 (Varduca, 1997).

Concerning the Quality Classification System in the Danube River Basin applied to pH values (**Fig. 8.1.1.4**), the following remarks can be done:

- the evaluation is based on data recorded from 87 monitoring sites (it means that out of the assessment is 16 monitoring sites from Phase I List of Monitoring Sites, in which no measurements of pH had been done in 1996-2000);
- more than 70 % of considered monitoring sites belong to Class II, with a maximum of 90.8 % in 1999;
- Class III is represented in all five studied years, with a maximum of 16.1 % in 1997; excluding Danube-Bazias (RO01-middle, rkm 1071), all cases of non-compliance with class II are caused by exceedance of upper limit set up for pH value. Therefore, the figures illustrating pH are concentrated on the “upper” border of target value.
- the percentage for monitoring sites with no reported data slowly decreases from 1996 to 2000.

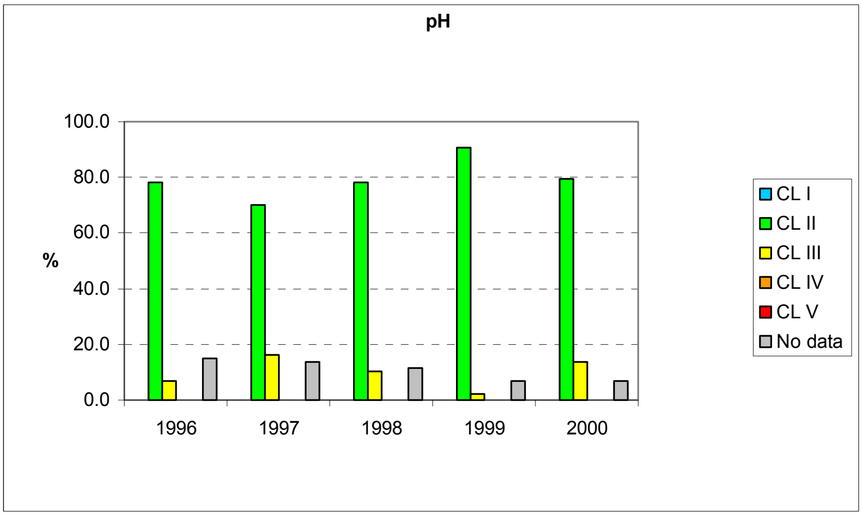


Fig. 8.1.1.4: Distribution of monitoring sites (%) according to the Quality Classification System in the DRB for **pH**

The spatial variation of pH values along the Danube River, shown in **Fig. 8.1.1.5a**, has the following pattern:

In the upper section, pH values show a slight alkaline medium; with the exception of only one value - 8.14 - in 1999 at Danube-Jochenstein (km 2204, D02), all the other values are in the range 8.20 – 8.60. Spatial distribution shows also that between Danube-Jochenstein (km 2204, D02) down to Danube-Wien-Nussdorf (km 1935, A03) an increasing tendency is present.

Taking into account the spatial pattern of 90%-iles of pH along the Danube River, just in the middle section is the majority of values not-satisfying the upper limit of pH target values. Between Danube-Medve (km 1806, H01) down to Danube-Hercegszanto (km 1435, H05) a maximum values were observed - pH in the range 8.6-8.8 - followed by a decreasing tendency of pH values down to 7.80 at

Danube-Borovo (km 1337, HR02). These long-term monitoring values correlate well with previous data (*Joint Danube Survey* Technical Report, 2002), this variation being caused mainly by the balance between the increased primary production followed by the increased organic matter decomposition.

The decreasing visible in the last part of the middle stretch seems to be valid also for the first part of the lower Danube, between Danube-Bazias (km 1071, RO01) and Danube-Pristol/NovoSelo (km 834, RO02), although a few values exceed pH 8.20. (Still, differences of 0.20-0.40 pH units could be detected between the recorded values for the same cross section - km 834: RO02/BG01). For the stretch located between Danube-ds. Svishtov (km 554, BG03) and Danube-us. Russe (km 503, BG04) spatial distribution presents a scattered profile: rather different values are recorded at the same location but in different years - 7.49 in 1996 and 8.52 in 1997 at Danube-us. Russe (km 503, BG04 M and R).

In the second part of the lower Danube, between Danube-us. Arges (km 432, RO03) down to the main arms of the Danube Delta (km 0, RO07 and RO08) an increasing tendency in pH values is recorded, especially in year 2000, when most pH values are within the range 8.42 – 8.50, showing the same slightly alkaline medium.

Selected tributaries do not show significant differences among the pH values – **Fig. 8.1.1.6a**.

- Concerning the number of pH values exceeding the target value (8.50) during the five evaluated years, 21 values are above this limit in the Danube itself and 7 values in selected tributaries - **Fig. 8.1.1.5b** and **8.1.1.6b.** In the Danube River can be seen that most of the pH values that exceed the target value are recorded in 1997, 1998 and rarely in 2000. Values exceeding the target value in tributaries are recorded in 1996 and 2000, on Dyje-Pohansko (CZ02), Sio-Szekszard-Palank (H06) and Prut-Lipcani (MD01).

The temporal pattern of pH values in the Danube River is illustrated in **Fig. 8.1.1.7** and in selected tributaries in **Fig. 8.1.1.8**.
The following remarks can be done in this respect:

- the upper section is practically without any trends;
- similarly in the middle section, temporal variation is rather scattered and no systematic trend is detectable;
- in the first part of the lower Danube, a decreasing tendency from 1996 to 2000 is visible at Danube-Bazias (km 1071, RO01); an increasing, also from 1996 to 2000 is visible at Danube-ds. Svishtov (km 554, BG03),;
- in the second part of the lower Danube, no temporal changes are present at Danube-us. Arges (km 432, RO03); most of the remaining sites in this stretch shows a tendency of increasing from 1996 to 2000 , maximum values reaching mostly in 2000.

Selected tributaries present the following temporal changes:

- an increasing was observed for the Arges-Conf. Danube (RO09) and Siret-Conf. Danube-Sendreni (RO10);
- a decreasing tendency is indicated in Sava-Jesenice (SL02).

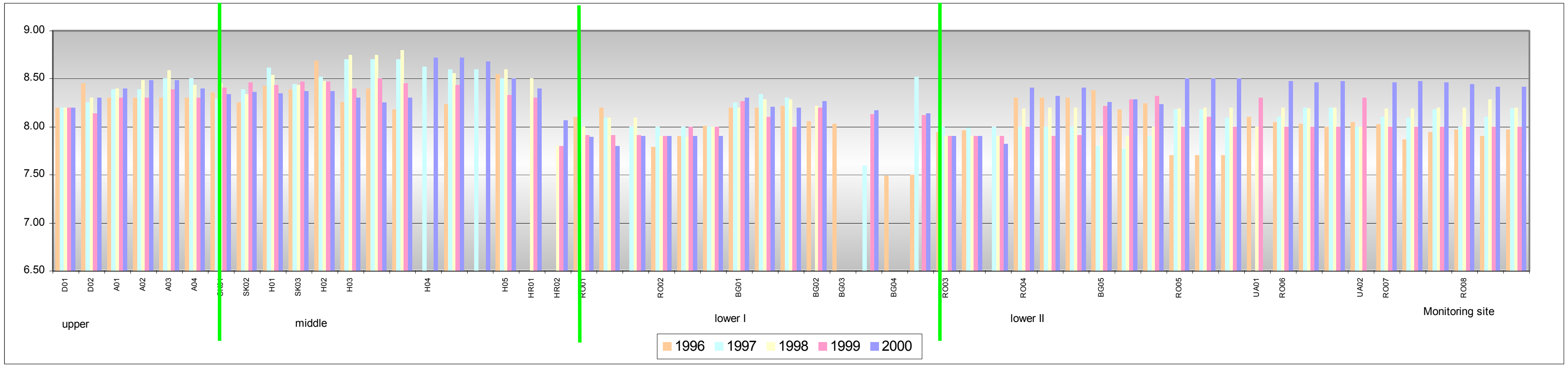


Fig. 8.1.1.5a: Spatial variation of pH – Danube River

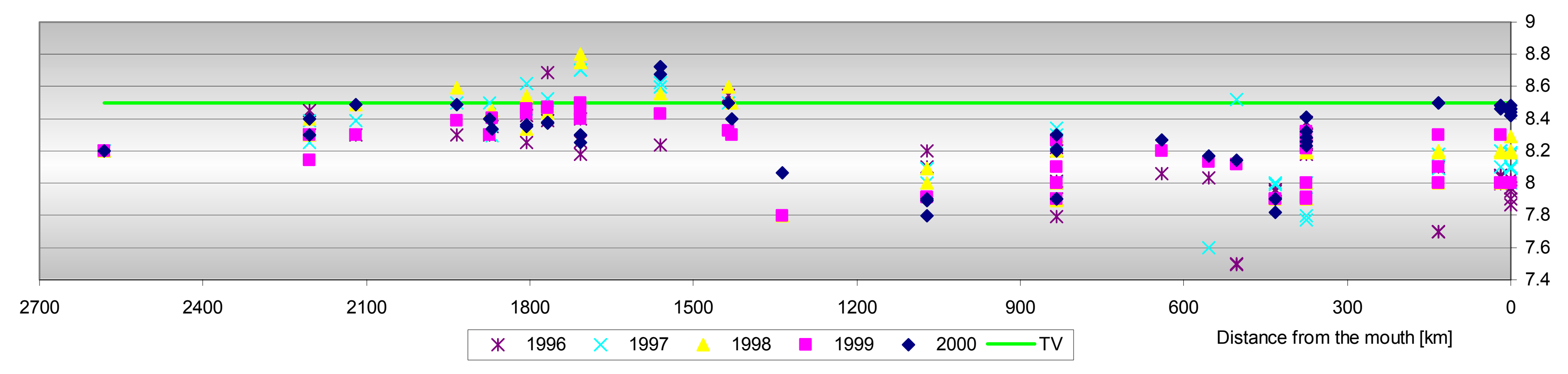


Fig. 8.1.1.5b: Spatial variation of pH – Danube River

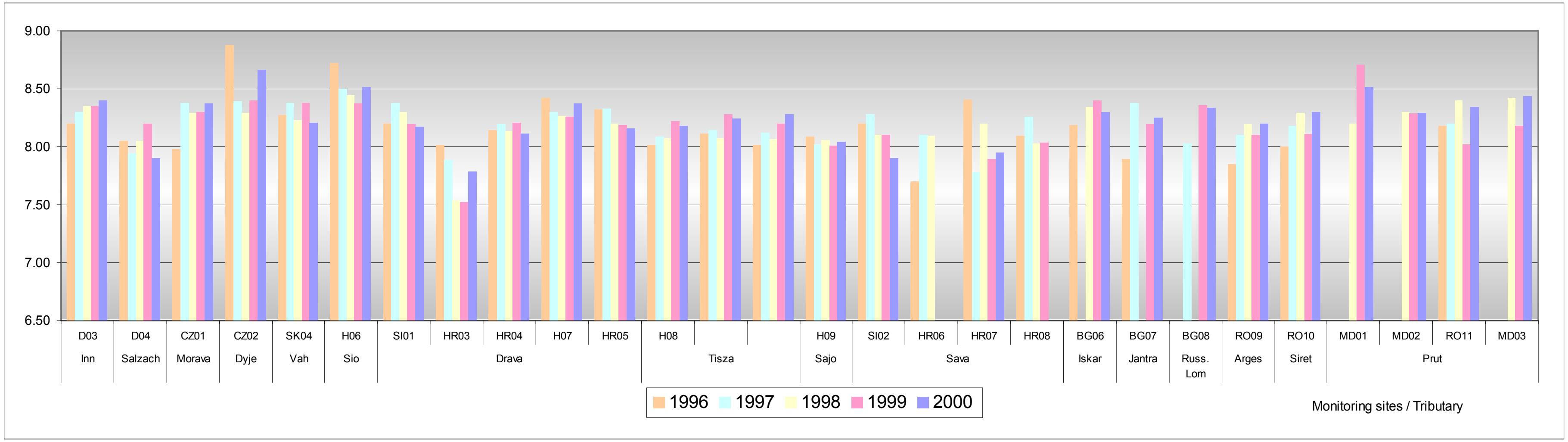


Fig. 8.1.1.6a: Spatial variation of pH – Tributaries

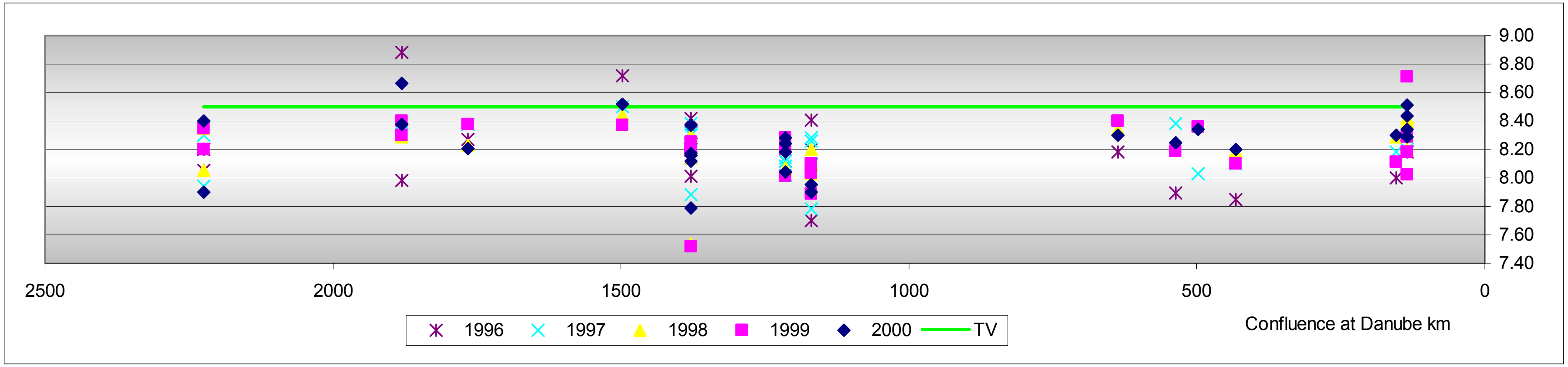


Fig. 8.1.1.6b: Spatial variation of pH – Tributaries

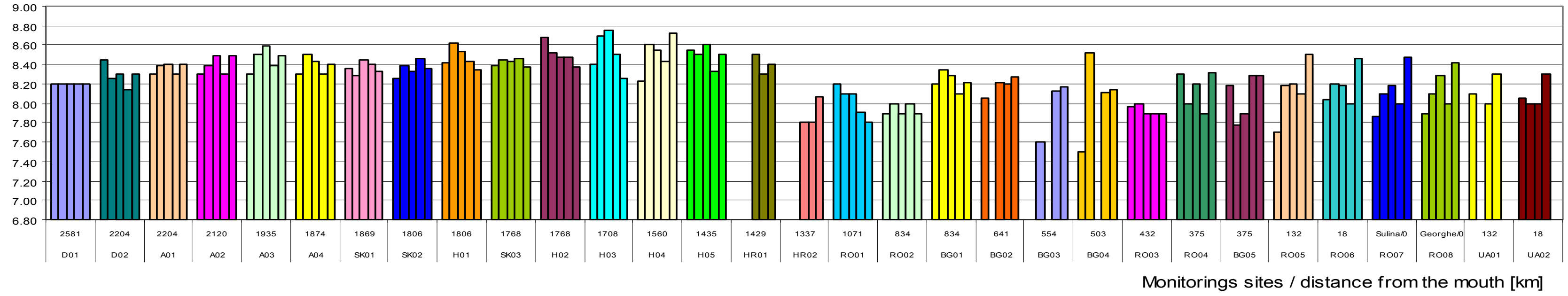


Fig. 8.1.1.7: Temporal trends of pH – Danube River

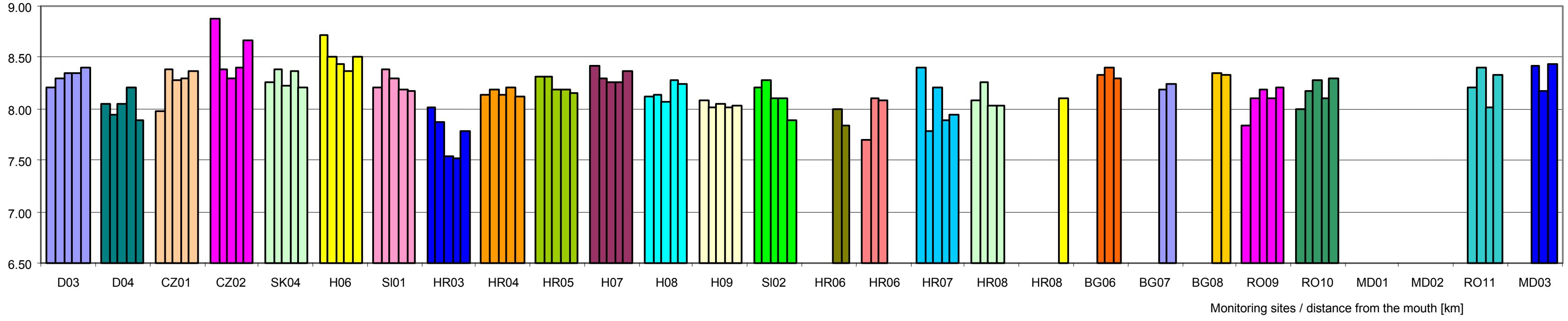


Fig. 8.1.1.8: Temporal trends of pH – Tributaries

Conductivity

Conductivity is one of the most frequently used determinands for assessing the mineralization degree of a natural watercourses as it is a measure of total dissolved salts in water column.

The spatial distribution of the conductivity values along the Danube River is shown in **Fig. 8.1.1.9a** and **8.1.1.9b.**
For the monitoring points located on the Danube in the upper section of the Danube itself, conductivity is within the range 400 – 539 µS/cm. From the above-mentioned figures can be seen the influence that the low salts content of the Inn-Kirchdorf (D03) has upon the downstream stretch.

The middle section of the river is characterized by small spatial variation. Only at Danube-Szob (km 1708, H03), a slight increasing pattern is noticeable, probably caused by an anthropogenic influence.

The first part of the lower Danube section shows no significant variation in spatial distribution between Danube-Bazias (km 1071, RO01) and Danube-us. Russe (km 503, BG04), only two values exceed the level of 500 µS/cm.
The pattern for the second part of the lower Danube is characterized by slightly higher values than in the first part; e.g. values increase from 405µS/cm in 2000 at Danube-us. Arges (km 432, RO03)up to 598µS/cm at Danube-Sulina/Sulina arm (km 0, RO07) in the same year.

Tributaries are generally characterized by higher conductivity levels than the Danube itself – **Fig. 8.1.1.10a** and **8.1.1.10b**:

- in the upper section, relatively higher values (637 µS/cm in 1996 – 784 µS/cm in 1998) were recorded on the Dyje but they are due to the low values of the flow (123.2 and 37.3 m^3/s, respectively). In 1997 there was higher conductivity than in 1996.
- the highest conductivity values belong to the Sio-Szekszard-Palank (H06), in the middle section (992 µS/cm in 1998 - 1195 µS/cm in 1997) in good correlation with flow discharges in respective years (63.9 m^3/s in 1998 and 49.0 m^3/s in 1997);
- in the lower Danube, the conductivity levels increase (e.g.: two c90 values, characterising Russenski Lom-Basarbovo (BG08), exceed 800 µS/cm - in 1997 and 1999). However, the highest values for tributaries along this stretch belong to the Prut-Conf. Danube Giurgiulesti (RO11) - 1100 µS/cm and 1110 µS/cm in 1997 and 1998, respectively.

The temporal trend for conductivity values in the Danube River is shown in **Fig. 8.1.1.11**, and in **Fig. 8.1.1.12** for selected tributaries:

- in the upper and the middle Danube, the general trend is decreasing from 1996 to 2000;
- in the first part of lower Danube, no general trend was observed; in the second part, the general tendency is increasing from 1996 to 1998 or 1999;
- selected tributaries from the upper river show a relative uniform temporal distribution of conductivity values; on the Morava-Lanzhot (CZ01) and Djye-Pohansko (CZ02) higher values are recorded in 1997 and 1998 respectively;
- the same uniform temporal pattern is valid also for the tributaries from the middle section, with few exceptions: on the Sio-Szekszard-Palank (H06), the maximum value appears in 1997 and on the Sava-us. Jesenovac (HR07) a decreasing trend from 1996 to 2000 is detectable.
- tributaries from the lower Danube present a scattered temporal profile, with no visible systematic trend.

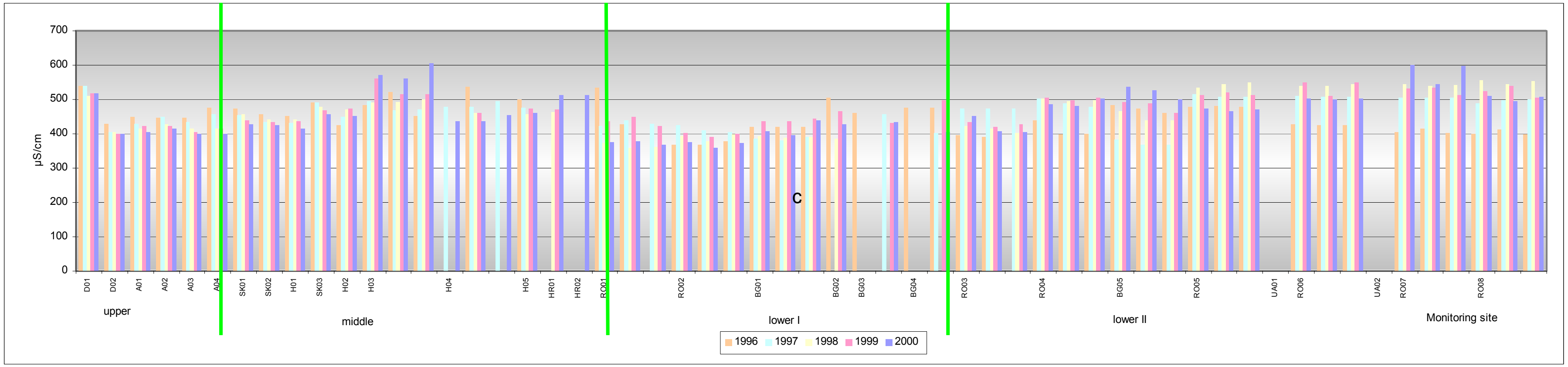


Fig. 8.1.1.9a: Spatial variation of Conductivity – Danube River

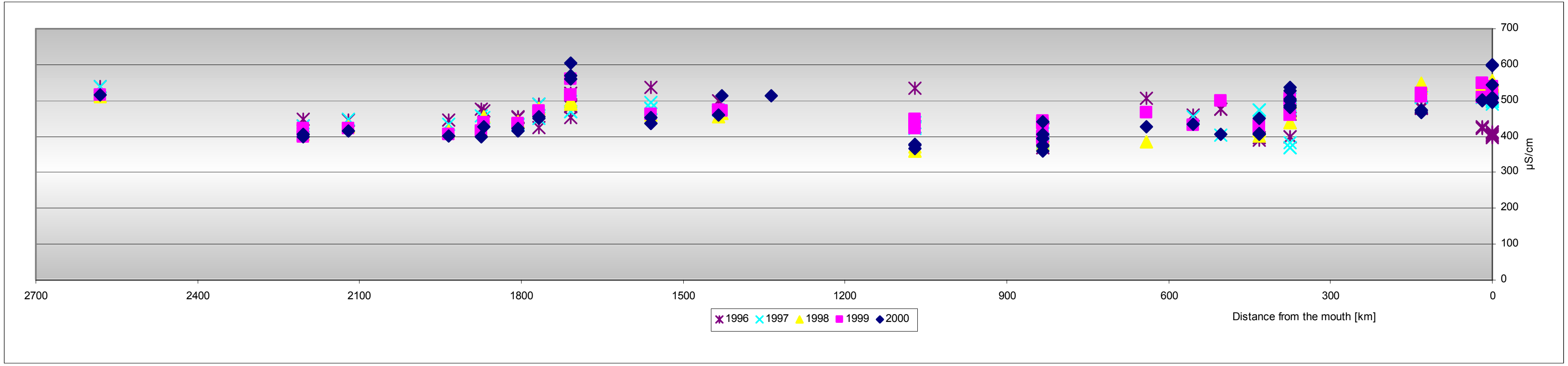


Fig. 8.1.1.9b: Spatial variation of Conductivity – Danube River

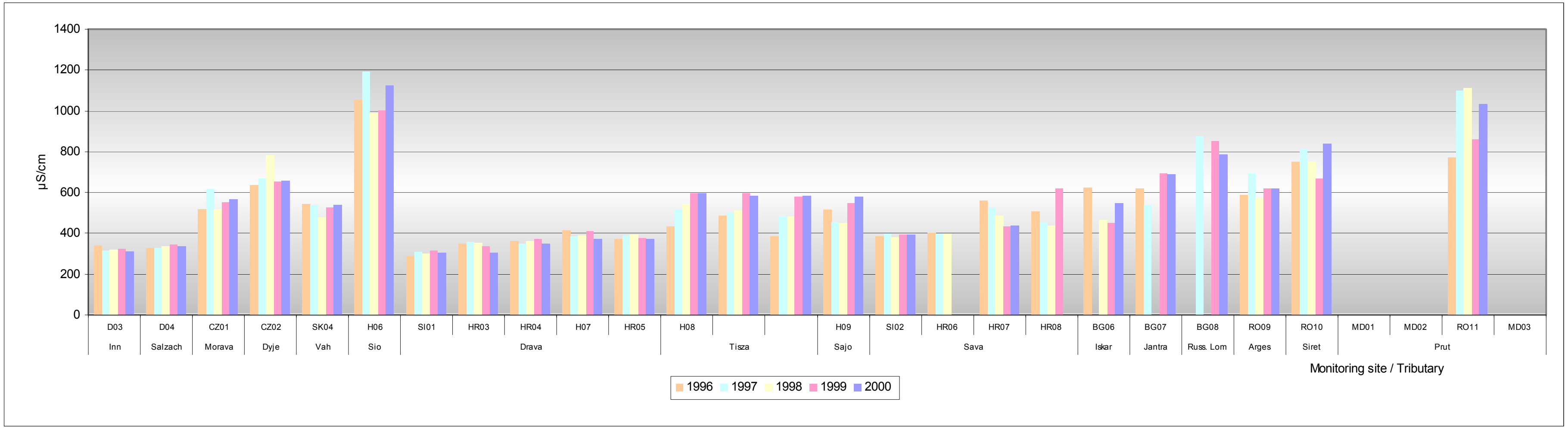


Fig. 8.1.1.10a: Spatial variation of Conductivity – Tributaries

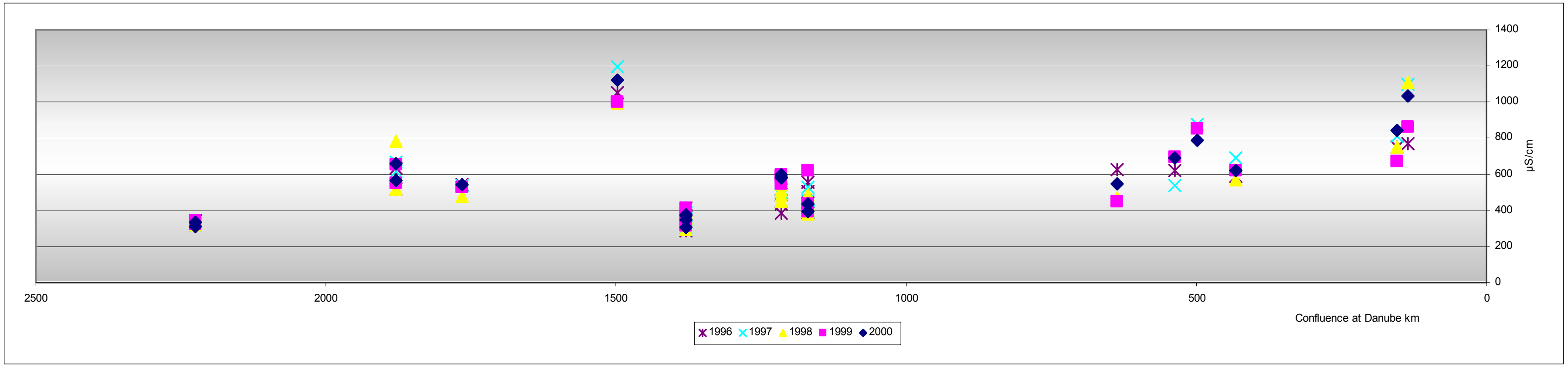


Fig. 8.1.1.10b: Spatial variation of Conductivity – Tributaries

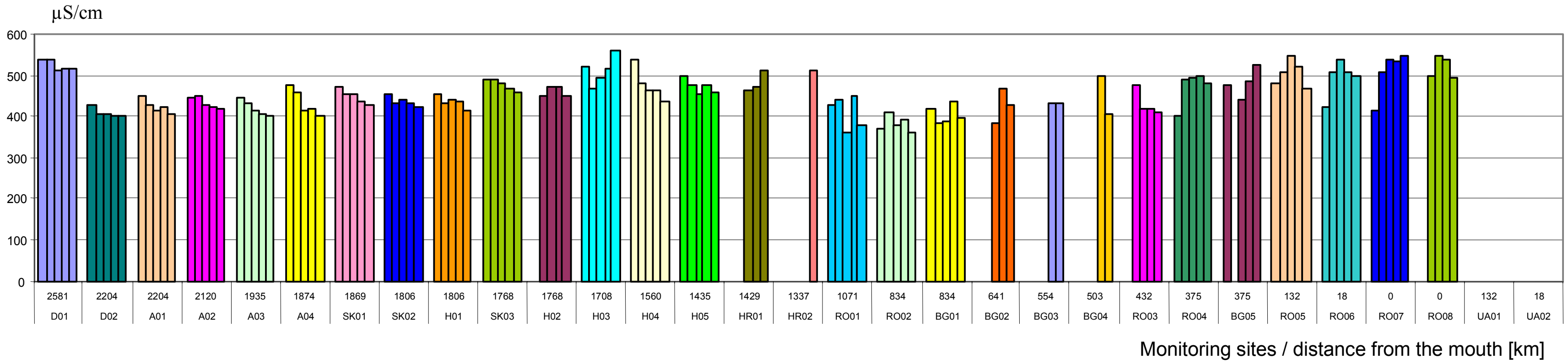


Fig. 8.1.1.11: Temporal trends of Conductivity – Danube River

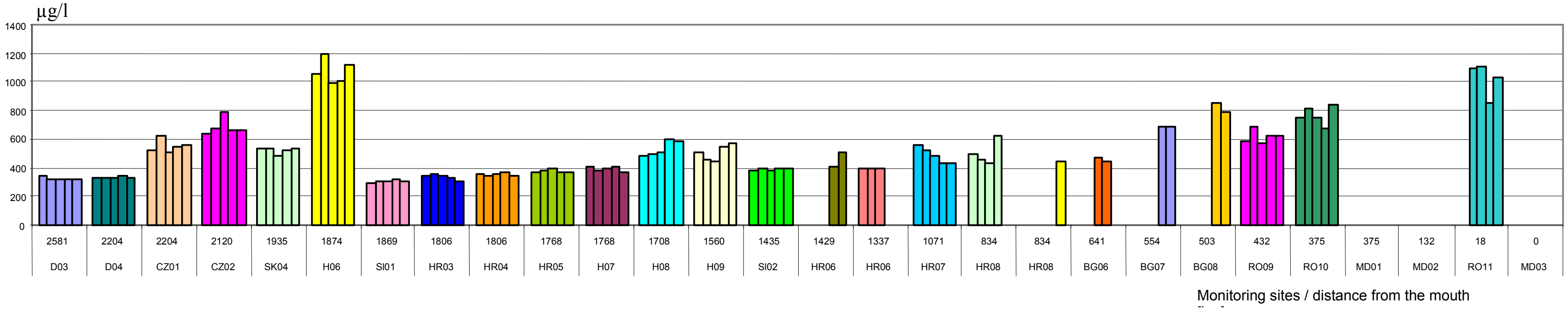


Fig. 8.1.1.12: Temporal trends of Conductivity – Tributaries

Alkalinity

Alkalinity is conditioned by the presence of acid carbonate, carbonate, hydroxide and only rarely by borate and silicate ions in water column. Values of “p” alkalinity (given by hydroxide and carbonate) and “m” alkalinity (given by acid carbonate) show the equilibrium status among the above-mentioned ions in water.

Spatial variation of alkalinity values along the Danube River is shown in **Fig. 8.1.1.13a** and **8.1.1.13b**.

For the upper section, unlike the first monitoring point, Danube-Neu-Ulm (km 2581, D01) where the alkalinity is in the range 4.6-4.8 mmol/l, all the other monitoring sites from this stretch are characterized by values in the range 3.5-3.9 mmol/l.

In the middle section, excepting two values, the range of alkalinity is 3.4 – 4.1 mmol/l. The exceptions are recorded at Danube-Batina (km 1429, HR01), where alkalinity values are 7.4 and 8.1 mmol/l in 1998 and 2000, respectively.

The spatial pattern of alkalinity in the first part of the lower section shows a slight increasing line from Danube-Bazias (km 1071, RO01) down to Danube-us. Iskar-Bajkal (km 641, BG02); at the following monitoring site, higher alkalinity value is recorded in 2000 (5.4 mmol/l).

In the second part of this lower stretch a slight increasing tendency of alkalinity values is present as well, with a maximum 4.9 mmol/l in 2000, at Danube-Silistra/Chiciu (km375, BG05).

The profile characteristic to selected tributaries presents maximum values on the Sio-Szekszard-Palank (H06), where the alkalinity values are within the range 6.4 – 8.5 mmol/l. Also the Jantra-Karantzi (BG07) and Russenski Lom-Basarbovo (BG08) show relatively higher values in 1999 and 2000 - between 5.6 and 7.5 mmol/l (see **Fig. 8.1.1.14a** and **8.1.1.14b)**.

From the temporal point of view, the following can be concluded based on illustration on **Fig. 8.1.1.15**, for the Danube River and in **Fig. 8.1.1.16** for selected tributaries:

- a uniform profile for upper and middle Danube, slight variations being noticeable at Danube-Medve/Medvedov (km1806, H01) and at Danube-Komarom/Komarno (km 1768, H02);
- in the first part of the lower Danube, a slight increasing trend from 1996 to 1999 or 2000 is present at Danube-Novo Selo/Pristol (km 834, BG01);
- in the second part of lower Danube, the temporal view is inhomogeneous, but it can be seen that higher values are recorded in 1997, 1998 or 2000, depending on the monitoring site.

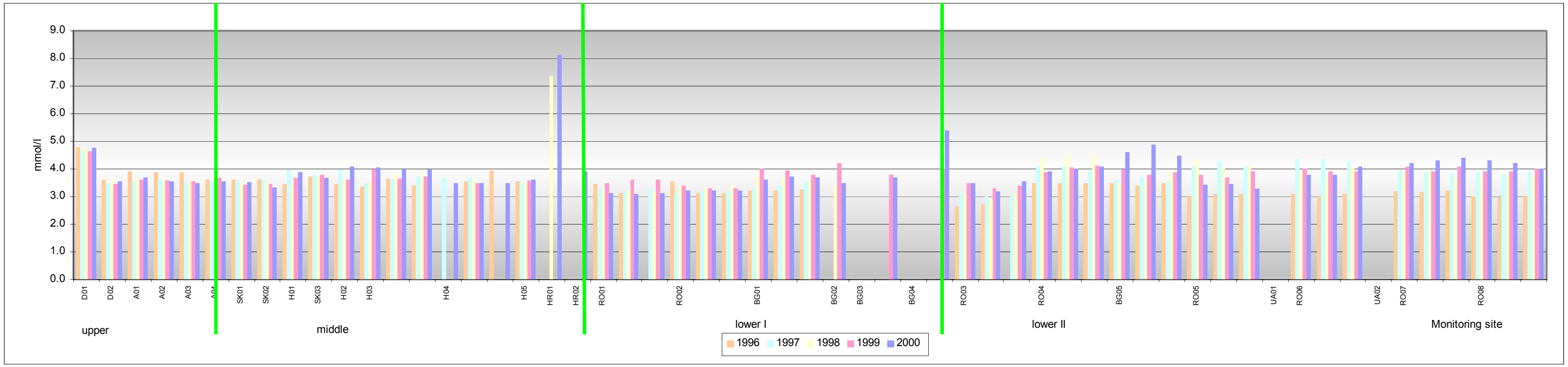


Fig. 8.1.1.13a: Spatial variation of Alkalinity – Danube River

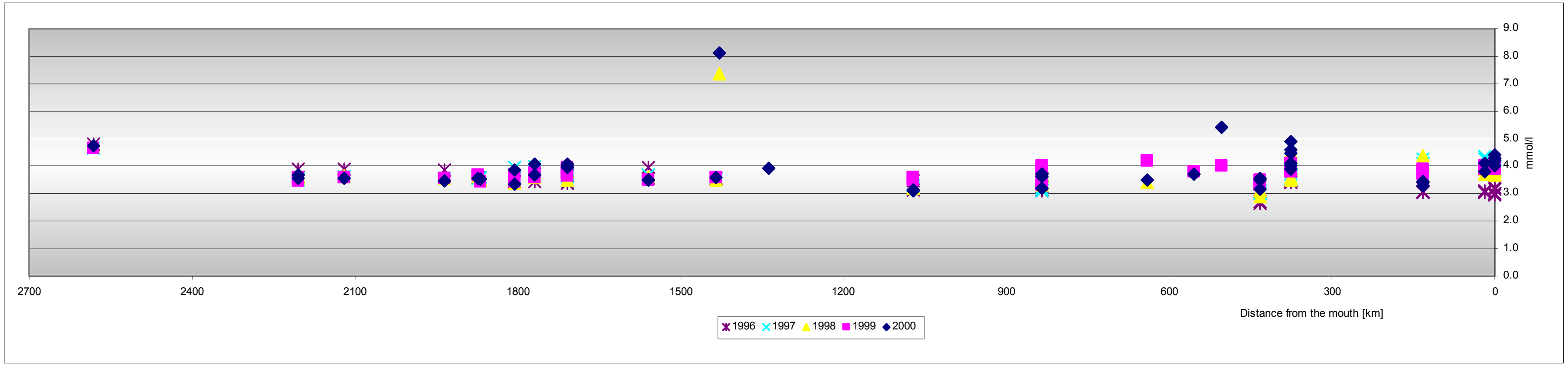


Fig. 8.1.1.13b: Spatial variation of Alkalinity – Danube River

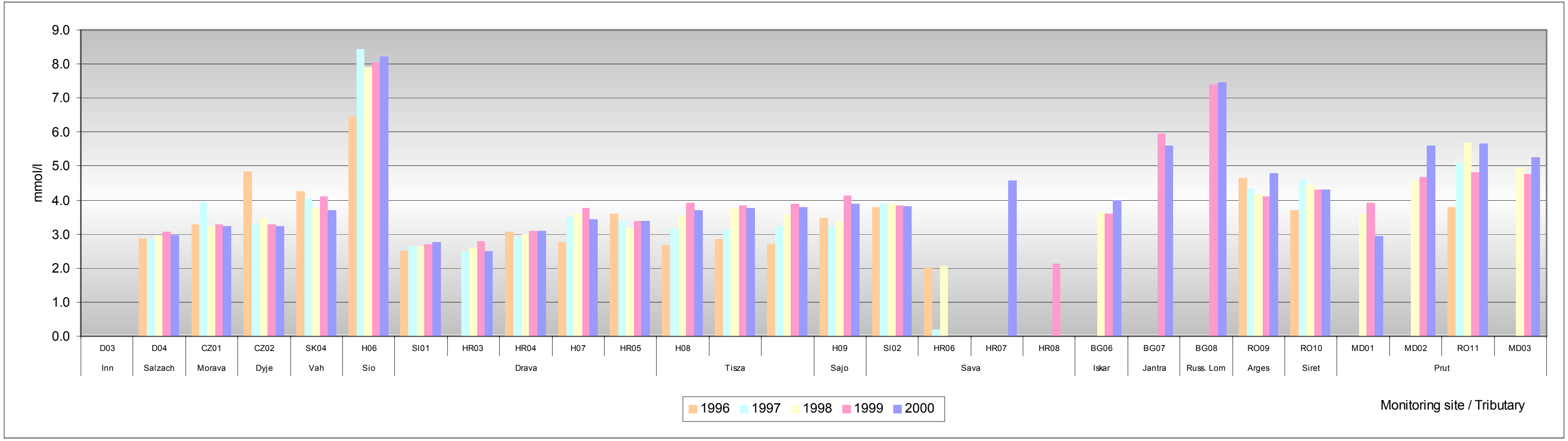


Fig. 8.1.1.14a: Spatial variation of Alkalinity – Tributaries

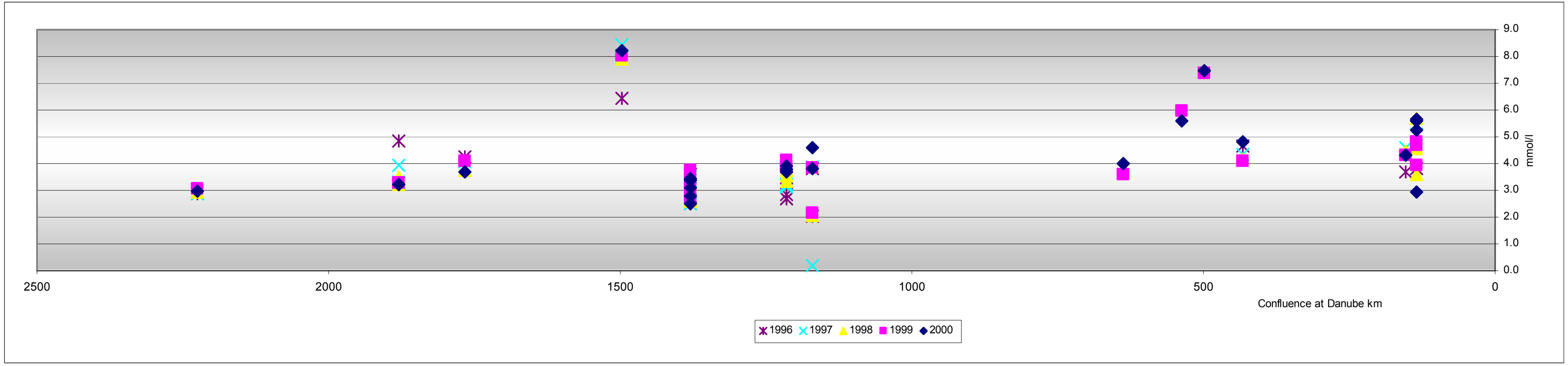


Fig. 8.1.1.14b: Spatial variation of Alkalinity – Tributaries

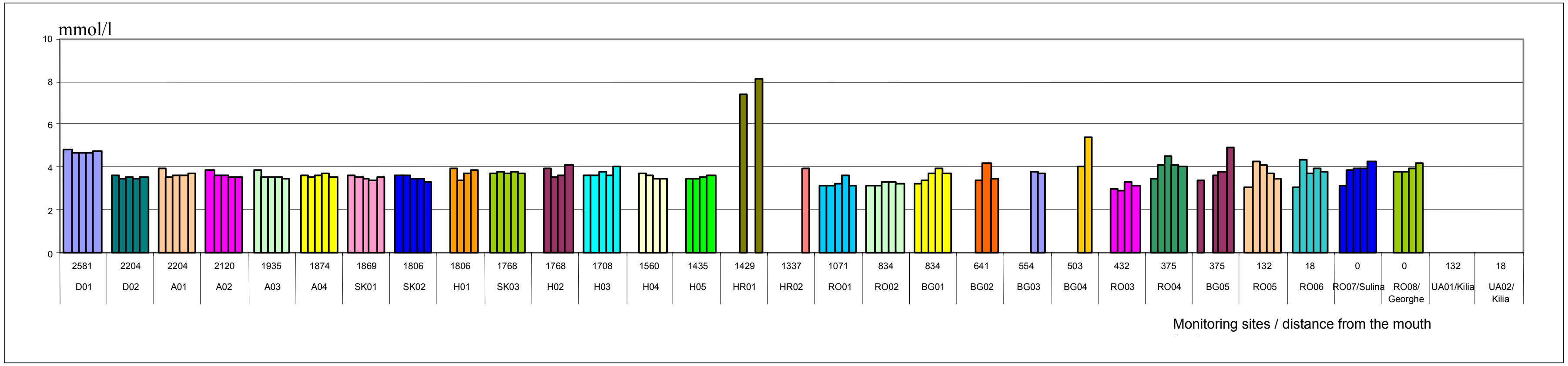


Fig. 8.1.1.15: Temporal trends of Alkalinity – Danube River

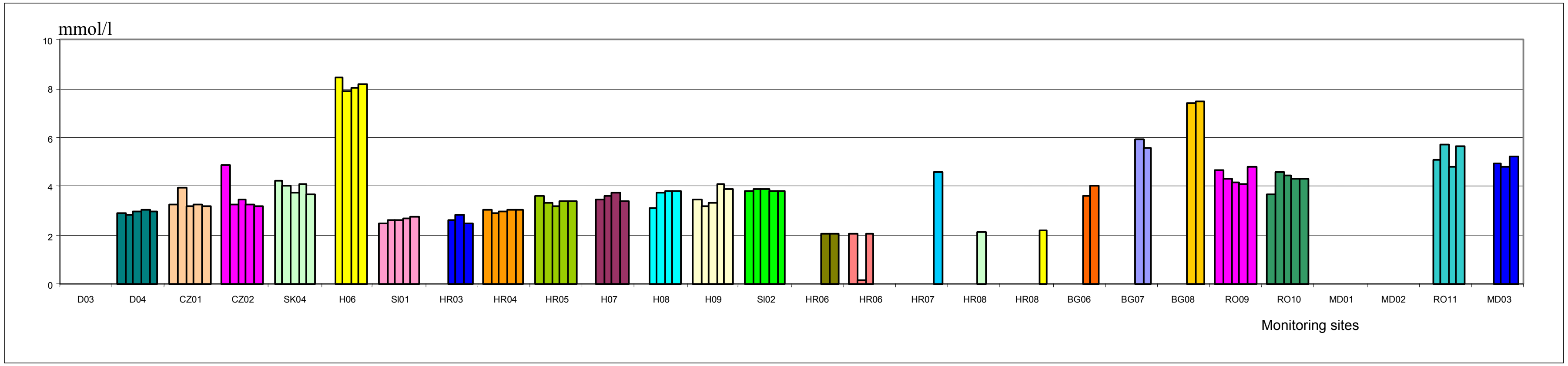


Fig. 8.1.1.16: Temporal trends of Alkalinity – Tributaries

8.1.2. Nutrients

Assessment of nutrients levels in water column has a particulate importance due to the fact that the input of nutrients into surface waters (mainly nitrogen and phosphorous), either from natural or anthropogenic sources, leads to the process being known as eutrophication. The direct consequences of eutrophication – increased algal bloom, accelerated biological activity (metabolism and decomposition), widespread reduction in dissolved oxygen concentration, growth of higher plants, changes in aquatic food chain and, eventually, a disturbed ecosystem and a deteriorated water quality – make the assessment of nutrients level to be one of the most important issue in assessment of water quality. Although the associated effects of eutrophication are characteristic particularly to lakes, reservoirs, coastal areas and large slowly flowing rivers as well, it could also be apparent in the case of the various conditions specific to the Danube River.

From the different fractions analyzed within the TNMN Programme, ammonium-N, nitrite-N, nitrate-N, ortho-phosphate-P and total phosphorous were chosen for spatial pattern assessment and trend assessment in the report.

Nitrogen

Dissolved inorganic nitrogen, particularly ammonium and nitrate, constitutes most of the total nitrogen in river waters. They derive mainly from the decomposition of protein compounds that enter the surface water along with urban and industrial waste discharge. Among the indirect sources of various nitrogen forms, erosion/runoff from agriculture and effluents from animal farms can be mentioned.

As it will be shown, nitrogen levels have a characteristic concentration distribution along the Danube and its tributaries.

Ammonium

Ammoniacal-nitrogen occurs in two forms: ammonia (NH_3) and ammonium (NH_4^+); the first one is a dissolved gas with much higher toxicity on aquatic ecosystem than the ionized form. The equilibrium between the two species depends on pH. Mediated by microorganisms, decomposition of protein organic matter has as final result release of ammonium. It can also emerge from decomposition of mineral and vegetal matters. Dissolved ammonium is further oxidized to nitrites and nitrates.

The distribution of monitoring sites according to the Classification System in the DRB for ammonium-N is shown in **Fig. 8.1.2.1**:

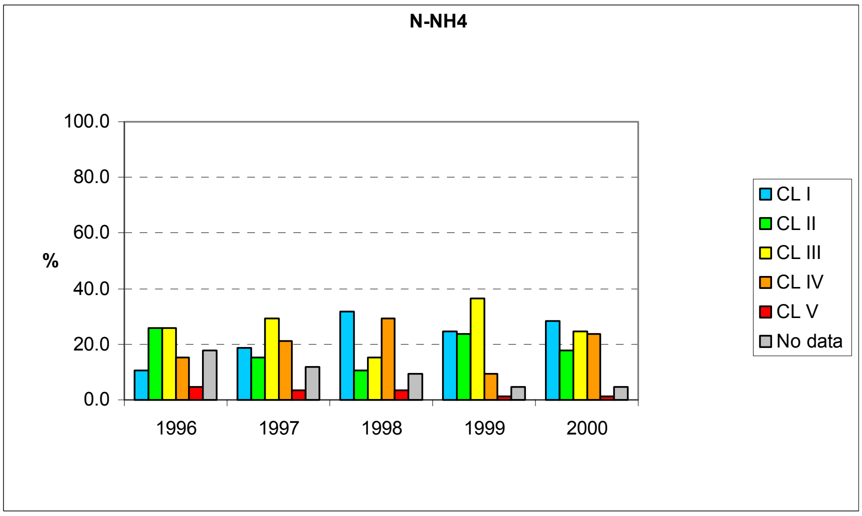


Fig. 8.1.2.1: Distribution of monitoring sites (%) according to the Quality Classification System in the DRB for **N-NH$_4$**

The quality assessment within the five-class system is made based on data reported from 85 monitoring sites (out of the assessment are 18 monitoring sites from Phase I List of Monitoring Sites, in which no measurements had been done in 1996-2000) and the following remarks can be done in this respect:

- the temporal distribution of monitoring sites within quality classes is generally uneven during five studied years, with no percentage above 50 % in one class;
- The percentage of sites in Class I varies between 10.6 % in 1996 and 31.8 % in 1998;
- The percentage of sites corresponding to Class II is in the range from 7 % (1998) to 26 % (1996);
- The maximum percentage of sites in Class III is in 1999 (36.5 %) and in Class IV in 1998 (29.4%)
- Only few monitoring sites (1.2 – 4.7 %) correspond to Class V;
- the number of measurements was increasing from 1996 to 2000.

The spatial variation of ammonium-N along the Danube River is shown in **Fig. 8.1.2.2a** and **8.1.2.2b**.

In the upper section of the river, ammonium-N concentrations have a homogenous level, with no value above the target value (0.30 mg/l).

In the middle section most of the concentrations are below 0.30 mg/l, too. Slightly higher values were recorded at Danube-Bratislava (km 1869, SK01), Danube-Medvedov/Medve (km 1806, SK02) and Danube-Komarno/Komarom (km 1768, SK03). It has to be mentioned that at the last two mentioned cross-sections (SK02/H01 and SK03/H02) results reported by the Hungarian part are significantly lower than results from Slovakia. Along this middle stretch, 18 c90 values are indicated as above the target value.

The ammonium-N spatial pattern changes in the first part of the lower Danube section, where the concentration level rises up to 0.75 mg/l between Danube-Bazias (km 1071, RO01) and Danube-Pristol/NovoSelo (km 834, RO02). An even higher value (1.09 mg/l) was observed at Danube-us. Iskar – Bajkal (km 641, BG02).
In the second part of lower Danube section, the general pattern shows an increasing of concentrations. Thus, the ammonium-N values recorded in 1998 in two arms of the Danube Delta (Sulina/Sulina arm and Sf. Gheorghe/Sf. Gheorghe arm) are 1.39 and 1.44 mg/l, respectively. For the entire lower Danube, 151 values were above the quality target in the period 1996-2000.

The large differences of the upper and the middle section ammonium-N levels against the ones from the lower Danube section are mainly attributable to the anthropogenic influence upon lower Danube on one hand (sewage effluent and runoff from agriculture) and to the general improvement in waste water treatment in the upper and the middle sections on the other hand.
Remarkable is high year-to-year variability in ammonium-N values in the monitoring sites of lower Danube section.

The spatial distribution of ammonium-N level for selected tributaries is illustrated in **Fig. 8.1.2.3a** and **8.1.2.3b**.

As it can be seen, for tributaries located in the upper and the middle section, rather high ammonium-N concentrations were recorded on the Morava-Lanzhot (CZ01), Dyje-Pohansko (CZ02), Vah-Komarno (SK04) and Sio-Szekszard-Palank (H06); most of these ammonium-N values (above 0.60 mg/l – the limit value for Class III) are mainly attributable both to urban waste waters and agricultural inputs. on
In case of Tisza and Sava tributaries, with only few exceptions the ammonium-N c90 level is below 0.60 mg/l. The water quality is totally different in tributaries located in the lower Danube: if in Iskar-Orechovitza (BG06) and Jantra-Karantzi (BG07) only one value correspond to Class IV and Class V,

respectively, in Arges-Conf. Danube (RO09), all ammonium-N concentrations - between 2.49 – 7.68 mg/l - are within Class V. These extreme high values, correlated with BOD_5 values, are mostly caused by non- or insufficiently treated waste waters from municipalities. Still very high ammonium-N concentrations (above 1.50 mg/l in 1996 – 1998) were observed on the Siret-Conf. Danube Sendreni (RO10) and Prut-Conf. Danube Giurgiulesti (RO11). In all selected tributaries, 67 concentrations are above the quality target for ammonium-N.

The temporal trends for ammonium-N concentrations along the Danube River are shown in **Fig. 8.1.2.4** and for tributaries in **Fig. 8.1.2.5**:

- for the upper Danube, a decreasing trend from 1996 to 2000 is visible;
- in the middle Danube, for monitoring sites located on left side of the river (the Slovakian part) there is a decreasing trend from 1996-1997 to 1998, followed by a stationary state until 2000; for the rest of monitoring sites located along this stretch, a relatively constant temporal profile is observed;
- in the first lower part of Danube River, temporal pattern is very scattered, with higher values recorded in 1997, 1998 and 2000. In the second part, situation is similar, with higher concentrations characteristic mainly to 1996, 1997 and 1998;
- in majority of tributaries located in the upper and middle Danube, generally ammonium –N seems to decrease, excepting Croatian sites located on the Sava River;
- for tributaries located in the lower Danube, the Arges-Conf. Danube (RO09) shows most critical ammonium-N values in 1996 and 2000; in Siret-Conf. Danube (RO10) and Prut-Conf. Danube Giurgiulesti (RO11) values observed in 1999-2000 were significantly lower than those measured in 1997 and 1998.

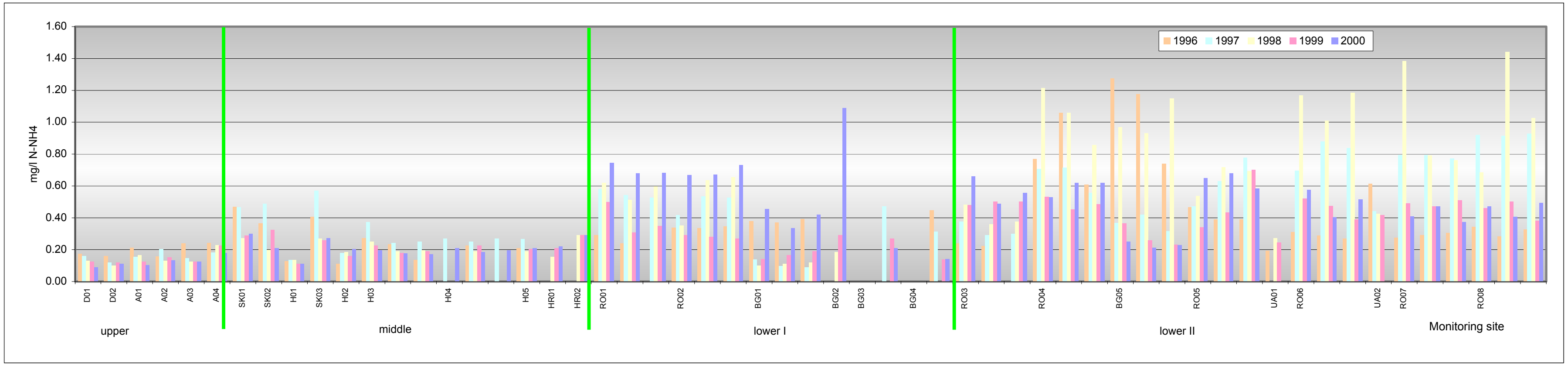


Fig. 8.1.2.2a: Spatial variation of N-NH$_4$ – Danube River

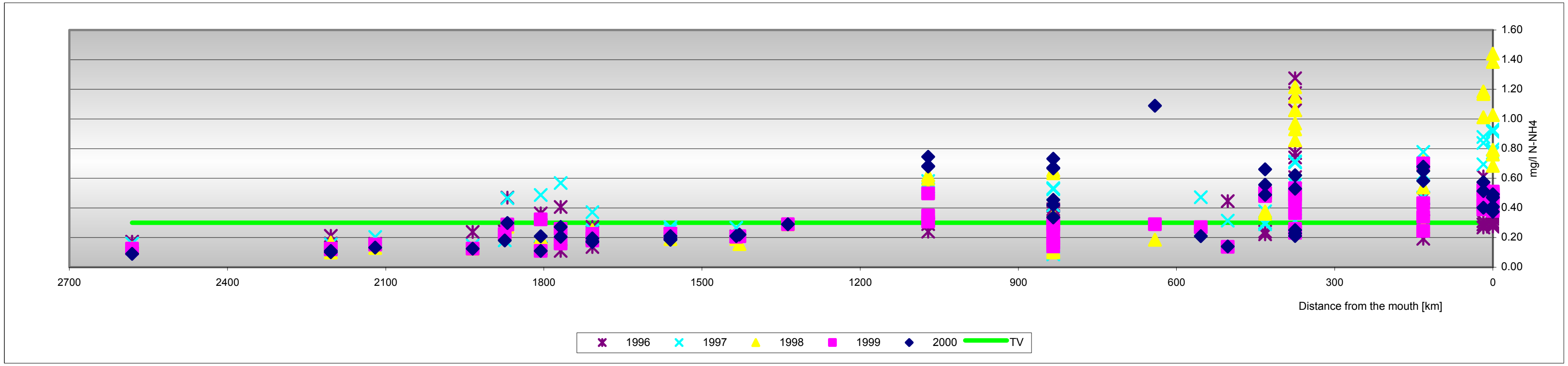


Fig. 8.1.2.2b: Spatial variation of N-NH$_4$ – Danube River

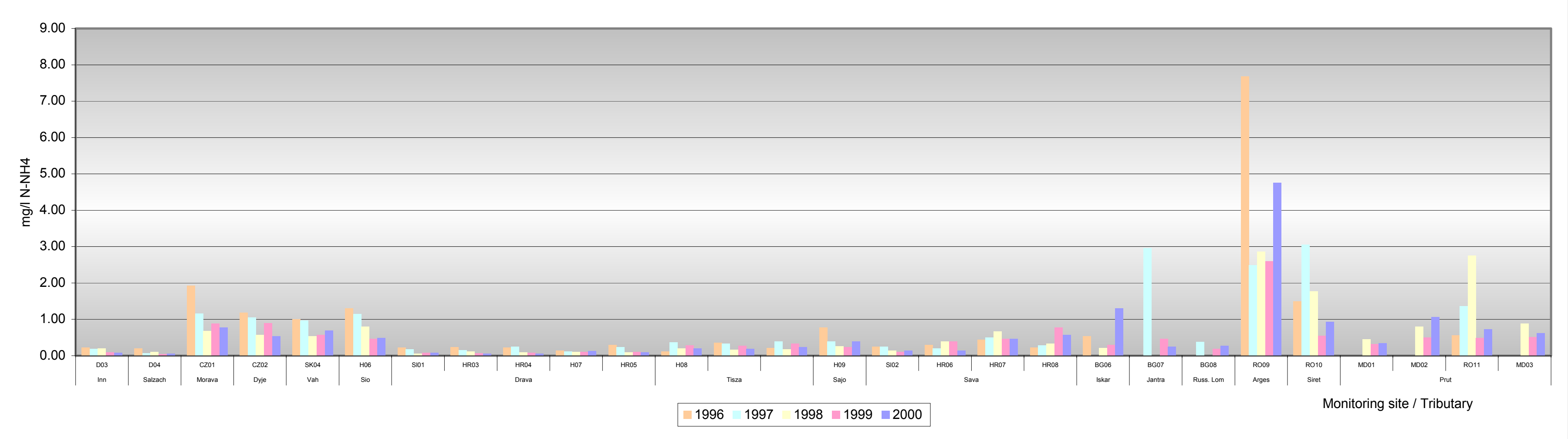


Fig. 8.1.2.3a: Spatial variation of N-NH_4 – Tributaries

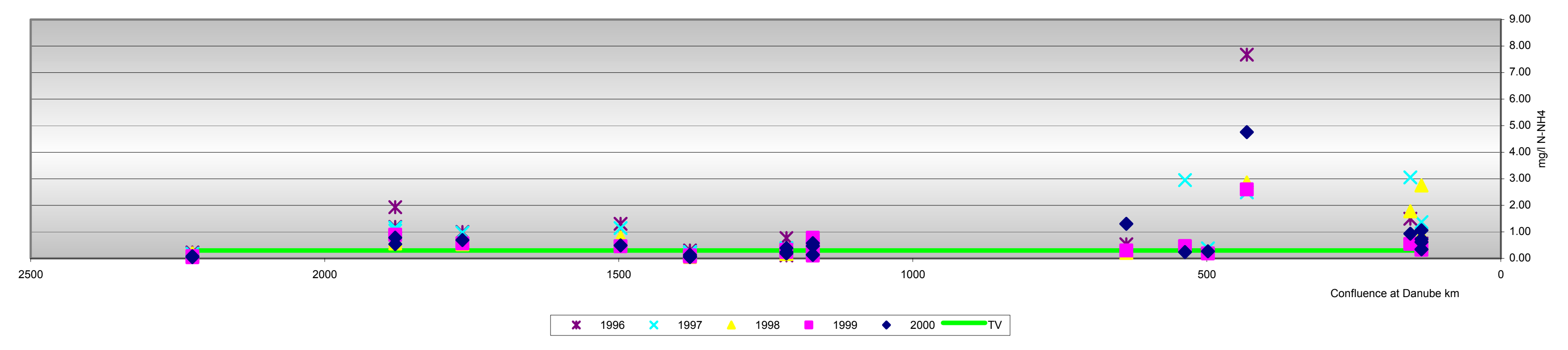


Fig. 8.1.2.3b: Spatial variation of N-NH_4 – Tributaries

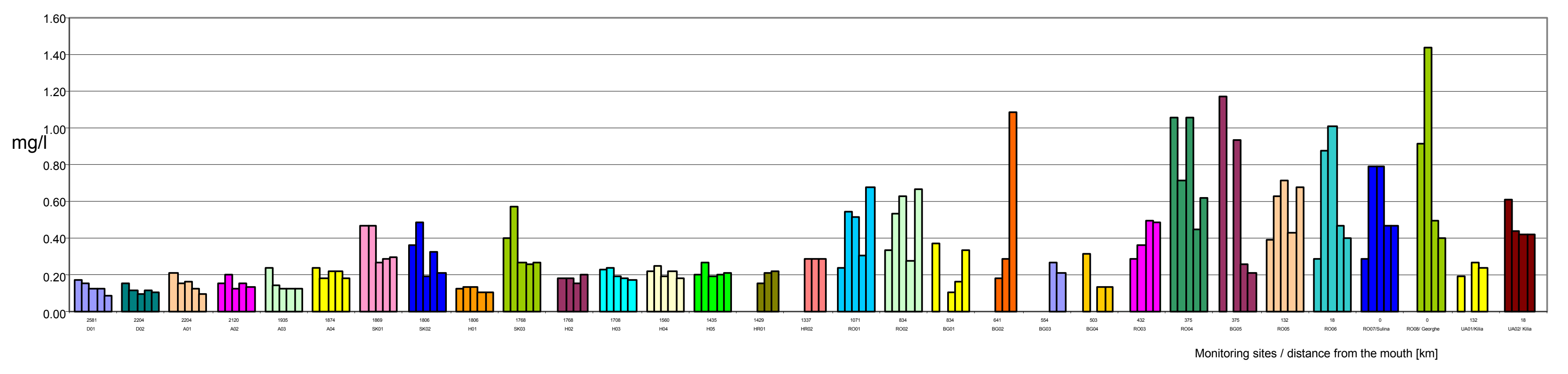


Fig. 8.1.2.4: Temporal trends of N-NH_4 – Danube River

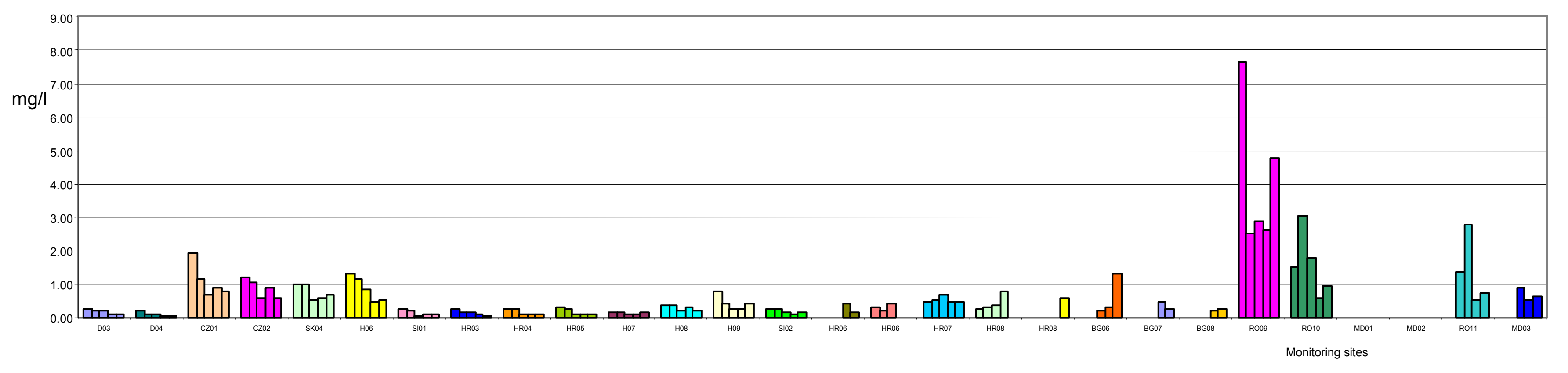


Fig. 8.1.2.5: Temporal trends of N-NH_4 – Tributaries

Nitrite

Nitrite is an intermediate nitrogen form in the oxidation/reduction process of the nitrogen dissolved forms.

The distribution of monitoring sites according to the Classification System in the DRB for nitrite-N is shown in **Fig. 8.1.2.6**:

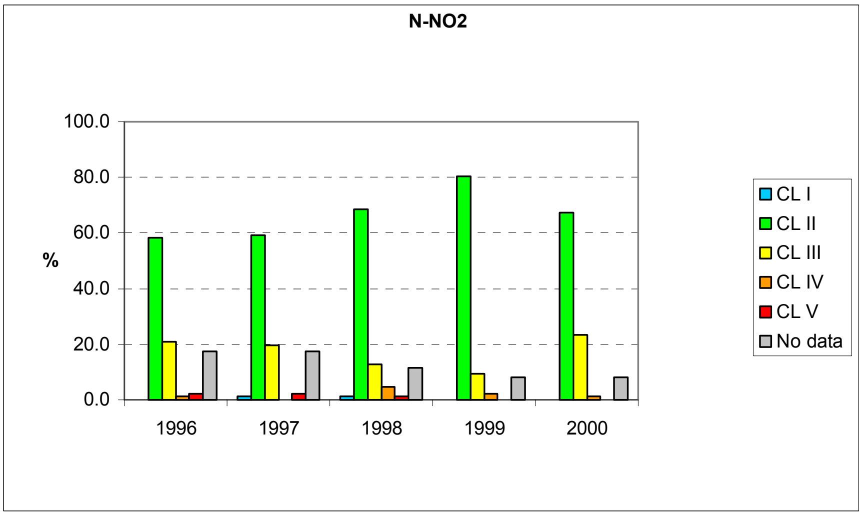


Fig. 8.1.2.6: Distribution of monitoring sites (%) according to the Quality Classification System in the DRB for **N-NO$_2$**

From the above-mentioned figure, based on data reported from 86 monitoring sites, (out of the assessment is 17 monitoring sites from Phase I List of Monitoring Sites, in which no measurements had been done in 1996-2000), it can be seen that:

- no site presents nitrite values corresponding to Class I
- more than 50 % of all sites are within Class II each year. The respective percentages increase from 1996 to 1999 and then decrease in 2000 in favour of Class III;
- the temporal profile corresponding to Class III is opposite to the previous one: decreases from 1996 to 1999 and increases in 2000;
- there are no sites corresponding to Class IV in 1997, the values representing other years are very low, with a maximum of 4.7 % in 1998;
- Class V is represented during 1996 – 1998 only, by a percentage of less than 3 % of all sites each year;
- number of measurements increased in evaluation period in a similar pattern as ammonium-N.

The spatial pattern for nitrite-N concentrations for the Danube River is shown in **Fig. 8.1.2.7a** and **8.1.2.7b** and it has the following features:

In the upper part of the Danube, almost no value exceeds 0.040 mg/l, which is less than the quality target (0.060 mg/l).

Approximately the same spatial pattern is present in the middle section of the river, where the nitrite-N concentrations vary within the range 0.020 – 0.051 mg/l. Apart an extreme value (0.233 mg/l) observed in 1998 at Danube-Bratislava (km 1869, SK01), along this stretch an increasing spatial variation is present; only 8 nitrite-N concentrations are above the target value.

In the first part of the lower Danube, nitrite-N concentrations are higher than in the middle stretch, reaching the 0.071 mg/l in 1996 at Danube-Pristol/Novo Selo (km 834, RO02).

In the second part of the lower Danube section, nitrite-N concentrations continue to rise up to 0.126 mg/l at Danube-Reni/Kilia arm/Chilia arm (km 132, UA01).

For the entire lower Danube, 58 values are above target value 0.060 mg/l.

For selected tributaries, (the spatial variation in **Fig. 8.1.2.8a** and **8.1.2.8b**), the concentrations vary within the range 0.009 – 0.720 mg/l. In the upper part, the Morava-Lanzhot (CZ01) and Dyje-Pohansko (CZ02) show values exceeding 0.060 mg/l in all five studied years. In the middle Danube, the Sio-Szekszard-Palank (H06) is characterized by high nitrite-N concentrations ranging between 0.147 and 0.435 mg/l. In a smaller extent, the Vah-Komarno (SK 04), Sajo-Sajopuspoki (H09), Sava-Jesenice and Sava-us. Una Jasenovac (HR06 and HR07) present concentrations above 0.060 mg/l.
The nitrite-N levels are different for the Jantra-Karantzi (BG07), Prut-Leuseni (MD02) and particularly for the Siret-Conf. Danube Sendreni (RO10): if for the first two ones the concentration reaches 0.280 mg/l in 1997 and 0.282 mg/l in 1998 respectively, the last one is characterized by a value of 0.720 mg/l recorded in 1998.
The total number of nitrite-N c90 values exceeding the target value in selected tributaries is 45.

The temporal trend (**Fig. 8.1.2.9**) shows no significant variation during 1996 – 2000 for upper Danube. In the middle Danube, a slight decreasing trend from 1996 to 2000 is present for Slovak results (SK02 and SK03), while for Hungarian results at the same cross sections the trend is quite opposite. In the first part of the lower Danube, a zigzag profile characterizes the Danube-Bazias and Danube-us. Iskar-Bajkal monitoring sites. At the cross section from Danube-Pristol/NovoSelo/Pristol (km 834 - RO02/BG01), temporal trends are different: according to RO02 results, higher values are recorded in 1996 and 1997 and according to BG01, in 1999. In the second part of the lower Danube section, the temporal profile is unevenly distributed among the five years, most of the sites showing a decreasing line from 1996 to 1999, followed by an increasing in 2000.

For selected tributaries, the temporal variation of the nitrite-N concentrations (**Fig. 8.1.2.10**) shows that for the Morava-Lanzhot (CZ01), Dyje-Pohansko (CZ02) and Vah-Komarno (SK04) a decreasing trend from 1996 to 2000 can be seen. For the Sio-Szekszard-Palank (H06) high values are recorded in 1996 and 1997, followed by decreasing values until 2000. The other tributaries from the middle section present no significant temporal variation during the studied period. In the lower Danube, the Arges-Conf. Danube (RO09) shows an increasing tendency from 1996 to 1999, while for the Siret-Conf. Danube Sendreni (RO10) the trend is opposite from 1996 to 2000.

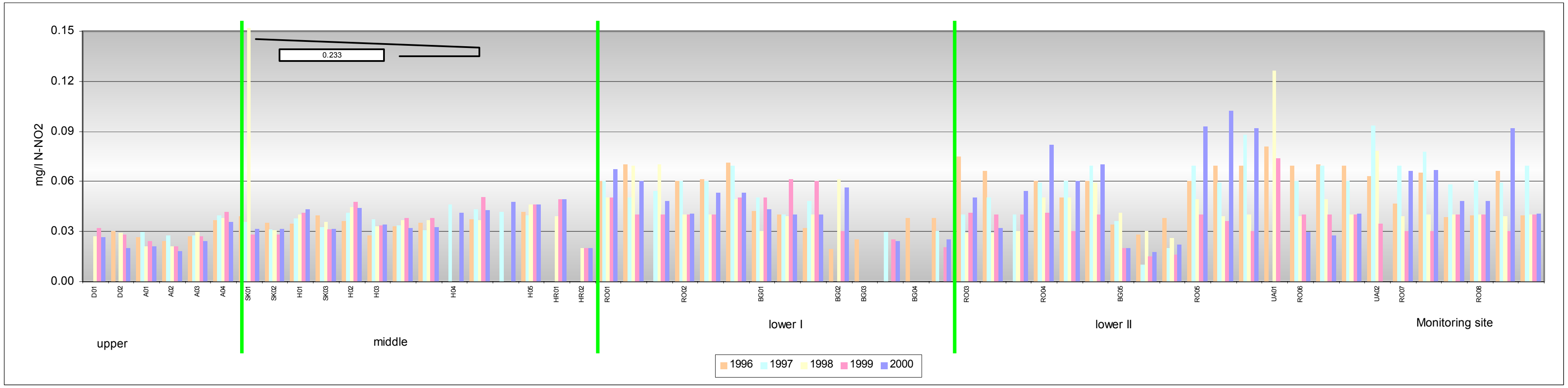


Fig. 8.1.2.7a: Spatial variation of N-NO_2 – Danube River

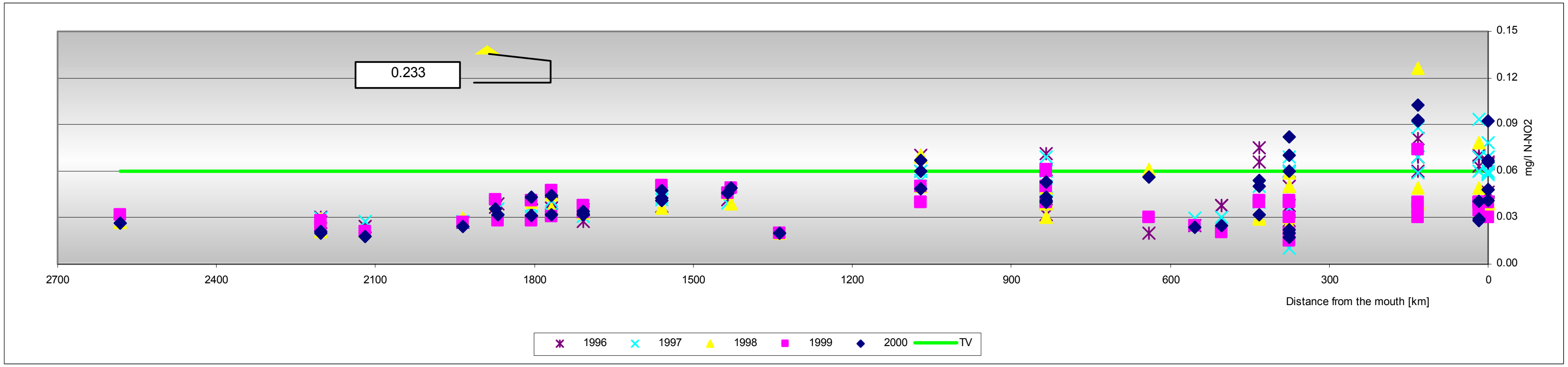


Fig. 8.1.2.7b: Spatial variation of N-NO_2 – Danube River

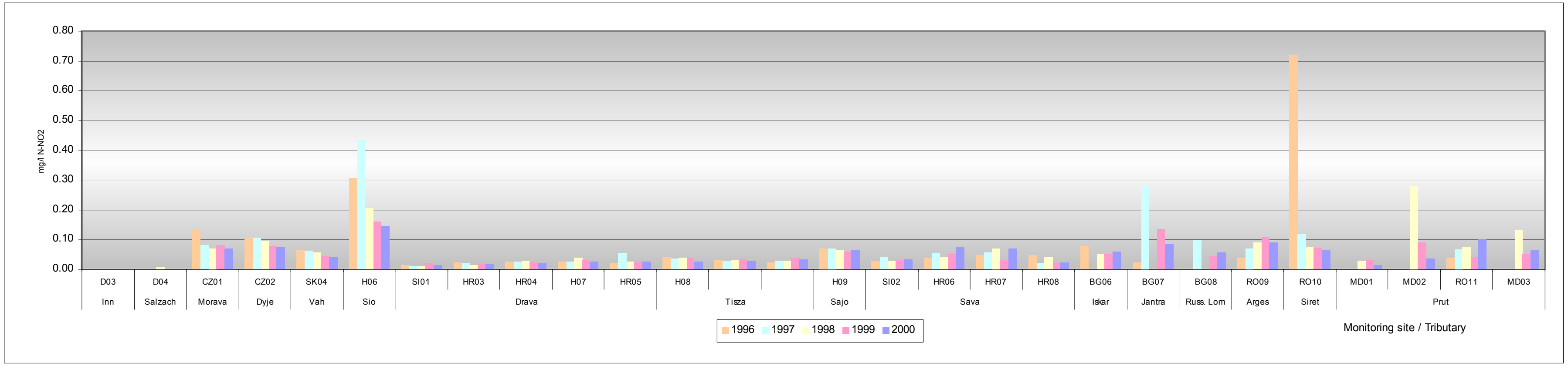


Fig. 8.1.2.8a: Spatial variation of N-NO_2 – Tributaries

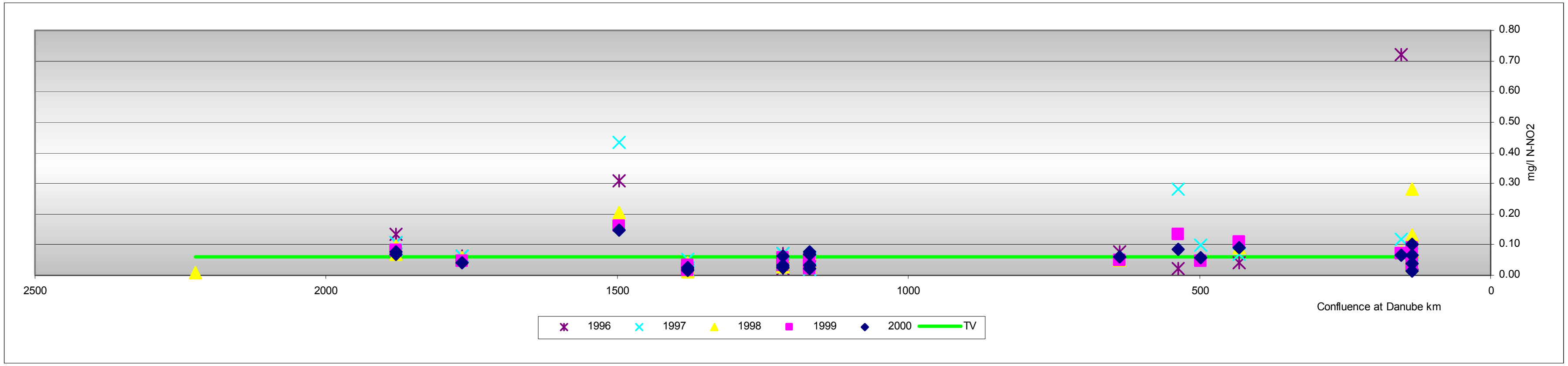


Fig. 8.1.2.8b: Spatial variation of N-NO_2 – Tributaries

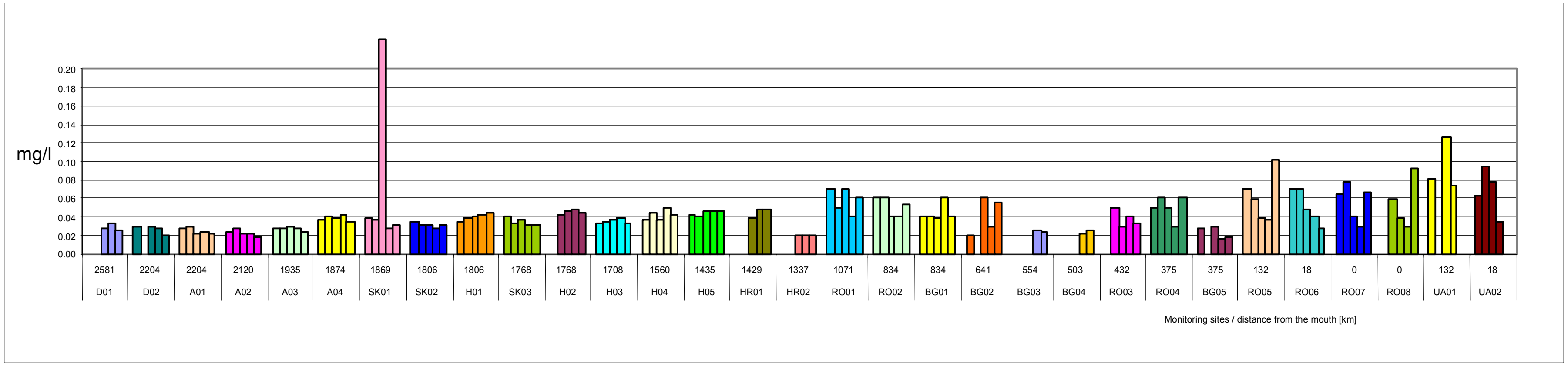


Fig. 8.1.2.9: Temporal trends of N-NO_2 – Danube River

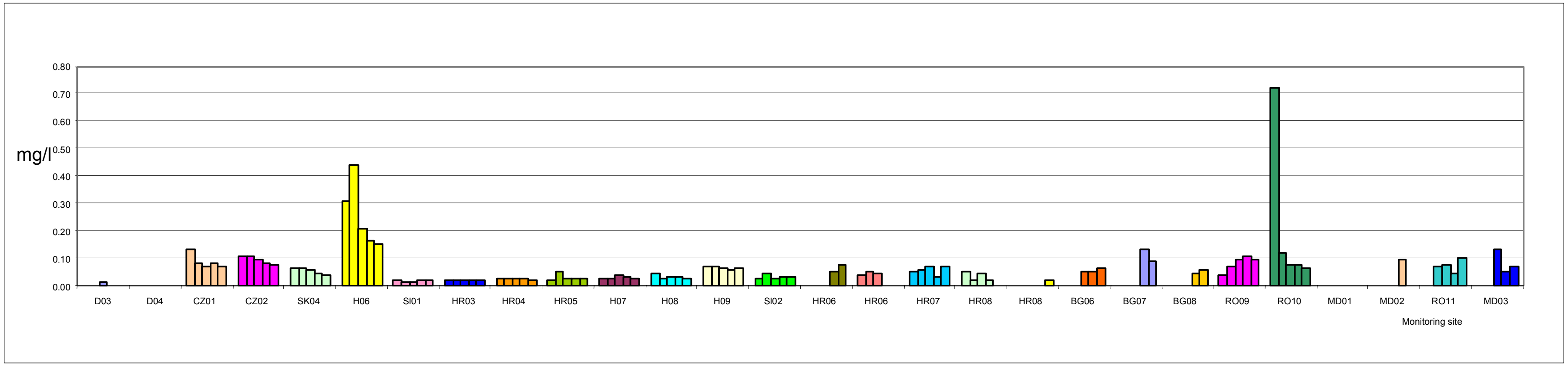


Fig. 8.1.2.10: Temporal trends of N-NO_2 – Tributaries

Nitrate

Nitrate is the final product of oxidation of N-components. Potential sources of nitrate include industrial wastes, animal wastes and fertilizers applied to agricultural crop land.

The distribution of monitoring sites according to the Classification System in the DRB for nitrate-N is shown in **Fig. 8.1.2.11**.

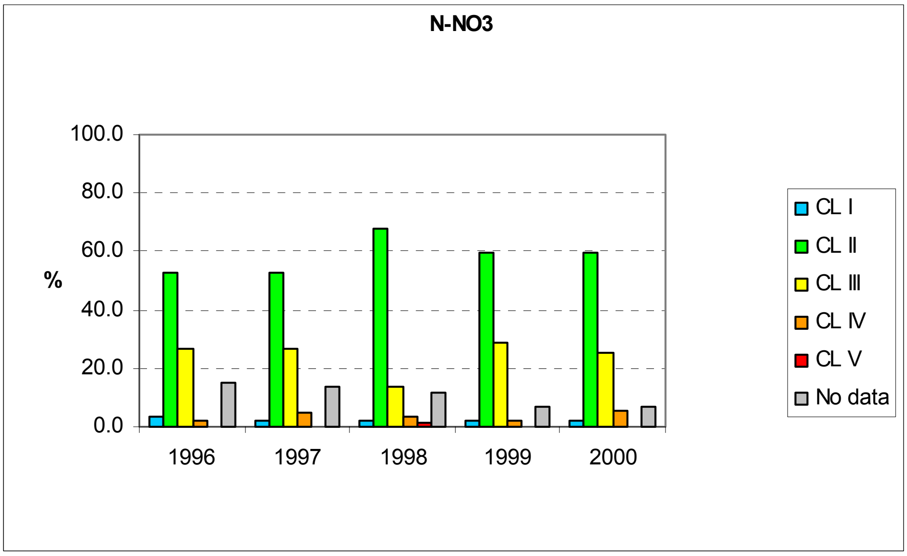


Fig. 8.1.2.11: Distribution of monitoring sites (%) according to the Quality Classification System in the DRB for **N-NO$_3$**

Based on data measured at 87 monitoring sites (therefore out of the assessment is 16 monitoring sites from Phase I List of Monitoring Sites, in which no measurements had been done in 1996-2000), the following pattern is valid:

- the number of sites within Class I is very low, actually between from 2.3 -3.4 %
- more than 50 % of all sites correspond to Class II each year, with a maximum of 67.8 % in 1998; almost 60 % of sites are characterised by this quality class during 1999 – 2000;
- representation of Class III has an inhomogeneous temporal variation, with a minimum percentage of 13.8 % in 1998 and a maximum of 28.7 in 1999;
- Class IV has less than 5 % of all sites during 1996 – 2000 and 5.7 % in 2000;
- Class V is present in 1998 only, with 1.1 % of sites.

The spatial variation for nitrate-N concentrations is shown in **Fig. 8.1.2.12a** and **8.1.2.12b**:

In the upper part of the Danube, 25 nitrate-N concentrations are above the quality target (3.00 mg/l), with the maximum value (4.76 mg/l) at Danube-Neu-Ulm (km 2581, D01). Probably the main cause of this profile is the base flow (*Nutrient Balances for Danube Countries* Project, 1991). Downstream this location, the concentrations level remains constant down to Danube-Wolfsthal (km 1874, A04).

In the middle section, the nitrate-N concentration level is quite homogenous, with 47 values exceeding the quality target.

In the first part of the lower Danube, nitrate-N level is lower than in the middle one, the influence of the Iron Gate reservoir being visible in this area. Rather high values appear at Danube-us. Iskar-Bajkal (km 641, BG02) and at Danube-ds. Svishtov (km 554, BG03)– 3.27 and 5.28 mg/l respectively. In the second part of the lower Danube, avoiding three high values within the range 4.70 – 5.80 mg/l, recorded at Danube-us. Arges (km 432, RO03), all the other concentrations are within the range 1.16 – 2.99 mg/l.

Tributaries are illustrated in **Fig. 8.1.2.13a** and **8.1.2.13b.** As it has already been shown also in case of previous nutrient forms, the tributaries from the upper and the middle Danube that are characterized by higher nitrate-N concentrations values are Morava-Lanzhot (CZ01), Dyje-Pohansko (CZ02), Sio-Szekszard-Palank (H06) and in a smaller extent Vah-Komarno (SK04). Thus, on Dyje and Sio rivers, nitrates level exceeds 6 mg/l, the limit value for Class III. (7.50 and 9.54 mg/l respectively). The next tributaries from the middle Danube present a uniform level of variation - below 3.00 mg/l - with exceptions occurring on the Sajo-Sajopuspoki (H09) and Sava-Jesenice (HR06), where several values are above this limit. As far as concerns the tributaries located in the lower Danube, the nitrates-N values are the highest from those observed in tributaries in Russenski Lom-Basarbovo (BG08) - 10.39 mg/l, Arges-Conf. Danube (RO09) - 10.40 mg/l and Prut-Conf. Danube Giurgiulesti (RO11 and MD03) - 10.37 and 11.10 mg/l, respectively. In all tributaries, there are 43 values above the quality target in evaluated period.

The temporal trend for the Danube River is shown in **Fig. 8.1.2.14** and for selected tributaries in **Fig. 8.1.2.15**. Thus, the following general trends are visible:

- for the upper Danube, no significant temporal changes of nitrate-N values are observed;
- in the middle Danube the situation is the same, but can be mentioned that in majority of monitoring sites in this section nitrate-N values were highest in 1996;
- in the lower Danube, temporal variation shows that in the first part the most elevated values are recorded in 1998 and 2000, while in the second part, the general trend is increasing from 1996 to 1999;
- tributaries from the upper Danube present a relatively stable state for Inn-Kirchdorf (D03) and Salzach-Laufen (D04); in Morava-Lanzhot (CZ01) and Dyje-Pohansko (CZ02) the nitrate-N values decrease;
- in the middle section, a decreasing trend from 1996 to 1998 followed by an increasing until 1999 or 2000 is valid for the Vah-Komarno (SK04) and for several monitoring sites located on Drava (Ormoz-SL01, Varazdin-HR03, Botovo-HR04 and D. Miholjac-HR05). A clear decreasing trend from 1996 to 1999 is visible on the Sio-Szekszard-Palank (H06). An opposite temporal variation appears on the Sajo-Sajopuspoki (H09). For the Sava tributary, no systematic temporal trend is noticeable;
- tributaries located in the first part of the lower Danube do not indicate any trend; in the second part, in Arges-Conf. Danube (RO09) an increasing trend from 1996 to 2000 is visible. For the Siret-Conf. Danube Sendreni (RO10) a relatively stable state is characteristic, while for the Prut tributary, two different monitoring sites (RO11 and MD03) show the highest values recorded in 2000 and 1998, respectively.

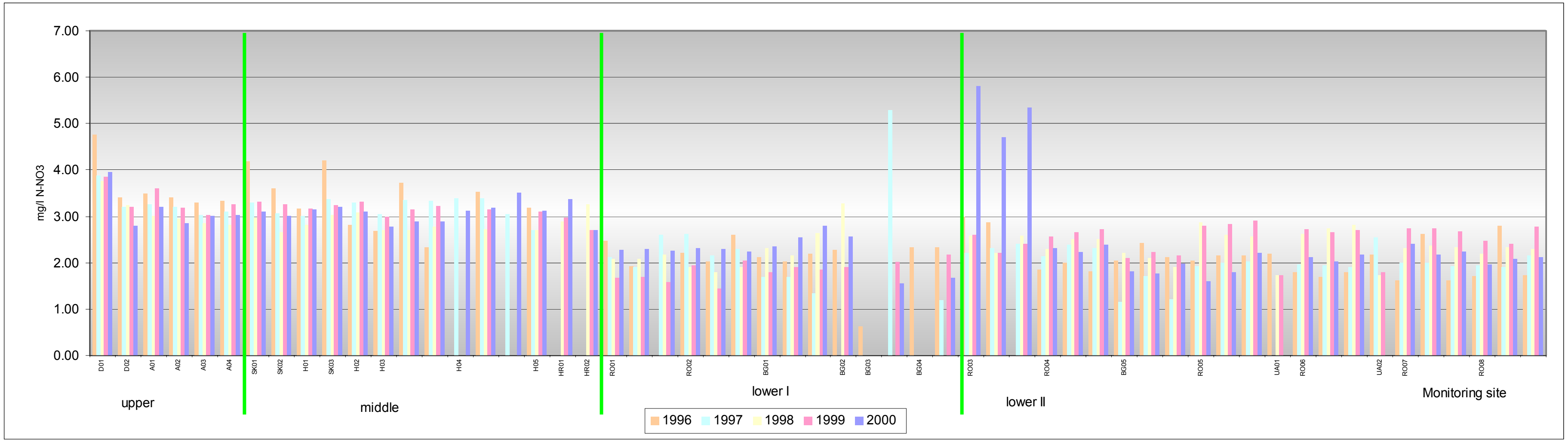


Fig. 8.1.2.12a: Spatial variation of N-NO_3 – Danube River

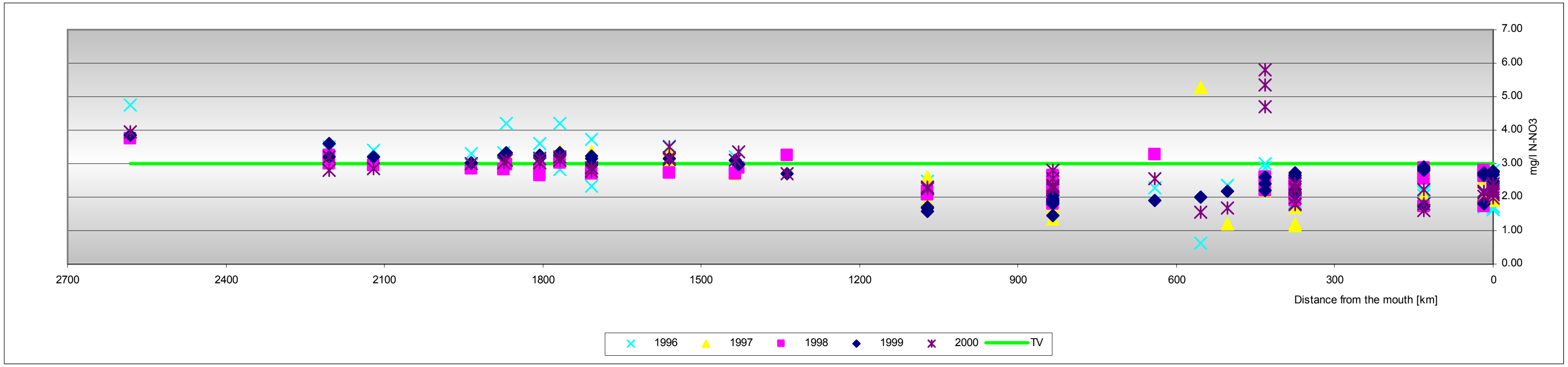


Fig. 8.1.2.12b: Spatial variation of N-NO_3 – Danube River

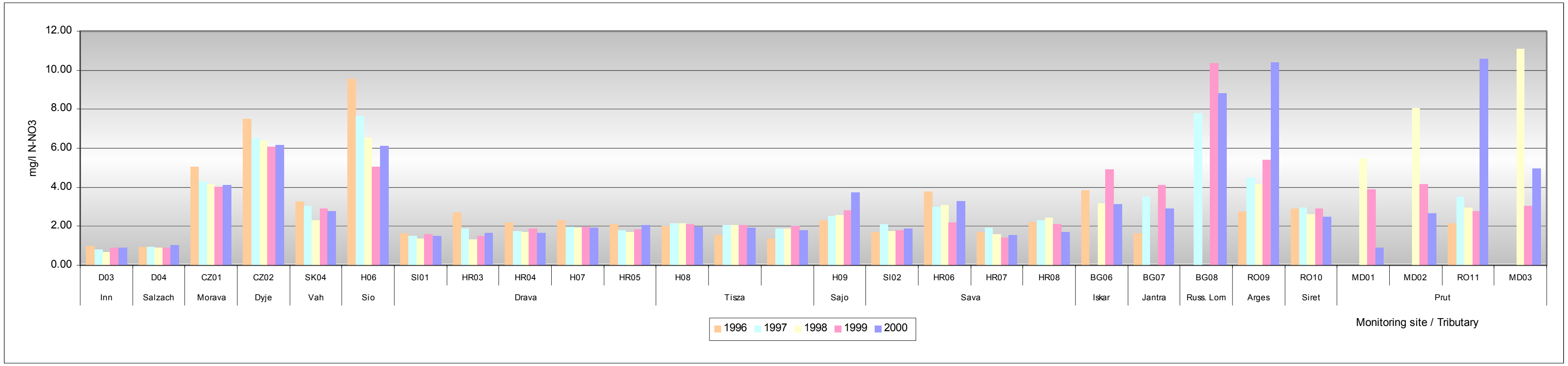


Fig. 8.1.2.13a: Spatial variation of $N\text{-}NO_3$ – Tributaries

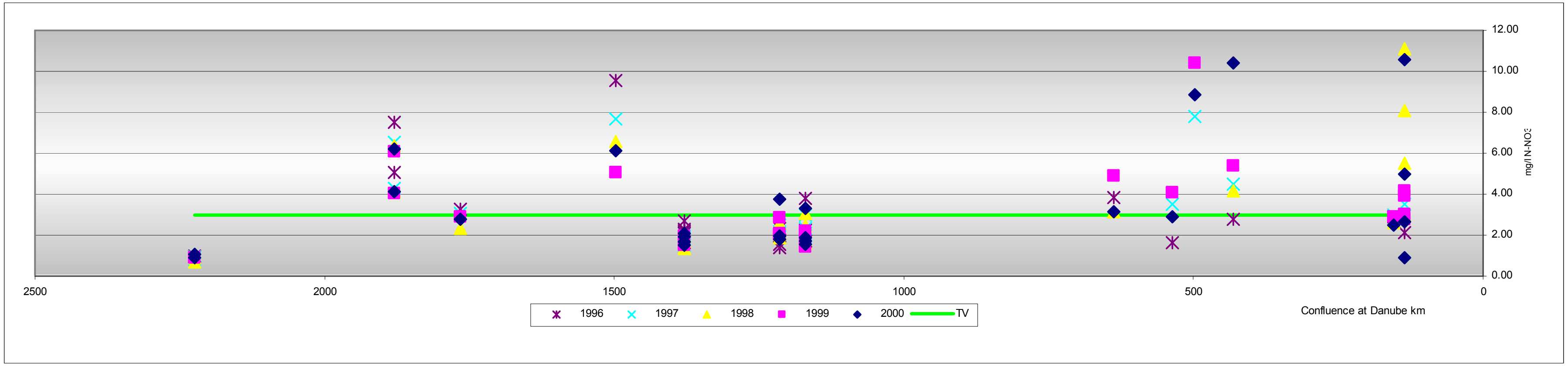


Fig. 8.1.2.13b: Spatial variation of $N\text{-}NO_3$ – Tributaries

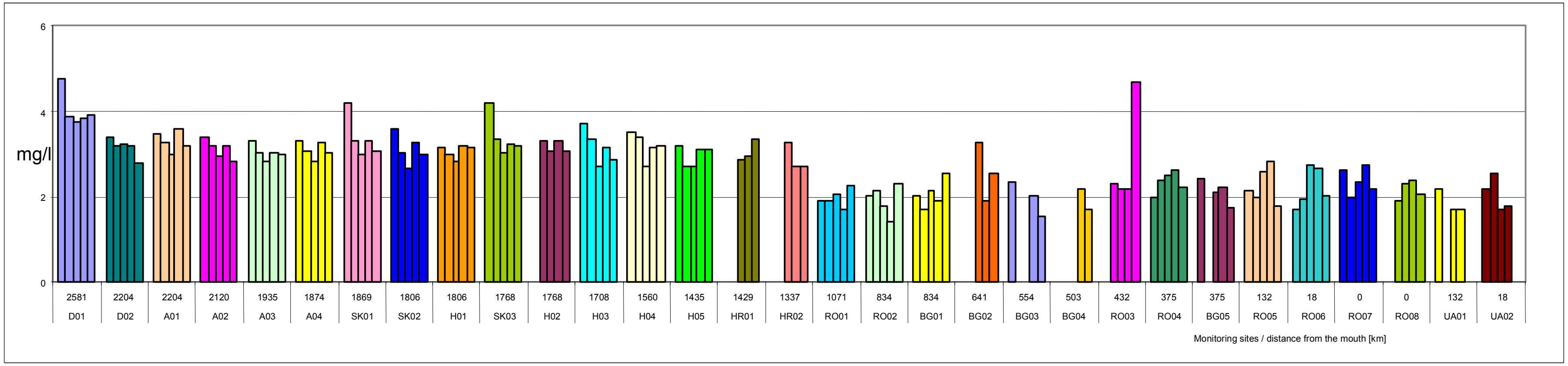


Fig. 8.1.2.14: Temporal trends of N-NO_3 – Danube River

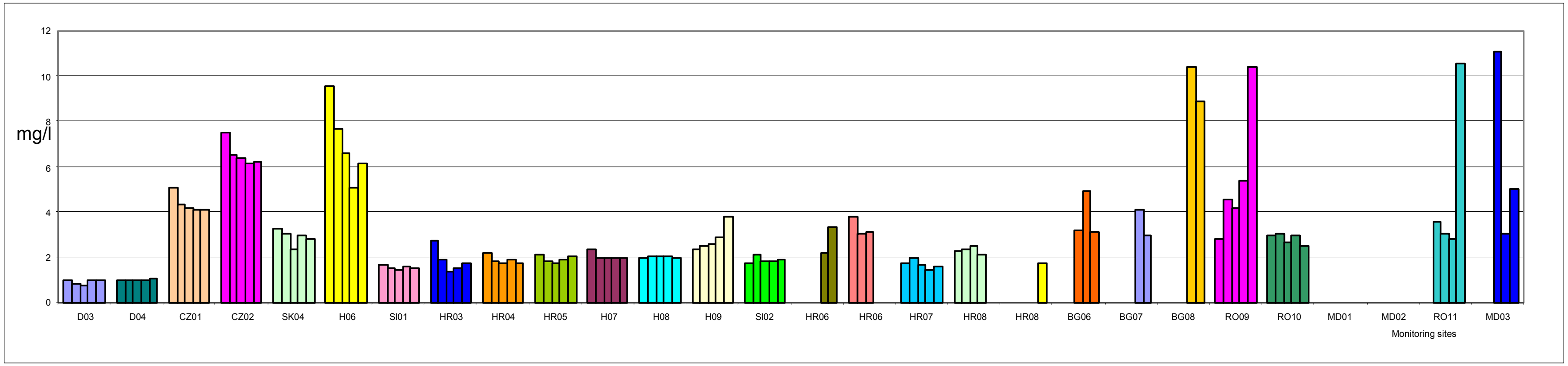


Fig. 8.1.2.15: Temporal trends of N-NO_3 – Tributaries

Phosphorous

Phosphorous is one of the main components in organic matter. It generally originates from mineralization from the soil and rocks (as natural sources) and from waste effluents, municipal wastewaters or drainage that contain fertilizers (as anthropogenic sources). Although phosphorous tends to be the nutrient that mostly limits plant growth in lakes in reservoirs, its presence assessment in flowing rivers is not of a less importance. If the natural background concentration of dissolved phosphorous is about 0.025 mg/l P, the polluted segment of a watercourse may contain up to 1 mg/l P or even more (*The Dobris Assessment, 1991*).

In TNMN Programme, phosphorous is measured both as total phosphorous and soluble reactive phosphate or ortho-phosphate. The latter form is the only biologicaly available form of phosphorous.

Ortho-phosphate

The distribution of monitoring sites according to the Classification System in the DRB for ortho-phosphate-P is shown in **Fig. 8.1.2.16**.

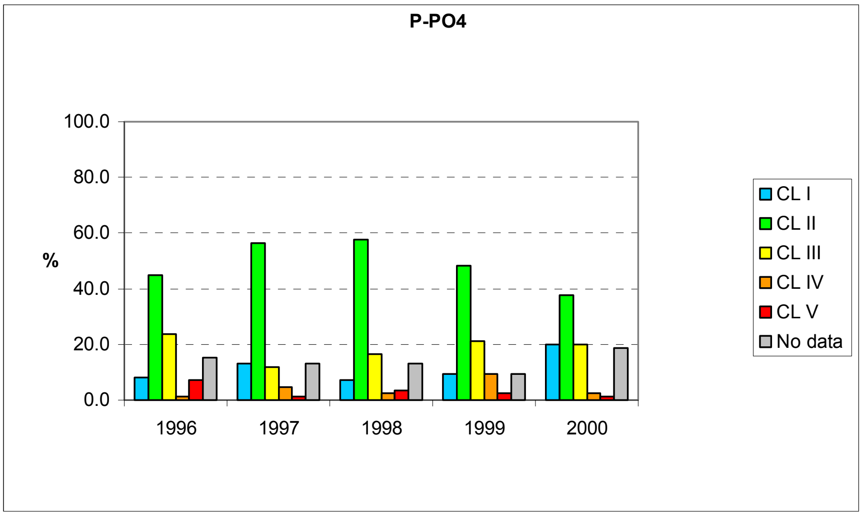


Fig. 8.1.2.16: Distribution of monitoring sites (%) according to the Quality Classification System in the DRB for **P-oPO$_4$**

On the bases on data reported from 85 monitoring sites (out of the assessment are 18 monitoring sites from Phase I List of Monitoring Sites, in which no measurements had been done in 1996-2000), the following can be concluded:

- the number of monitoring sites within Class I shows an uneven temporal variation, with a minimum of 7.1 % in 1998 and a maximum of 20% in 2000;
- Class II comprises the maximum percentages in each year, with an increasing line from 1996 to 1998, followed by a decreasing until 2000. Percentage of sites in Class II varies from 38% (2000) to 58% (1998);
- the percentage of monitoring sites within Class IV is low, with maximum value of 9.4% in 1999;
- similarly low percentage if sites correspond to Class V, with a maximum of 7.1% in 1996.

The spatial assessment of orthophosphate-P concentration along the Danube River is shown in Fig. **8.1.2.17a** and **8.1.2.17b**.

In the upper Danube, ortho-phosphate concentrations level is nearly 0.050 mg/l at all monitoring sites, so no value is above the target value for this nutrient (0.10 mg/l).

In the middle Danube, spatial profile is slightly changed, with most of the values within the range 0.060 – 0.126 mg/l. Comparing with the quality target value, there are 18 values above it.

In the first part of the lower Danube, the ortho-phosphate-P concentrations are higher than in the middle Danube, the variation range of c90 is 0.070 – 0.186 mg/l for the first 200 km of this stretch. Although high values from Danube-Bazias (km 1071, RO01) were recorded in 2000, the previous four years do not show many values above the 0.100 mg/l level. An extreme high value (0.446 mg/l) was observed at Danube-us. Russe (km 503, BG04) in 1996.

In the second part of the lower Danube, ortho-phosphate-P c90 values seldom exceed 0.100 mg/l level. However, the big difference between the recorded data at the same cross section (RO04/BG05 and RO06/UA02) gives an inhomogeneous picture of the spatial distribution. Leaving apart this incoherence, a slight decreasing spatial tendency is visible from Danube-us. Arges (km 432, RO03) down to the three main arms of the Danube Delta (RO06, RO07 and RO08).

Along the entire lower Danube, 51 ortho-phosphate-P concentrations are above the quality target.
The spatial pattern of ortho-phosphate-P concentrations in selected tributaries is shown in **Fig. 8.1.2.18a** and **8.1.2.18b**.

- in the upper and middle section of the Danube, in two tributaries only ortho-phosphate values exceed 0.20 mg/l (the limit value for Class III) in evaluated period: Dyje-Pohansko (CZ02) and the Sio-Szekszard-Palank (H06). In strong correlation with other data from the group of nutrients, these values are caused mainly by anthropogenic inputs.
- in the lower section, there are far more elevated values for ortho-phosphate, characteristic to Class V: 1.322 and 1.072 mg/l in 1996 and 1998 on the same tributary - Iskar-Orechovitza (BG06). High values were also recorded in 1996 and 1999 on the Jantra-Karantzi (BG07) – 0.460 and 0.484 mg/l, Russenski Lom-Basarbovo (BG08) – 0.850 mg/l and Arges-Conf. Danube (RO09) – 0.675 mg/l and 0.850 mg/l;
- in TNMN tributaries, 57 values are above the target value in period 1996-2000.

Temporal trend for ortho-phosphate-P is shown in **Fig. 8.1.2.19** for the Danube River and in **Fig. 8.1.2.20** for selected tributaries. The following can be concluded:

- for monitoring sites located in the upper Danube, no significant temporal variation is visible;
- in the middle Danube, a decreasing trend from 1996 to 1999 is characteristic from Danube-Bratislava (km 1869, SK01) down to Danube-Szob (km 1708, H03); an exception appears at Danube-Medvedov/Medve (km 1806, SK02). For the rest of the sites in this stretch, the temporal distribution is almost stationary.
- as regards the first part of the lower Danube section, from Danube-Bazias (km 1071, RO01) down to Danube-Pristol/Novo Selo (km 834, RO02) an increasing tendency from 1996 to 2000 is present if the Romanian results are taken into account; according to the Bulgarian data, the temporal trend for Danube-Novo Selo/ Pristol (km 834, BG01) is opposite - decreasing from 1996 to 1999;
- in the second part of lower Danube section, in most of the monitoring points the values are reather varying. In addition, rather high differences exist between the reported data for the same cross section – Danube-Silistra/Chiciu/Silistra (RO04/BG03, km 375). At the Danube-us. Arges (km 432, RO03) an increasing line from 1997 to 2000 is noticeable;
- selected tributaries show inhomogeneous temporal trends: the Morava-Lanzhot (CZ01) and Dyje-Pohansko (CZ02) have high values recorded in 1996 and 1998 respectively, while the Sio-Szekszard (H06) is characterized by high values in 1997 and 2000. Except a decreasing trend observed in Drava-Varazdin (HR03) the rest of monitoring sites located on this tributary present a relatively stable state. No temoral changes were observed in Tisza tributary, even the variation between years is low. The picture shows differently for the Sava, where no systematic temporal trend is detectable, but year-to-year variation is much higher there.

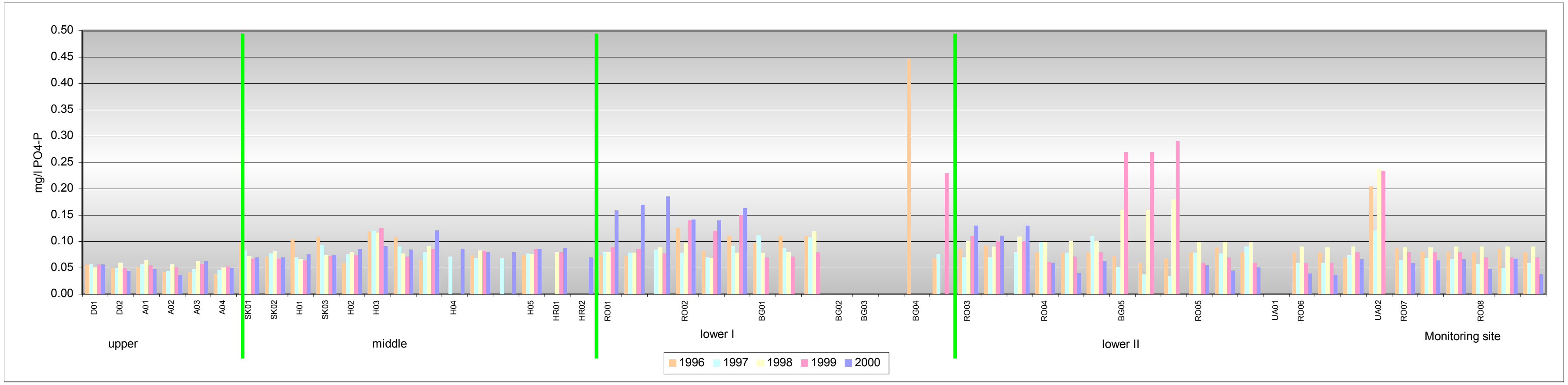


Fig. 8.1.2.17a: Spatial variation of P-oPO_4 – Danube River

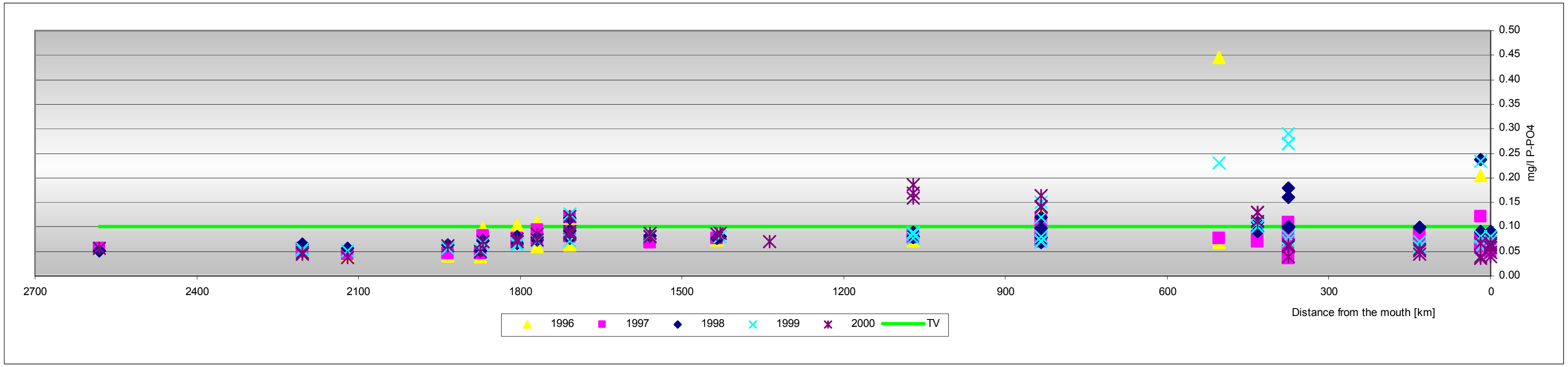


Fig. 8.1.2.17b: Spatial variation of P-oPO_4 – Danube River

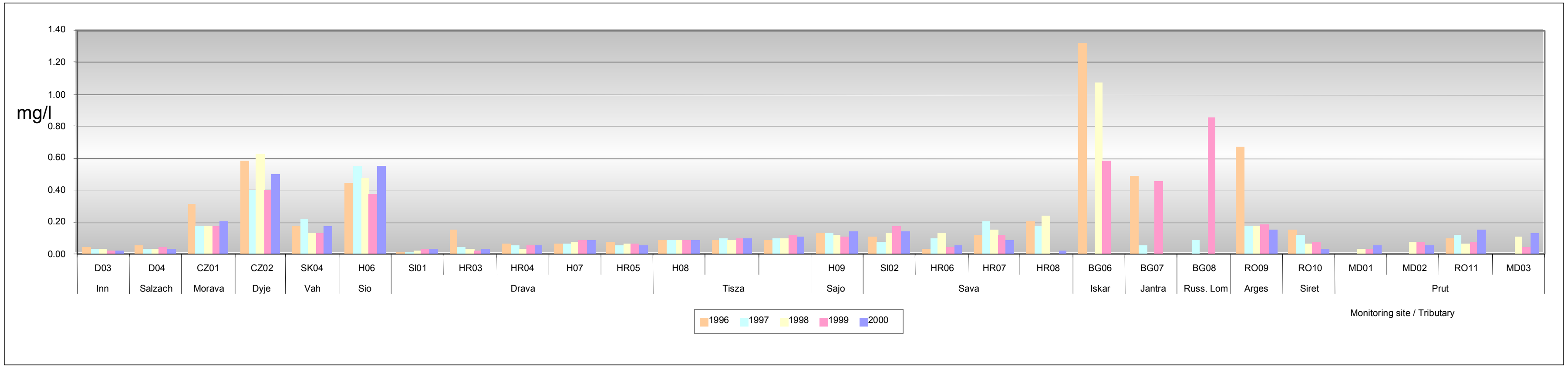


Fig. 8.1.2.18a: Spatial variation of P-oPO$_4$ – Tributaries

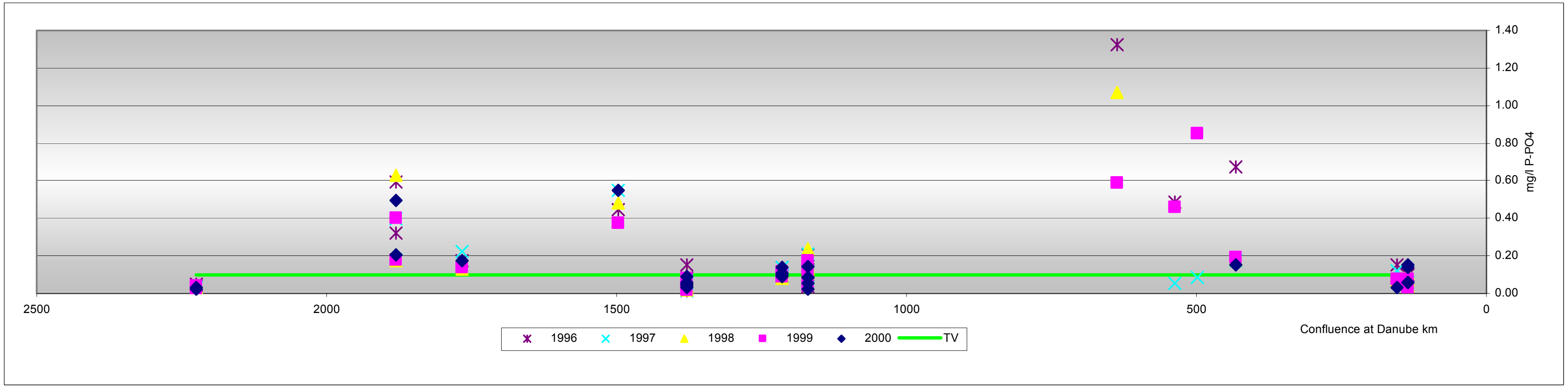


Fig. 8.1.2.18b: Spatial variation of P-oPO$_4$ – Tributaries

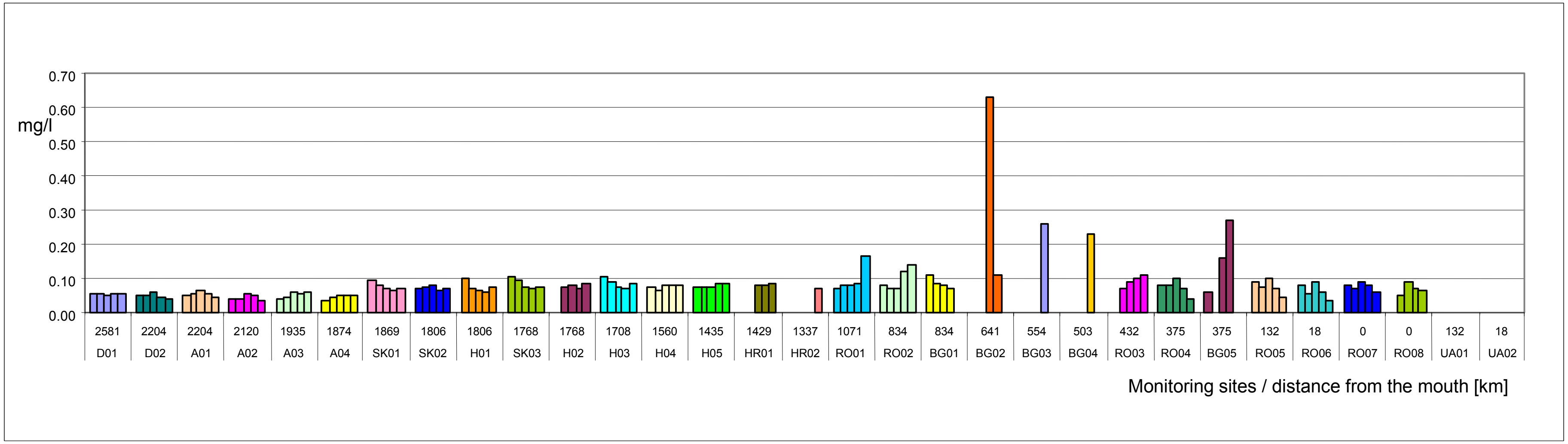


Fig. 8.1.2.19: Temporal trends of P-oPO$_4$ – Danube River

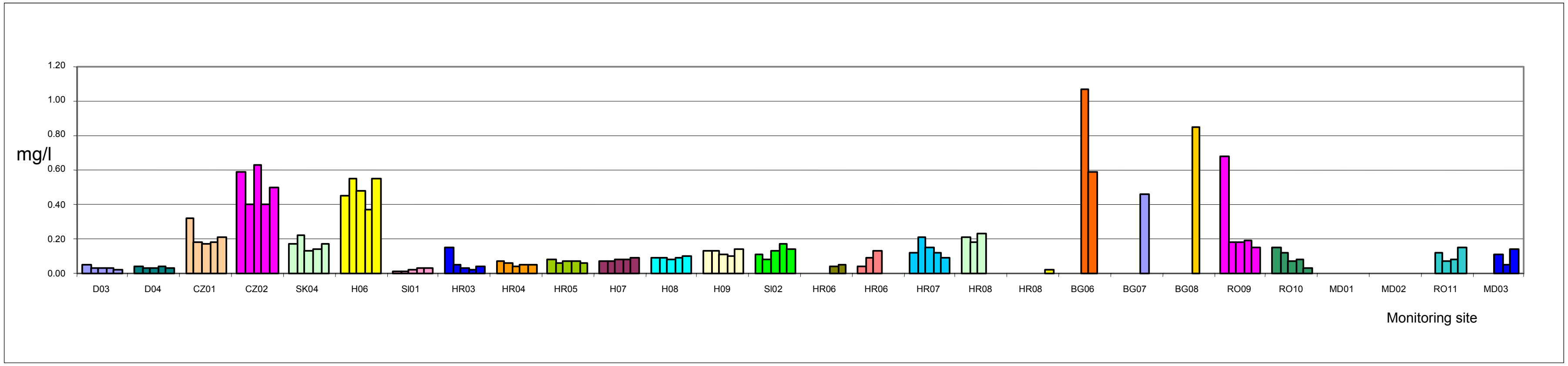


Fig. 8.1.2.20: Temporal trends of P-oPO$_4$ – Tributaries

Total Phosphorous

The distribution of monitoring sites according to the Classification System in the DRB for Total P is shown in **Fig. 8.1.2.21**.

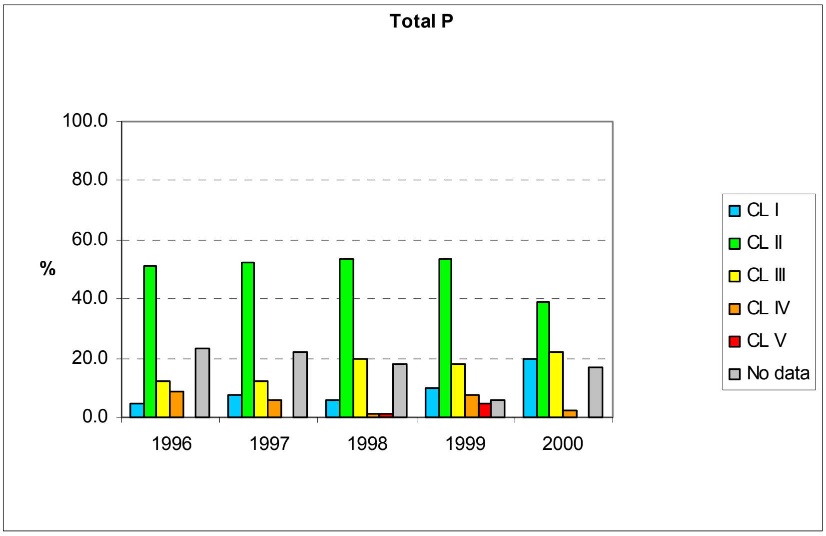


Fig. 8.1.2.21: Distribution of monitoring sites (%) according to the Quality Classification System in the DRB for **Total P.**

Based on data recorded at 824 monitoring sites (it means that out of the assessment is 21 monitoring sites from Phase I List of Monitoring Sites, in which no measurements had been done in 1996-2000), the following remarks can be done:

- Class I comprises less than 20 % of all monitoring sites, with a minimum of 6.0 % in 1996 and 1998;
- during 1996 – 1999, more than 40 % of all sites belong to Class II, but in 2000 the percentage decreases to 38.1 %;
- the number of sites within Class III increases from 1996 to 2000, the maximum value being 21.4 %;
- the number of sites within Class IV decreases during 1996 – 1998 and from 1999 to 2000 and increases from 1998 – 1999; the variation range is 1.2 % - 8.3 %;
- Class V is represented in 1998 and 1999 only, by 1.2 % and 4.8 % of all sites respectively;
- “no data” category” from 84 monitoring sites has a constant variation around 20 %, excepting 1999 when only 6 % of all sites are included in this category.

The spatial variation of Total P concentration along the Danube River is shown in **Fig. 8.1.2.22a** and **8.1.2.22b.**

Unlike the spatial variation for ortho-phosphate in the upper Danube, the total P concentrations increase from Danube-Neu-Ulm (km 2581, D01), where the variation range is 0.106-0.140 mg/l to Danube-Wolfsthal (km1874, A04), where the range is 0.120-0.302 mg/l. There are five c90 values of total P above the quality target (0.200 mg/l) .

In the middle section of the river the maximum value was located in Danube-Szob (km 1708, H03L) – 0.310 mg/l in 1998, being the sampling site where Danube leaves Slovakia. Along this stretch, 23 values are above the target limit.

In the first part of the lower Danube, after Danube-Bazias (km 1071, RO01) where the concentrations values reach 0.240 mg/l, a decreasing is observed down to Danube-us. Iskar-Bajkal (km 641, BG02), where the concentration is 0.144 mg/l. Although the missing data cannot provide enough information

for the next stretch, a high value (0.765 mg/l) is visible at Danube-ds. Svishtov (km 554, BG03) in 1999.
In the second part of the lower Danube, Total P values follow a relatively uniform line regarding spatial variation, only three values being outside of this profile, recorded at Danube-Silistra/Chiciu (km 375, BG05). However, a slight decreasing is noticeable below Danube-us. Arges (km 432, RO03) down to the three main arms of the Danube Delta.

For the entire lower Danube, 21 values are above the quality target 0,2 mg/l.

Total P in the selected tributaries has an inhomogeneous profile, mainly in accordance to extent of human influences in the river basins of these tributaries – **Fig. 8.1.2.23a** and **8.1.2.23b**. Thus, relatively high Total P values, corresponding to Class IV and V, were recorded on the following watercourses:

- the Dyje-Pohansko (CZ02) – all values exceeding 0,5 mg/l with maximum 0.917 mg/l in 1998;
- the Sio-Szekszard-Palank (H06) – all values exceeding 0,9 mg/l with maximum 1.370 mg/l in 1998;
- the Jantra-Karantzi (BG07) – with c90 value of 0.942 mg/l in 1999 (only the data from this year available);
- the Russenski Lom-Basarbovo (BG08) – with c90 value of 1.805 mg/l in 1999 (only the data from this year available);
- the Arges-us. Arges (RO09) – with c90 value of 0.865 mg/l in 1996.

There are 63 Total P values above the quality target.

Temporal trend for Total P concentrations is illustrated in **Fig. 8.1.2.24** for the Danube River and in **Fig. 8.1.2.25** for selected tributaries. Concerning total phosphorus the variance between the years is much higher than that of orthophosphates because of its connection to short-time process. When samples are taken during high-flow period, 90 %-iles of that year are supposed to be on a higher level. In many cases the years showing high values of suspended solids have high values of total phosphorus, too. Regarding temporal assessment, the following can be concluded:

- in the upper Danube, slight continuous increasing is visible in Danube Wien-Nussdorf (A03, rkm 1935)
- in the middle part of the Danube, Total P temporal distribution is rather scattered, with no indication of general increasing or decreasing trend;
- similar situation is in the first part of the lower Danube; at the cross section Danube-Pristol NovoSelo/ Pristol, the changes in time are opposite, depending on whether results provided by Romania or Bulgaria are taken into account;
- in the second part of the lower Danube, if at Danube-us. Arges (km 432, RO03) Total P concentrations increase from 1997 to 2000 and at Danube-Reni-Chilia/kilia arm (km 132, RO05) values decrease from 1997 to 2000; for almost all remaining sites, the maximum values are recorded in 1996 and 1998;
- there is only one tributary, in which an indication of an increase is observable - Inn – Kirchdorf (D03), but this “change” in time can be explained by suspended solids content in a water in 2000 (see also Fig. 8.1.1.4). The decrease is visible in Arges (RO09) and Siret (RO10), especially taking into account high values reached in 1996 that did not occur later in the evaluated period.

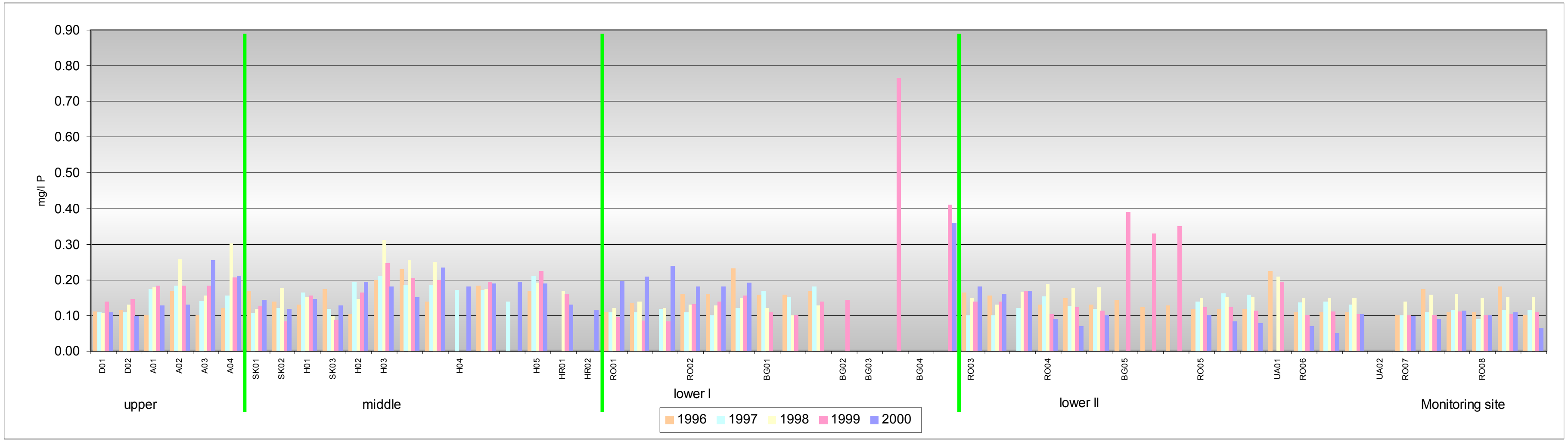


Fig. 8.1.2.22a: Spatial variation of Total P – Danube River

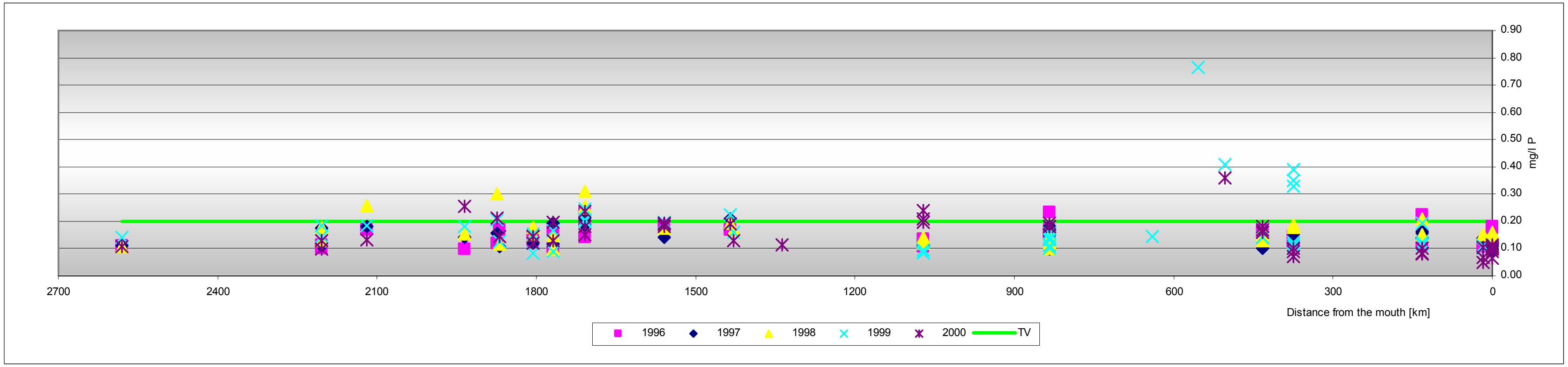


Fig. 8.1.2.22b: Spatial variation of Total P – Danube River

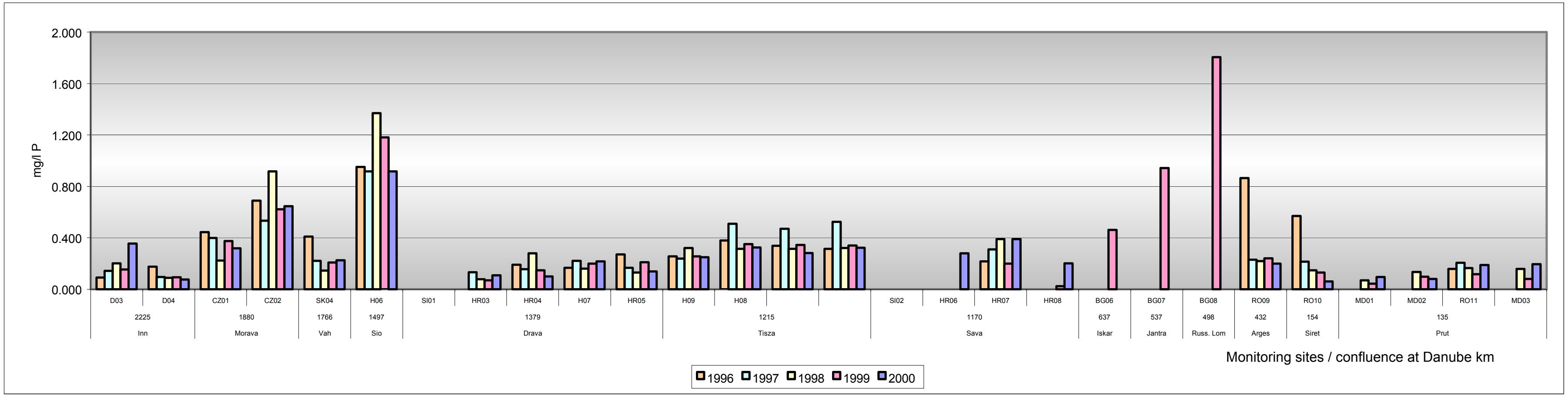


Fig. 8.1.2.23a: Spatial variation of Total P – Tributaries

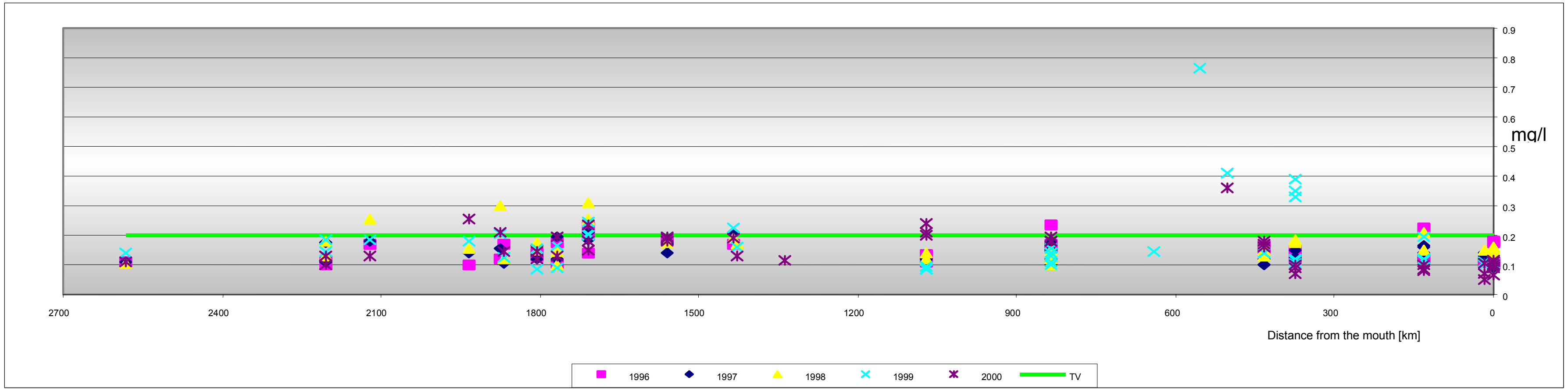


Fig. 8.1.2.23b: Spatial variation of Total P – Tributaries

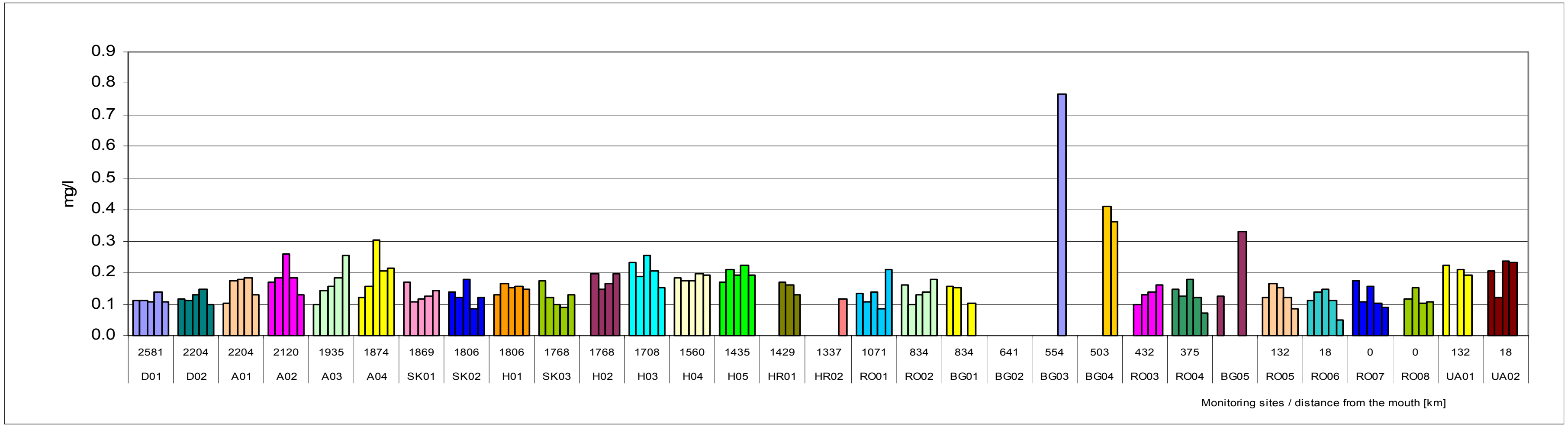


Fig. 8.1.2.24: Temporal trends of Total P – Danube River

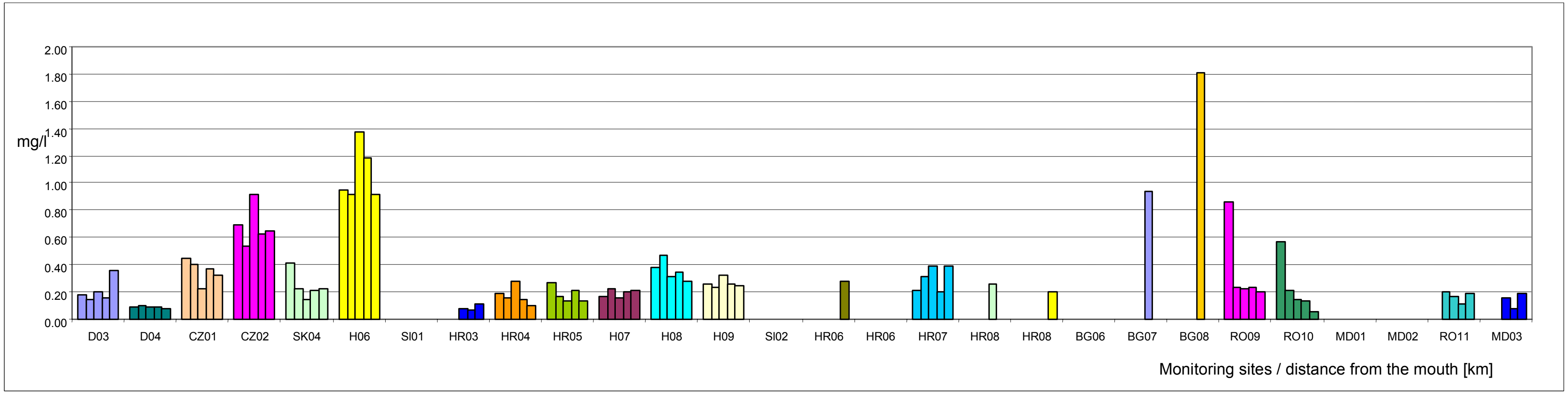


Fig. 8.1.2.25: Temporal trends of Total P – Tributaries

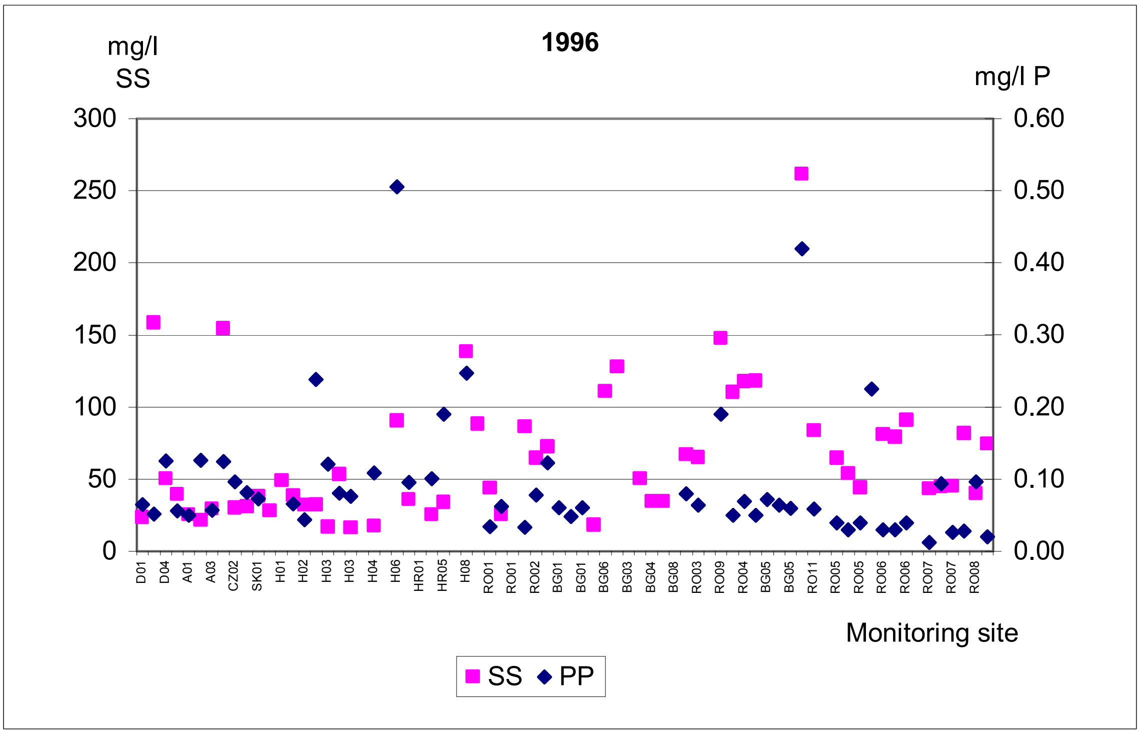
Regarding exceedance of the target limit of Total-P, set up on the level of 0.2 mg/l, 18.0 % of c90 values are above this limit in the Danube River and 57.3 % in selected tributaries – **Fig. 8.1.2.22b and 8.1.2.23b**.

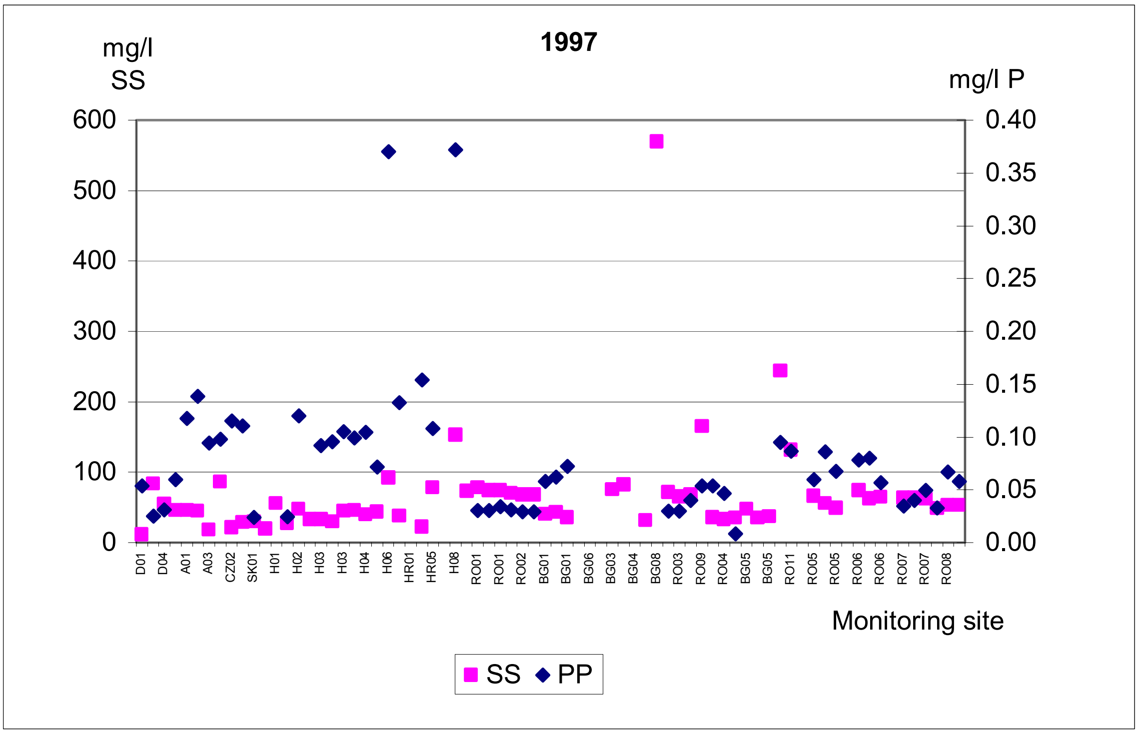
If the orthophosphate is a reliable indicator of bioavailability, total phosphorous concentration can be related with suspended solids content, due to the fact that phosphorous compounds tend to be adsorbed on particulate matter. In this respect, the charts illustrating the spatial distribution of suspended solids versus so-called “particulate phosphorous”, approximated as the difference between total P and ortho-phosphate P (where available), was done for each studied year (see **Fig. 8.1.2.26 - 8.1.2.30)**. Results present a large variability in longitudinal profile of the Danube itself and the only conclusive data are visible for several sites, listed in **Table 8.1.2.1**.

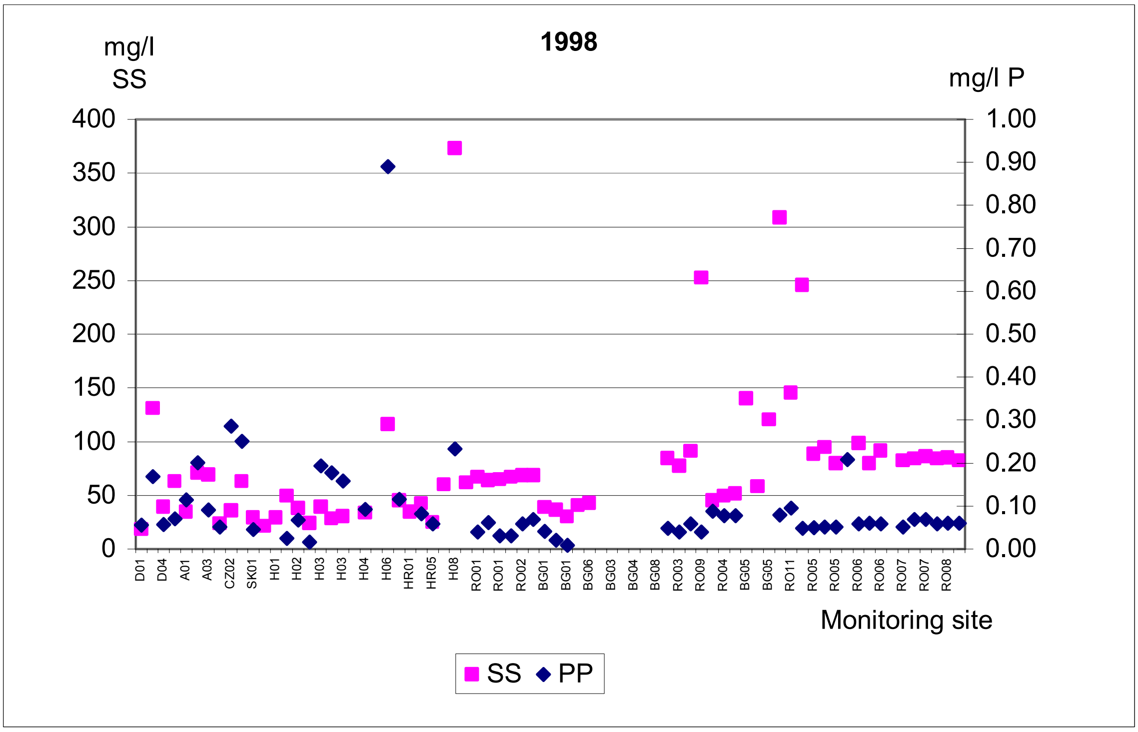
Table 8.1.2.1: Several correlations between the particulate phosphorous (PP) and suspended solids content (SS):

Year	Monitoring site	PP (mg/l)	SS (mg/l)
1996	H08	0.247	138.4
	RO09	0.190	147.5
	RO10	0.420	261.5
1997	HO8	0.372	153.4
1998	D03	0.169	131.0
1999	H06	0.805	140.8
	H08	0.254	125.3
	BG08	0.955	300.6
	UA01	0.194	108.7
2000	D03	0.335	315.0
	H08	0.183	217.4

Fig. 8.1.2.26 - 8.1.2.30: Suspended solids content vs. particulate phosphorous




1997
mg/l
SS
mg/l P
600
500
400
300
200
100
0
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
D01
D04
A01
A03
CZ02
SK01
H01
H02
H03
H03
H04
H06
HR01
HR05
H08
RO01
RO01
RO02
BG01
BG01
BG06
BG03
BG04
BG08
RO03
RO09
RO04
BG05
BG05
RO11
RO05
RO05
RO06
RO06
RO07
RO07
RO08
Monitoring site
■ SS ◆ PP


1998
mg/l
SS
mg/l P
400
350
300
250
200
150
100
50
0
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
D01
D04
A01
A03
CZ02
SK01
H01
H02
H03
H03
H04
H06
HR01
HR05
H08
RO01
RO01
RO02
BG01
BG01
BG06
BG03
BG04
BG08
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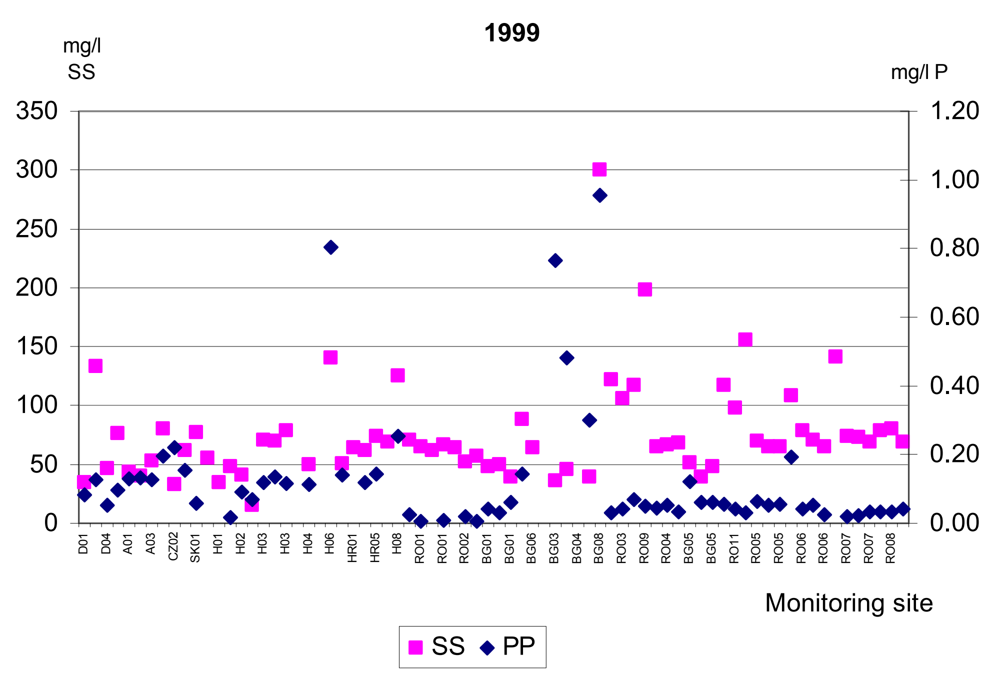
RO08
Monitoring site
■ SS ◆ PP


1999
mg/l
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D01
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CZ02
SK01
H01
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H04
H06
HR01
HR05
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RO01
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RO02
BG01
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Monitoring site
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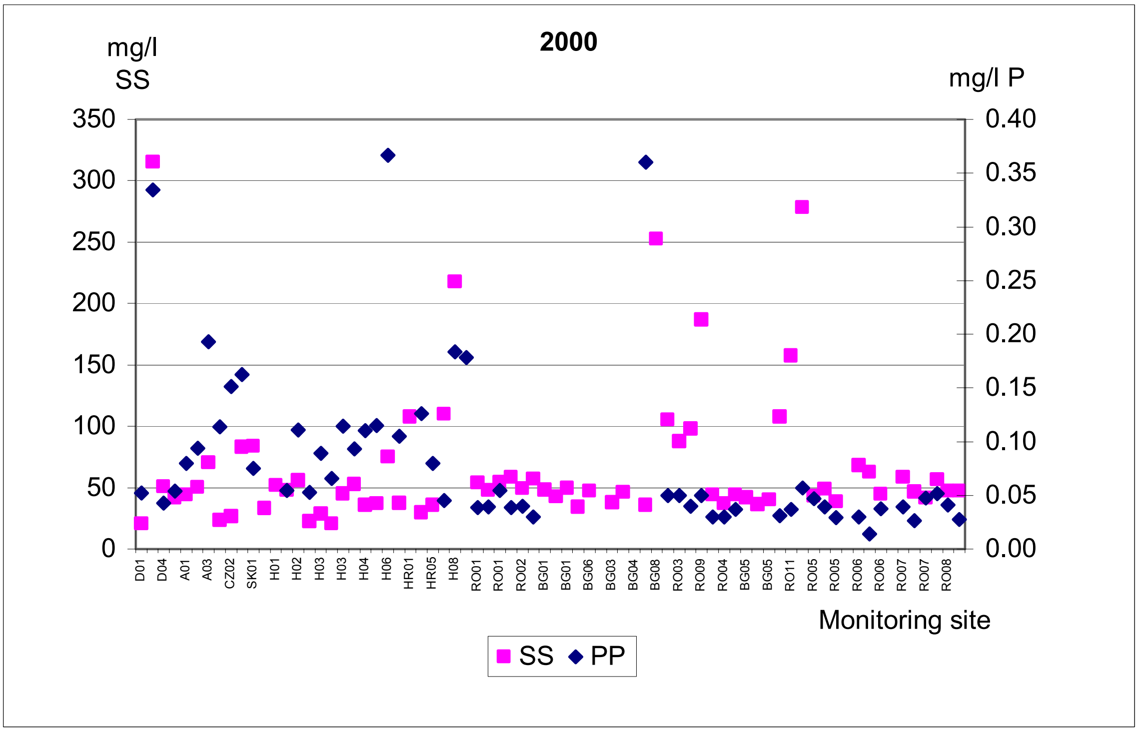
2000
mg/l
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mg/l P
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0.25
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0.10
0.05
0.00
D01
D04
A01
A03
CZ02
SK01
H01
H02
H03
H03
H04
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HR05
H08
RO01
RO01
RO02
BG01
BG01
BG06
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RO03
RO09
RO04
BG05
BG05
RO11
RO05
RO05
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RO07
RO07
RO08
Monitoring site
SS
PP

8.1.3. Heavy Metals

All heavy metals exist in surface waters in colloidal, particulate and dissolved phases, although dissolved concentrations are generally low (*Kennish, 1992*). The colloidal and particulate metal may be found in hydroxides, oxides, silicates and sulfides or adsorbed to clay, silica or organic matter. The soluble forms are generally ions or unionized organometallic chelates or complexes. The solubility of trace metals in surface waters is predominately controlled by pH, the type and concentration of ligands on which the metal could adsorb and the oxidation state of the mineral components and redox environment of the system (*Connel et al., 1984*). The water chemistry also controls the rate of adsorption and desorption of metals to and from sediment. Thus, metals can be desorbed from the sediment if the water increases in salinity, decreases in redox potential or decreases in pH.

In surface waters system, heavy metals can be from natural and anthropogenic sources, but currently human inputs of metals exceed the natural ones. As natural sources, chemical and physical weathering of rocks and soils can be mentioned, further decomposition of plants and animal detritus, wind erosion, atmospheric deposition of airborne particles (Kennish, 1992). As antropogenic non-point sources, the most important are surface runoff from mining operations, urban storm water runoff, combustion of fossil fuels; as anthropogenic point sources, among the most important are domestic wastewater effluents, corrosion of water pipes and industrial effluents (Connel et al., 1984).

Within the TNMN Programme, a number of 11 heavy metals are routinely analyzed in water samples, both as total water concentration and as dissolved fraction. The ration of these fractions in water varies from substance to substance. The concentration of heavy metals is strongly dependent on quantity and nature of suspended solids. This is the reason of natural variations and trends which hide the effect of anthropogenic contaminations. High values often reflect situations with high loads of suspended solids and flood events – statistical parameters ike 90 %-ile, using also in the assessment in this report, are therefore influenced by these processes. To eliminate such effects it is preferred to determine heavy metals dissolved in water as well as concentrations in suspended solids.

Referring to the five-years synthesis report, the main focus is directed to the total heavy metals content in water samples during 1996 – 2000, because dissolved fraction data are available for recent years only, and collected data do not even cover the whole river basin.

Iron

The spatial distribution of Iron concentrations along the Danube River is shown in **Fig. 8.1.3.1a** and **8.1.3.1b**:

In the upper section, Iron concentrations vary within the range 0.208 – 1.190 mg/l, with a slight spatial increasing from Danube-Neu Ulm (km 2581, D01) down to Danube-Wolfsthal (km 1874, A04), reaching 1.19 mg/l.

In the middle section, the spatial profile is relatively constant down to Danube-Szob (km 1708 H03), where the highest values range between 0.82 – 0.99 mg/l. Downstream this monitoring site, a significant decreasing is visible.

In the first part of the lower section, iron concentration profile is higher than in the middle stretch. The maximum recorded value from the whole Danube River appears at Danube-Bazias (km 1071, RO01) – 4.40 mg/l.

In the second part of the lower Danube, iron concentrations generally increase. Taking into account whole Danube River, here are the highest concentration of iron, increasing frequently over 1.00 mg/l. The highest c90 values from this sub-section (2.78 mg/l) is present at Danube-Silistra/Chiciu (km 375, BG05)

Iron concentrations for selected tributaries is shown in **Fig. 8.1.3.2a** and **8.1.3.2b**:

- for those located in the upper section, the Inn-Kirchdorf (D03) and, in a smaller extent, the Salzach-Laufen (D04) and Morava-Lanzhot (CZ01) present values above 2.00 mg/l;
- most of the tributaries located in middle stretch of the Danube are characterized by low Iron concentrations, only on the Tisza-Tiszasziget (H08) and the Sava-ds. Zupanja (HR08) two values exceed 2.00 mg/l;
- there is a change in the lower section, where three tributaries show quite high concentration levels, as follows:
    - the Russenski Lom-Basarbovo (BG08) – 6.59 and 6.86 mg/l;
    - the Arges-Conf. Danube (RO09) – 8.14 mg/l;
    - the Siret-Conf. Danube Sendreni (RO10) – with the maximum recorded value for tributaries - 18.73 mg/l.

The temporal trends for the Danube River are shown in **Fig. 8.1.3.3a** and **8.1.3.3b** for the Danube River and in **Fig. 8.1.3.4** for selected tributaries:

- from sites located in Danube River, only in Danube-Szob (rkm 1708, H03) there is an indication of increase;
- from tributaries, decreasing in period 1996-2000 is observable in Morava-Lanzhot (CZ01), Drava-Varazdin (HR03), Drava-Botovo (HR04), Arges (RO09) and Siret (RO10).

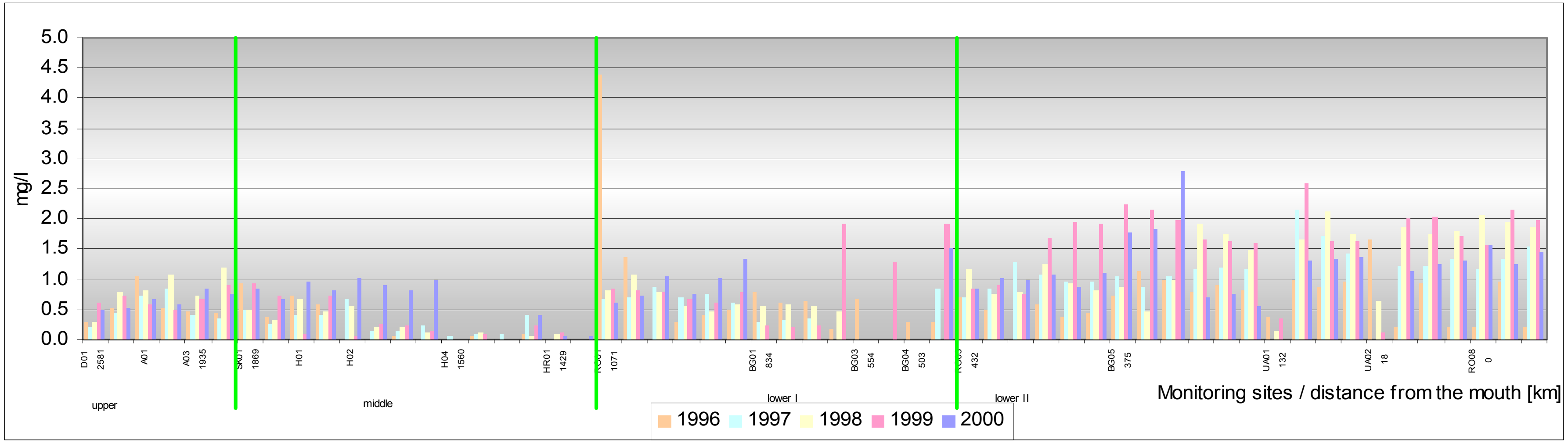

Fig. 8.1.3.1a: Spatial variation of Fe – Danube River

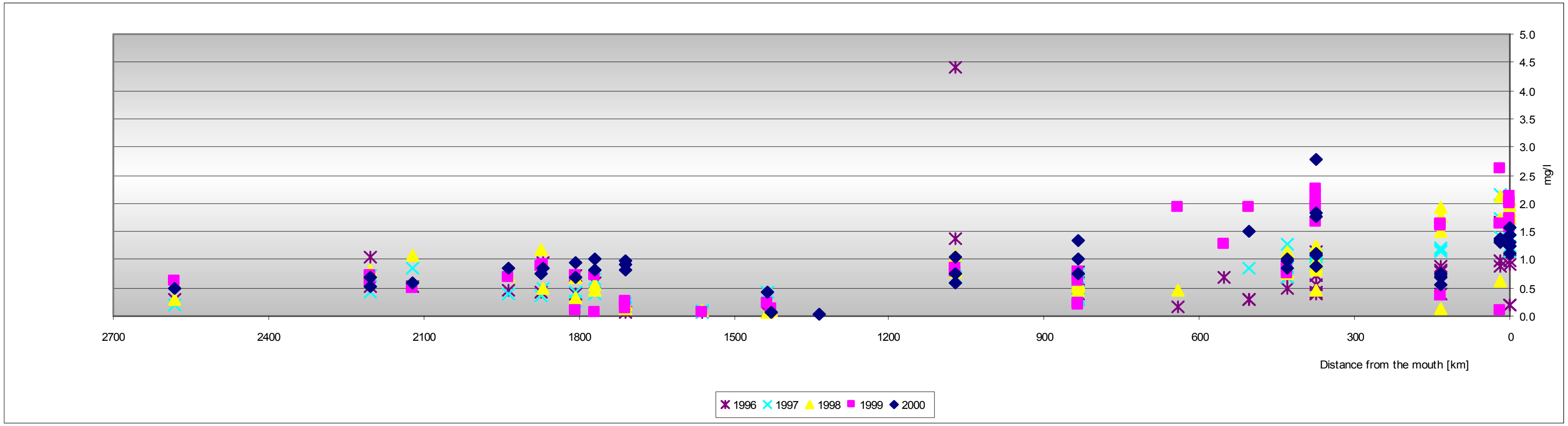

Fig. 8.1.3.1b: Spatial variation of Fe – Danube River

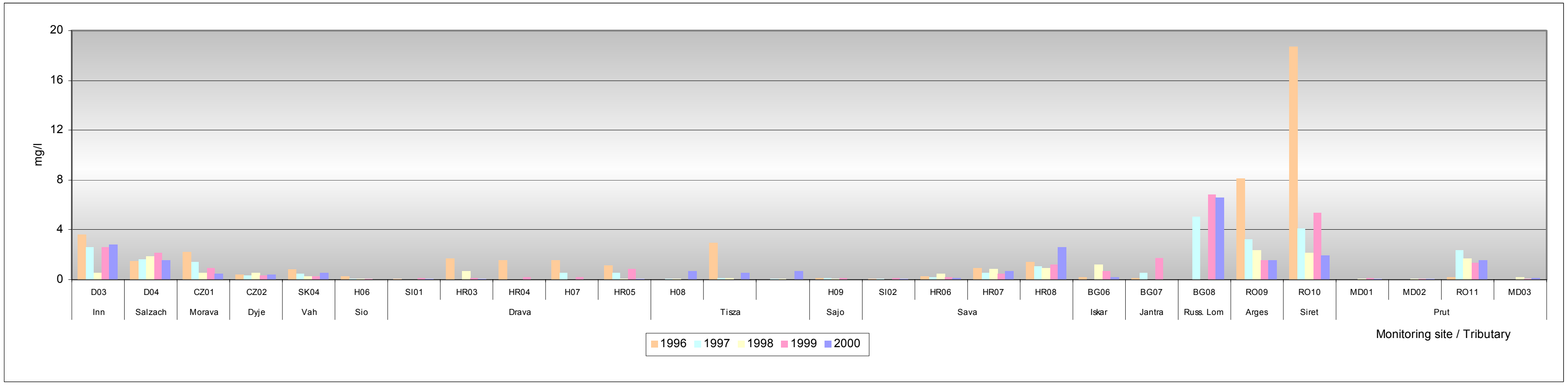

Fig. 8.1.3.2a: Spatial variation of Fe – Tributaries

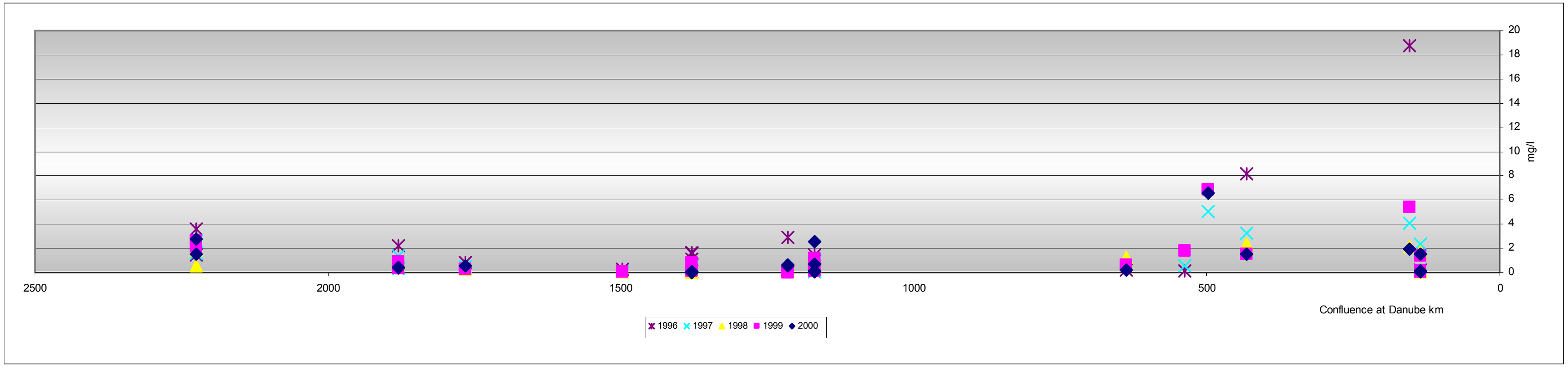

Fig. 8.1.3.2b: Spatial variation of Fe – Tributaries

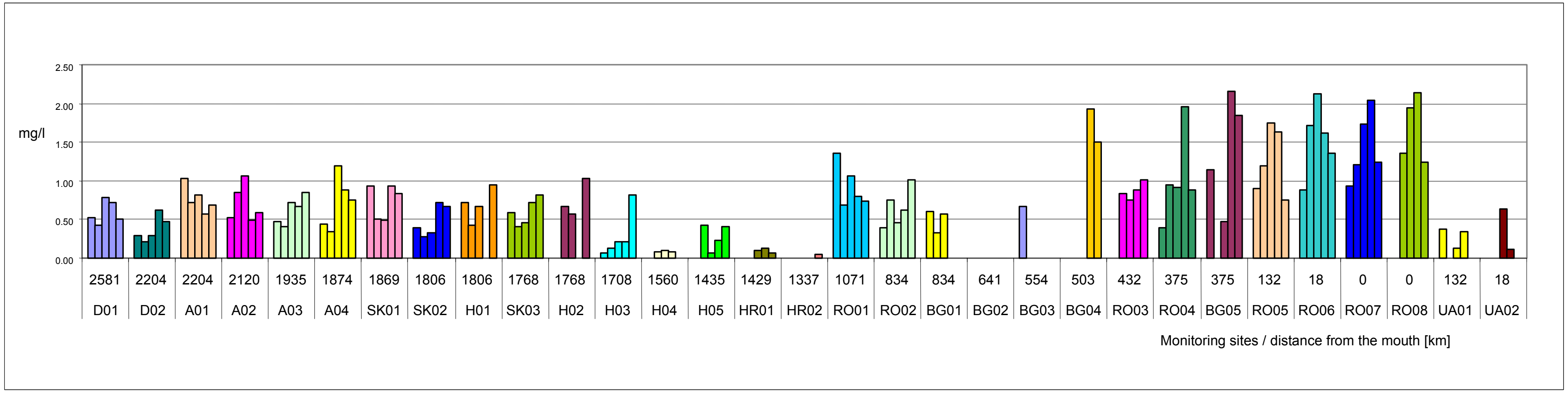

Fig. 8.1.3.3: Temporal trends of Fe – Danube River

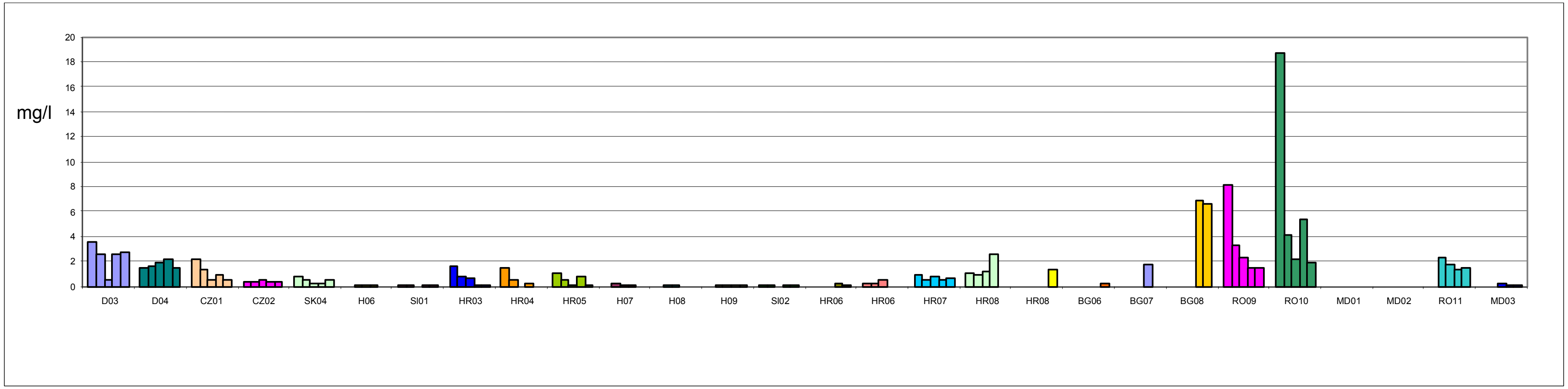

Fig. 8.1.3.4: Temporal trends of Fe – Tributaries

Manganese

For the Danube River itself, the spatial distribution of manganese concentrations is shown in **Fig. 8.1.3.5a** and **8.1.3.5b.**

In the upper section of the Danube, spatial distribution is relative uniform, with only one concentration value reaching 0.10 mg/l, at Danube-Wolfsthal (km 1874, A04).

In the middle stretch, spatial variation assessment depends on which data are taken into account: it results in a uniform spatial pattern in accordance to Slovak data (SK02 and SK03), but higher values in accordance to the Hungarian ones (H01 and H02). A significant decreasing of manganese values is visible from Danube-Szob (km 1708, H03) to Danube-Borovo (km 1337, HR02). Taking into account Hungarian data, in the section between rkm 1800 – 1700 are the highest manganase values along the Danube River.

The first part of the lower Danube shows a scattered profile of manganese concentrations: from Danube-Bazias (km 1071, RO01) to Danube-us. Iskar Bajkal (km 641, BG02), nearly half of the values are equal to or exceed the 0.10 mg/l level. The next two monitoring sites in this sub-section, Danube-ds. Svishtov (km 554, BG03) and Danube-us. Russe (km 503, BG04), indicate much lower values.

The second part of the lower Danube section is characterized by a relatively uniform distribution, with few exceptions. Thus, the maximum manganese value (0.27 mg/l in 2000) is recorded at Danube-us. Arges (km 432, RO03); also several values along this stretch exceed the 0.20 mg/l level.

The spatial distribution of manganese c90 values on selected tributaries is shown in **Fig. 8.1.3.6a** and **8.1.3.6b**. Regarding those located in the upper Danube, the Morava-Lanzhot (CZ01) and Dyje-Pohansko (CZ02) present concentration above 0.20 mg/l. In the middle stretch, only the Tisza-Tiszasziget (H08) shows rather high values, reaching 0.87 mg/l in 1996. In the lower section, majority of tributaries is characterized by high values, but some of them exceed 1.00 mg/l: 1.02 mg/l on the Iskar-Orechovitza (BG06), 1.01 and 1.26 mg/l on the Siret-Conf. Danube Sendreni (RO10).

The temporal trends of manganese concentrations are shown in **Fig. 8.1.3.7** for the Danube River and in **Fig. 8.1.3.8** for selected tributaries:

- in the upper Danube, temporal pattern is without significant changes, also variation between years is rather low there;
- in the middle Danube, increase of iron in Danube-Szob (rkm 1708, H03) is in coincidence with increse of manganese;
- in the lower Danube, an increasing is observed in Danube-Bazias (km 1071, RO01), and decrease in Danube-Novo Selo/Pristol /rkm 834, BG01);
- for two tributaries located in the upper Danube, the Morava-Lanzhot (CZ01) and Dyje-Pohansko, the temporal trends are opposite: decreasing for the first one and increasing in the same sense for the second. Also relative decreasing trends are valid for tributaries located in the middle and lower Danube: the Vah-Komarno (SK04), Arges-Conf. Danube (RO09) and the Prut-Conf. Danube Giurgiulesti (RO11).

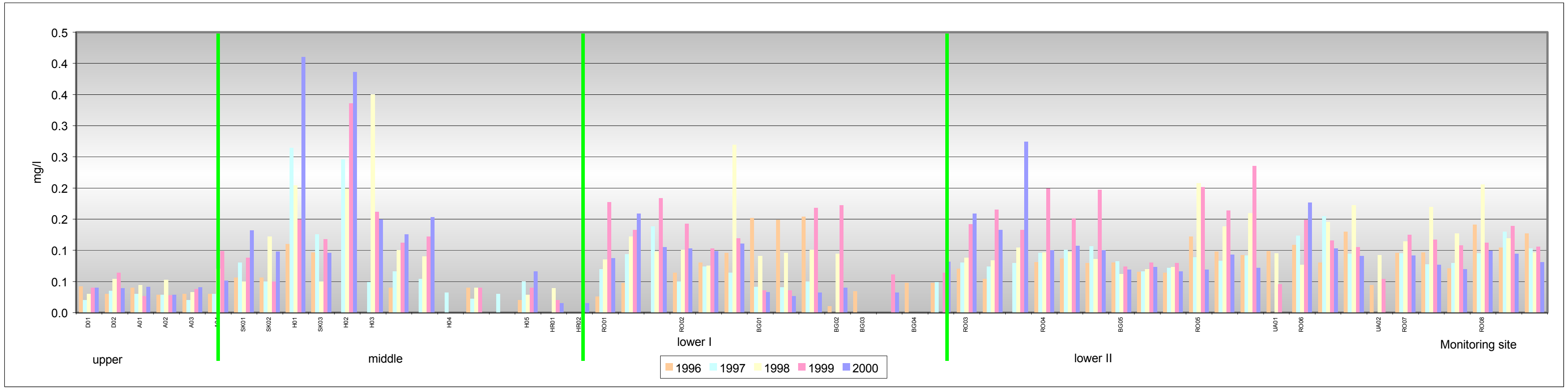

Fig. 8.1.3.5a: Spatial variation of Mn – Danube River

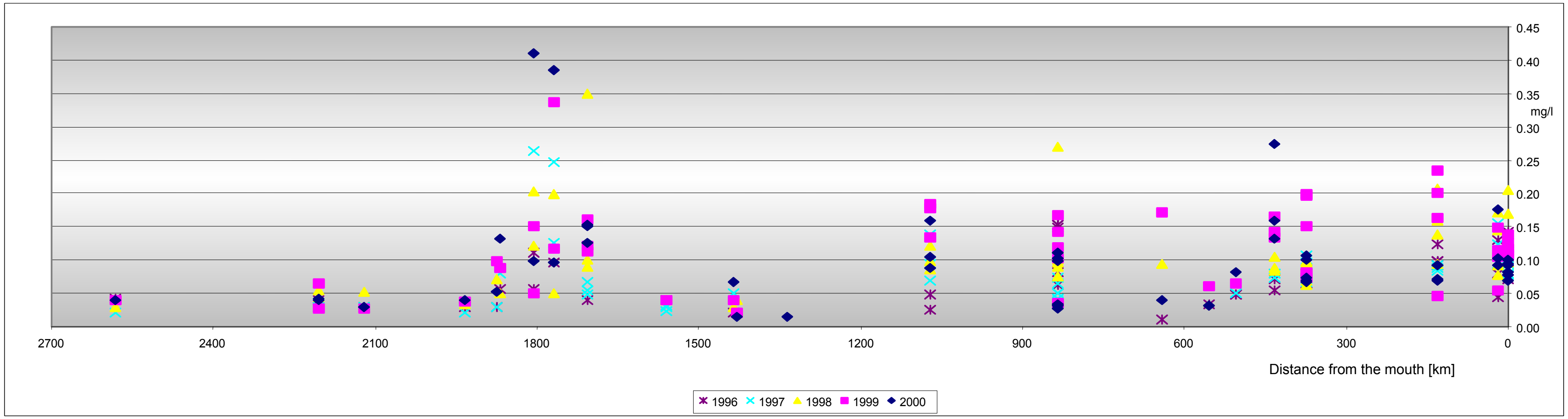

Fig. 8.1.3.5b: Spatial variation of Mn – Danube River

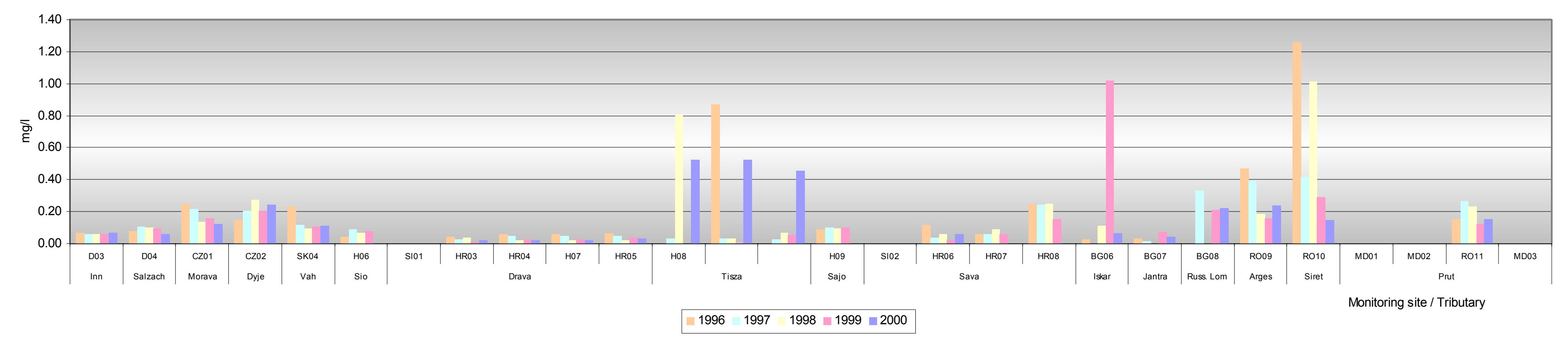

Fig. 8.1.3.6a: Spatial variation of Mn – Tributaries

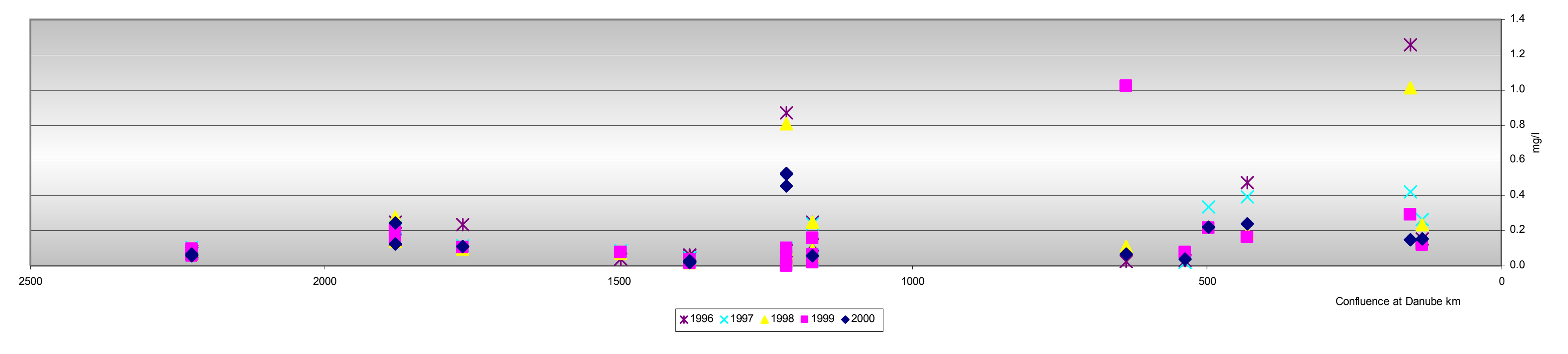

Fig. 8.1.3.6b: Spatial variation of Mn – Tributaries

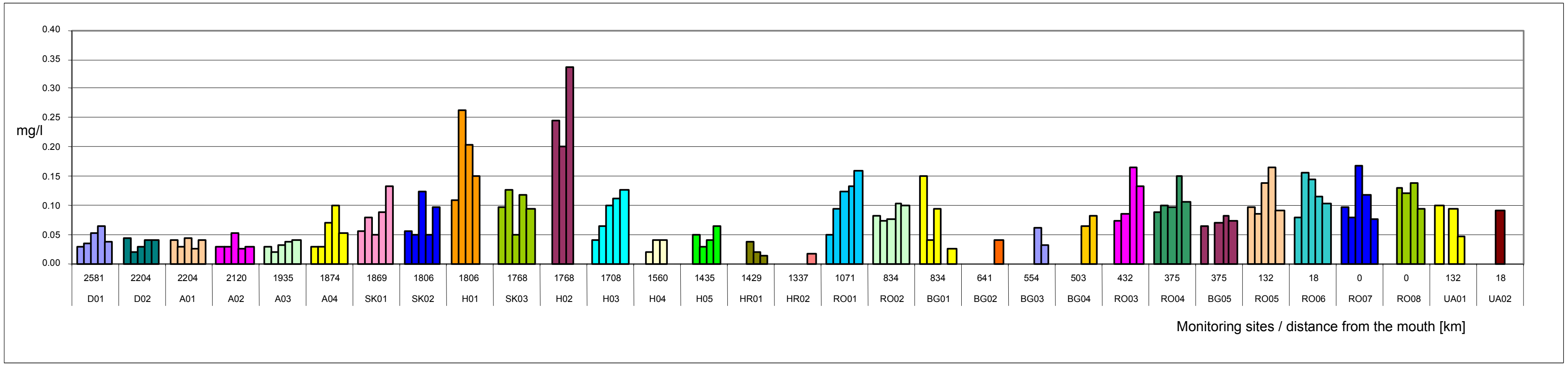

Fig. 8.1.3.7: Temporal trends of Mn – Danube River

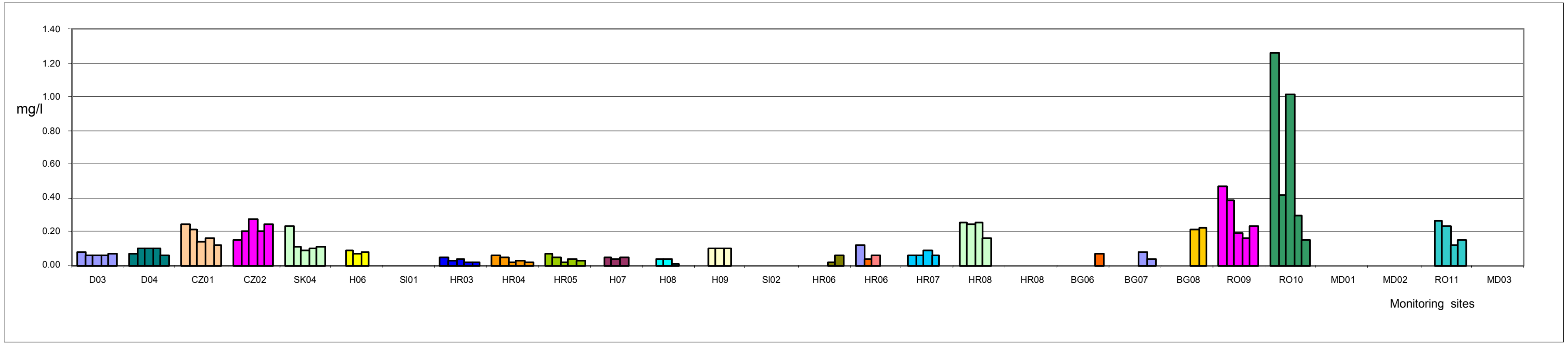

Fig. 8.1.3.8: Temporal trends of Mn – Tributaries

Arsenic, cadmium, chromium, copper, lead, mercury, nickel and zinc in unfiltered water samples (total forms)

The heavy metals like arsenic, cadmium, chromium, copper, lead, mercury, nickel and zinc are of a particular concern to surface water systems. The Water Quality Classification for DRB set up limit values for five classes for total forms and only guidelines values for dissolved forms at the border between class II and class III.

For heavy metals in unfiltered water samples (total forms) data are available for the entire time period 1996 – 2000 and for dissolved forms during 1998-2000 only. In addition, data on dissolved forms are available only for part of river basin.

Arsenic

Arsenic can be found naturally in small concentrations. It occurs in soil and minerals and it may enter air, water and land by wind-blown dust and water run-off. Arsenic is a component that is extremely hard to convert to water-soluble or volatile products. Because arsenic is naturally a quite mobile component, it means that large concentrations are not likely to appear on one specific site. However, the negative fact is that arsenic pollution becomes a wider issue because it easily spreads. In the aquatic systems, arsenic ends up through effluents from industrial production of copper, lead and zinc and also through insecticide applications on land. Although arsenic may be found in surface water, ground water is the main source of arsenic in water.

The distribution of monitoring sites according to the Classification System in the DRB for arsenic is shown in **Fig. 8.1.3.9**:

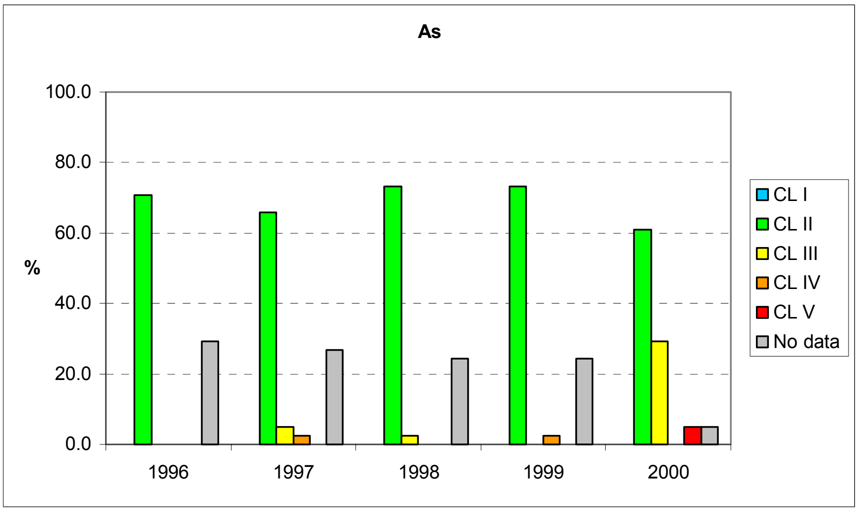

Fig. 8.1.3.9: Distribution of monitoring sites (%) according to the Quality Classification System in the DRB for **As**

Based on data reported from 41 monitoring sites (out of the assessment is 62 monitoring sites from Phase I List of Monitoring Sites, in which no measurements had been done in 1996-2000), it can be concluded that most of the monitoring sites are within Class II (61.0 % – 73.2 %). Other classes are represented in very small percentages, with an exeption 30 % of sites in Class III in 2000.

The spatial pattern for arsenic concentrations along the Danube River is shown in **Fig. 8.1.3.10a** and **8.1.3.10b** and in **Fig. 8.1.3.11a** and **8.1.3.11b** for selected tributaries.

In the upper section, arsenic is detectable starting from Danube-Jochenstein (km 2204, A01), but no monitoring site from this section has arsenic concentration exceeding the target value (5 µg/l).

In the middle section, an increasing spatial pattern is present from Danube-Bratislava (km 1869, SK01) to Danube-Szob (km 1708, H03), followed by a decreasing to Danube-Borovo (km 1337, HR02); along this stretch no value is above the target limit as well.

Lower section is characterized mainly by lack of reported data for arsenic. However, the existing values are higher than in previous river sections, the maximum concentration (11.02 µg/l) being recorded at Danube-us. Iskar – Bajkal (km 641, BG02). Along the entire part of lower Danube 9 values exceed the target value set up for arsenic.

Selected tributaries present 8 concentration values exceeding the target value:

- the Salzach-Laufen (D04) – 8.00 µg/l (in 2000);
- the Vah-komarno (SK04) – 5.17 µg/l (in 2000);
- the Sio-Szekszard-Palank (H06)– 90 %-iles during the whole period exceeded target value and were in a range from 5.24 - 12.32 µg/l;
- the Iskar-Orechovitza (BG06) – 79.36 µg/l (in 2000);
- the Russenski Lom-Basarbovo (BG08) – 10.00 µg/l (in 2000).

The temporal trends for the Danube River are illustrated in **Fig. 8.1.3.12a** and **8.1.3.12b** and in **Fig. 8.1.3.13** for selected tributaries:

- for upper Danube, Austrian sites show slight increasing tendency;
- for middle Danube, most of the sites show a decreasing trend from 1997 to 2000;
- for entire lower Danube, even if the missing data cannot give a complete picture, it can be seen that all the high values are specific to year 2000;
- from tributaries, a slight increasing was in Dyje-Pohansko (CZ02) and Tisza-Tiszasziget (H08); a decreasing trend in the same sense in Inn-Kirchdorf (D01) and Sajo-Sajopuspoki (H09).

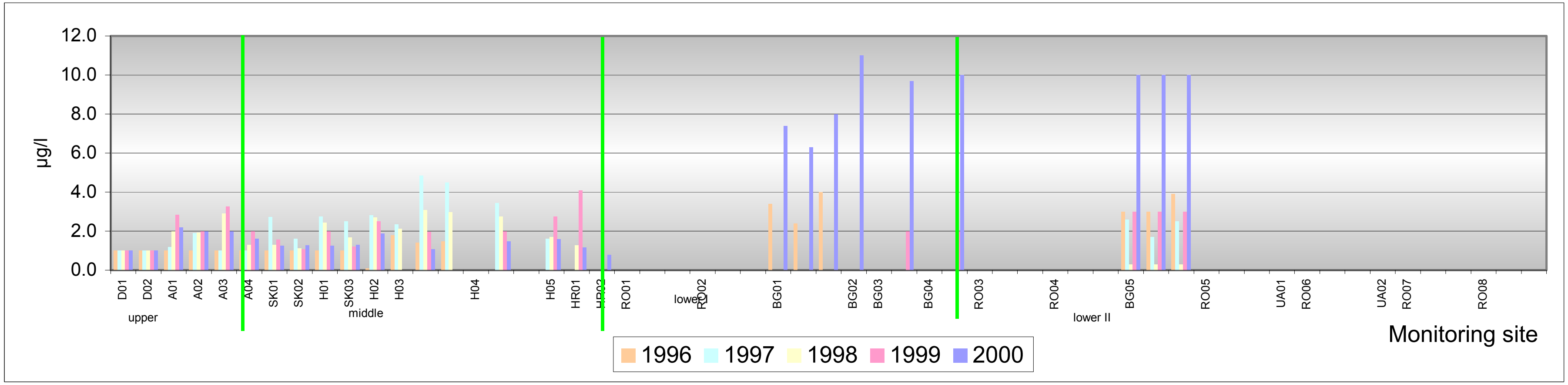

Fig. 8.1.3.10a: Spatial variation of As – Danube River

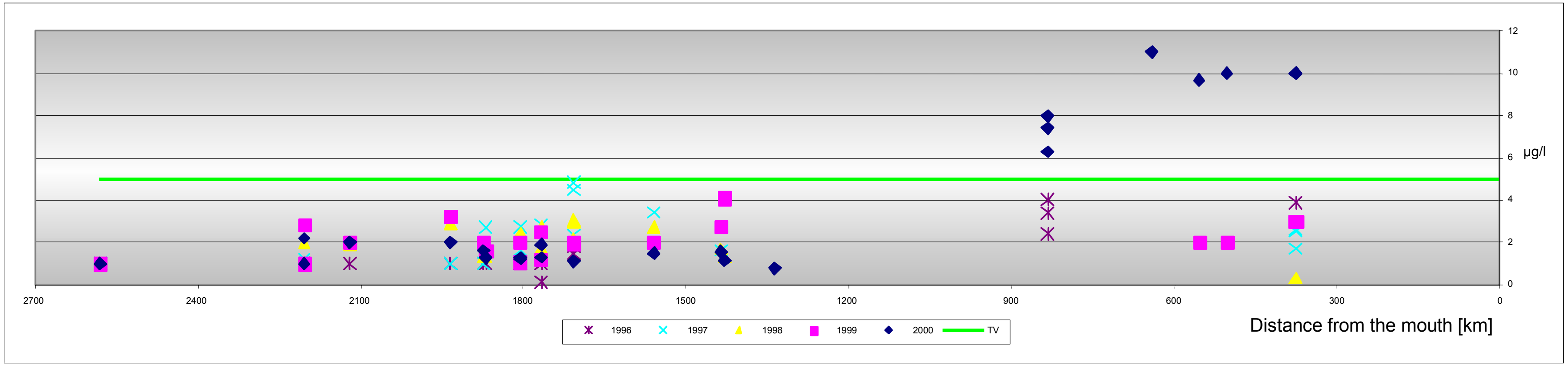

Fig. 8.1.3.10b: Spatial variation of As – Danube River

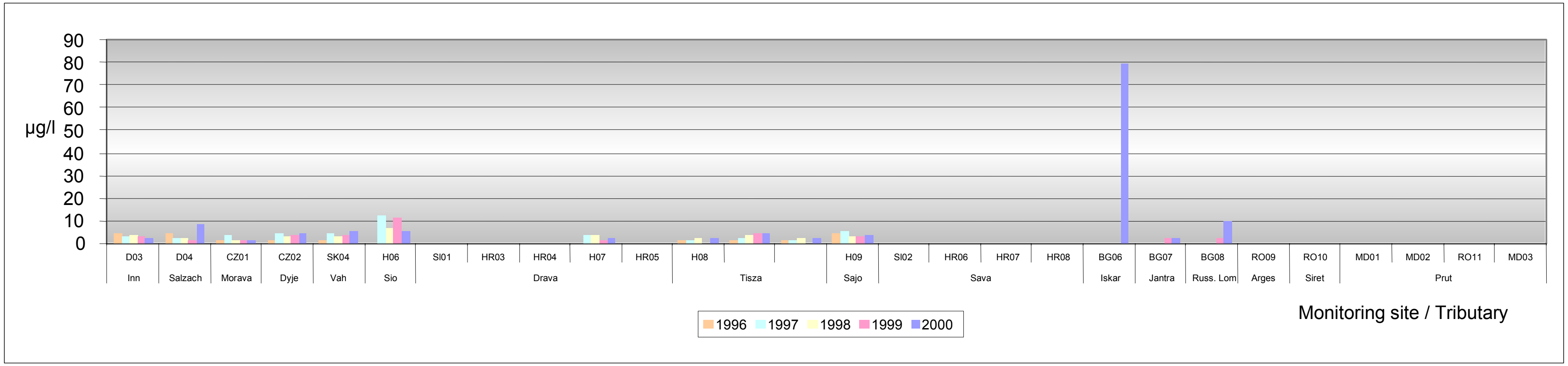

Fig. 8.1.3.11a: Spatial variation of As – Tributaries

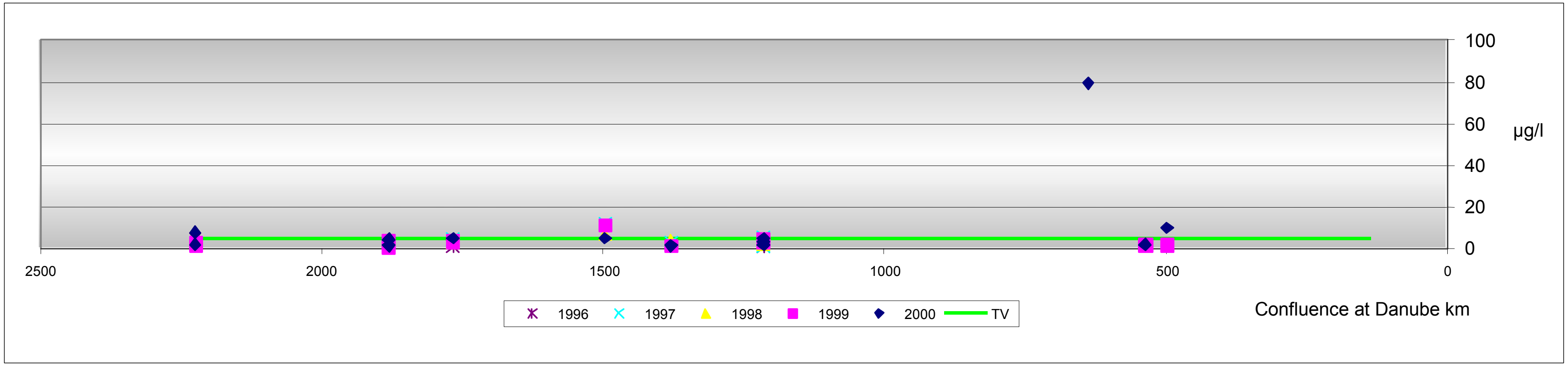

Fig. 8.1.3.11b: Spatial variation of As – Tributaries

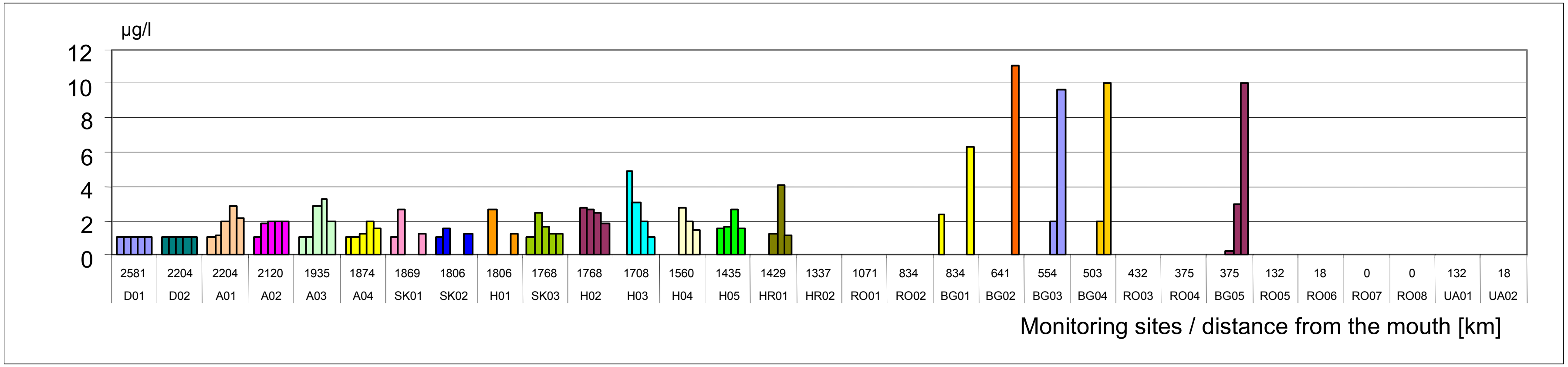

Fig. 8.1.3.12: Temporal trends of As – Danube River

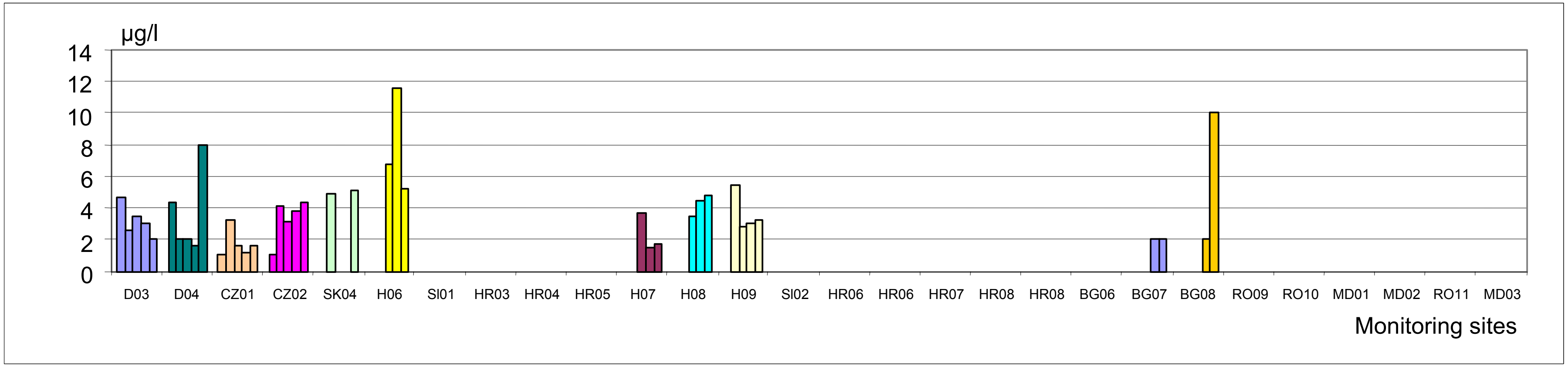

Fig. 8.1.3.13: Temporal trends of As – Tributaries

Cadmium

Cadmium is one of the most hazardous heavy metal pollutants. Naturally, it can mainly be found in the earth's crust and it always occurs in combination with zinc. Cadmium enters the environment mainly through the ground, because it is found in manure and pesticides. Cadmium is released into rivers through weathering of rocks and human activities, such as manufacturing. An important source of cadmium emission is also the production and applying of phosphate fertilizers. In natural waters, unaffected by anthropogenic impacts, the cadmium concentration is less than 1 µg/l (*The Dobris Assessment, 1991*).

The distribution of monitoring sites according to the Classification System in the DRB for cadmium is shown in **Fig. 8.1.3.14**:

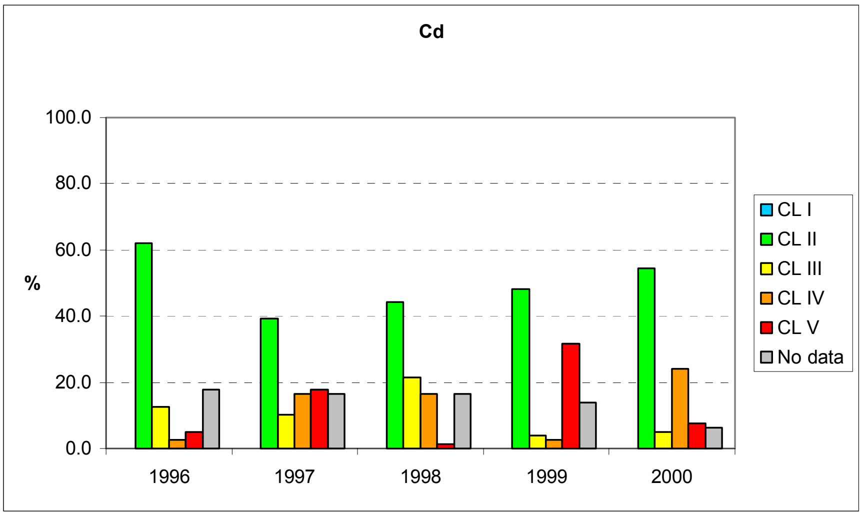

Fig. 8.1.3.14: Distribution of monitoring sites (%) according to the Quality Classification System in the DRB for **Cd**

Based on data reported from 79 monitoring sites (out of the assessment is 24 monitoring sites from Phase I List of Monitoring Sites, in which no measurements had been done in 1996-2000), it can be concluded that:

- most of monitoring sites belongs to Class II (39.2 % - 62.0%) and this percentage increases from 1997 to 2000
- percetage of sites corresponding to Class III decreases from 1998 to 2000;
- distribution corresponding to Class IV is uneven during the five years period;
- in 1999 more than 30% of the monitoring points are within Class V, but this figure decreased in 2000.

The spatial distribution of cadmium concentrations is shown in **Fig. 8.1.3.15a** and **8.1.3.15b** for the Danube River and in for tributaries.

In the upper section, level of cadmium is low at all monitoring points; the maximum value recorded on this stretch is 0.66 µg/l at Danube-Abwinden-Asten (km 2120, A02), but no value is above the target limit for cadmium (1 µg/l).

In the middle section, between Danube-Medve/Medvedov (km 1806, H01) and Danube-Szob (km 1708, H03), 9 cadmium c90 values exceed the target value. Downstream to Danube-Szob, cadmium level is again very low.

First part of the lower section is characterized by high values from Danube-Bazias (km 1071, RO01) to Danube-Pristol/Novo Selo (km 834, RO02), but also with very high variability among the years. Cadmium c90 values reach up to 16.81 µg/l and 17.70 µg/l there according the Romanian data. On the other hand, at the cross section from km 834, the Bulgarian data show undetectable cadmium concentrations. For the rest of the stretch, excepting one high value of 8.00 µg/l, recorded at Danube-us. Russe (km 503, BG04), cadmium presence is also undetectable. From the reported data, only three values along this stretch are below the target value.

The second part of the lower Danube section shows even higher cadmium concentrations than the first one: thus, 76 values are above the target limit. The highest c90 value for this stretch, which is also the highest value for the entire Danube - 29.10 µg/l - was recorded at Danube-us. Arges (km 432, RO03) in 1997.

The spatial variation for selected tributaries, shown in **Fig. 8.1.3.16a** and **8.1.3.16b**. It is seen that 34 values exceeded the target value. It is also visible that tributaries at the lower part of river basin are characterised by much higher cadmium values than those in the upper and middle section. Going to more details, it can be concluded that:

- in the upper section, only on the Dyje-Pohansko (CZ02) concentrations slightly exceed the target value;
- in the middle Danube, in Sava-ds. Zupanja (HR08) and Drava River excepting Drava-Ormoz (SL01), cadmium concentrations are above 1µg/l;
- as was already indicated, the situation is much worse regarding the tributaries from the lower Danube, where actually all of them are characterized by very high cadmium concentrations, leading to the following c90 values:
    - the Iskar-Orechovitza (BG06) – 10.00 µg/l in 1996;
    - the Jantra-Karantzi (BG07) – 9.10 µg/l in 1996;
    - the Russenski Lom-Basarbovo (BG08) – 8.00 µg/l in 2000;
    - the Arges-Conf. Danube (RO09) – 24.18 µg/l (1996), 9.25 µg/l (1997) and 8.96 µg/l (1999);
    - the Siret-Conf. Danube Sendreni (RO10) – 8.46 µg/l in 1999);
    - the Prut-Conf. Danube Giurgiulesti (RO11) – 8.36 µg/l (in 1998).

The temporal trend for cadmium concentrations is shown in **Fig. 8.1.3.17** for the Danube River and in **Fig. 8.1.3.18** for selected tributaries:

- for the upper Danube, no systematic temporal trend is visible;
- a slight decreasing tendency from 1997 to 2000 is valid for most of the sites located in the middle Danube from Danube Medve/Medvedov (rkm 1806, H01) to Danube-Szob (rkm 1708, H03);
- in the lower Danube, most of monitoring sites are characterized by high values recorded in 1997 and 1999, significant decrease is observed in 2000;
- from selected tributaries, only several monitoring sites indicate temporal changes: decreasing is observed in Drava River, Jantra (BG07), Arges (RO09) and Prut-Conf. Danube-Giurgiulesti (RO11).

JDS results from analysis of cadmium (0.2 – 0.8 µg/l in total sample) indicated that Danube River can be regarded as unpolluted by this metal. However, TNMN results does not confirm this finding, great differences are especially in the lower part of the Danube River.

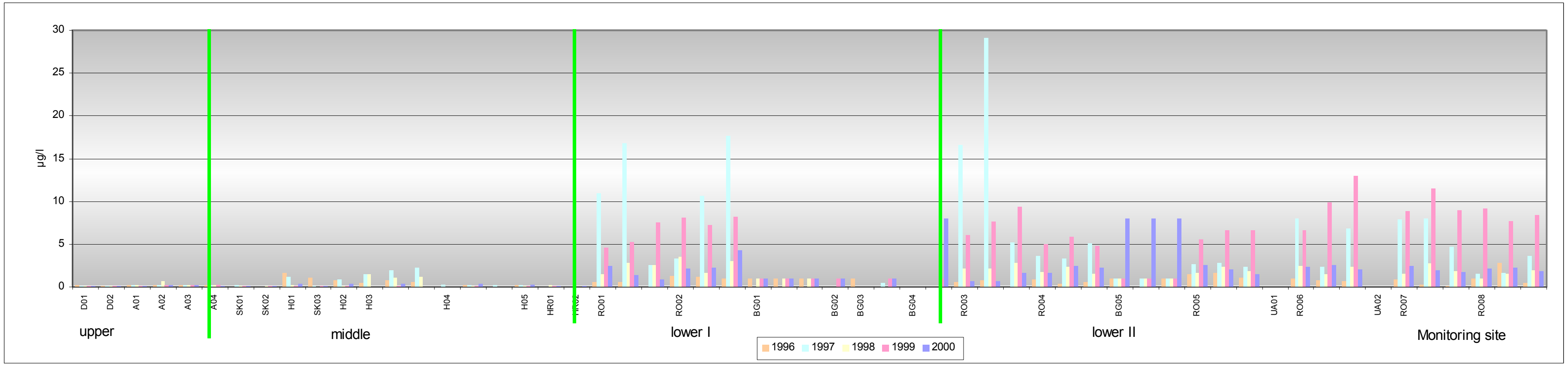

Fig. 8.1.3.15a: Spatial variation of Cd – Danube River

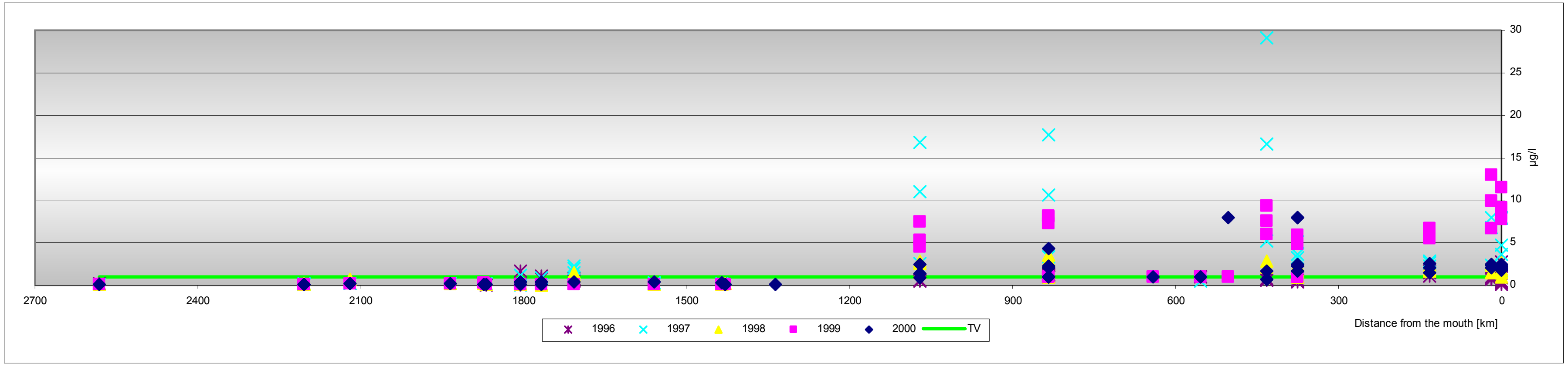

Fig. 8.1.3.15b: Spatial variation of Cd – Danube River

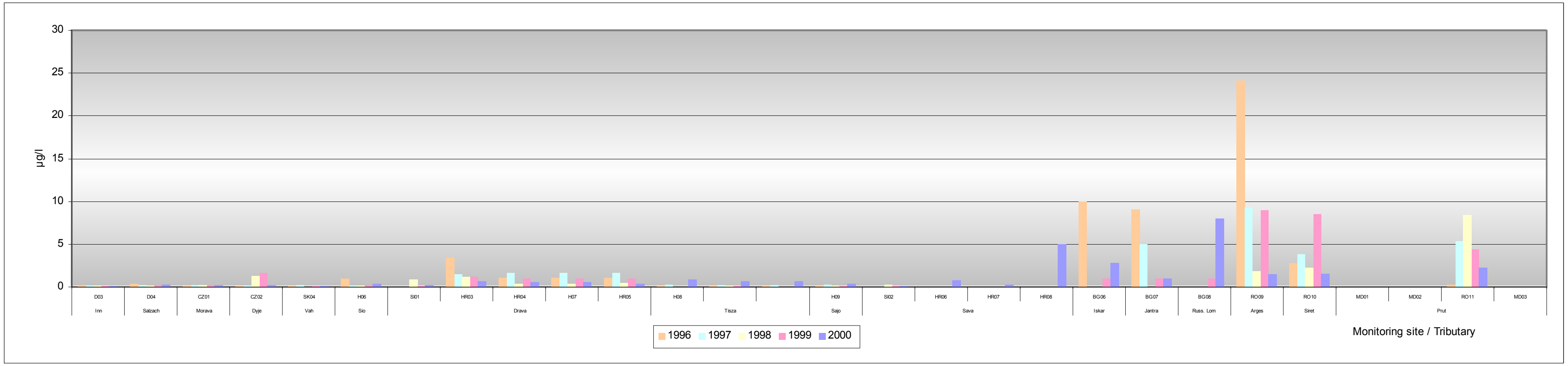

Fig. 8.1.3.16a: Spatial variation of Cd – Tributaries

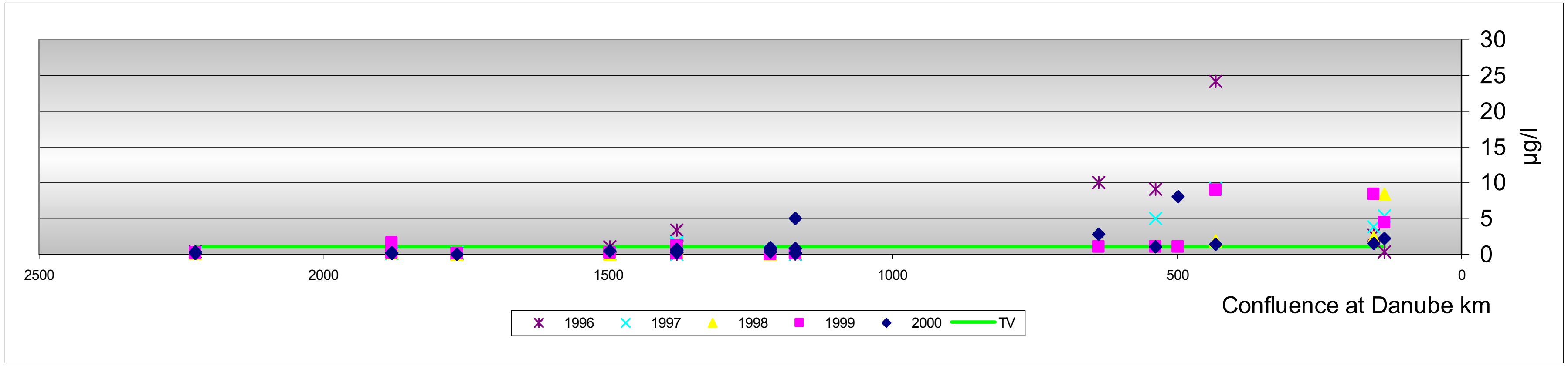

Fig. 8.1.3.16b: Spatial variation of Cd – Tributaries

Note: In HR08 (2000) the value in the graph represents limit of detection that is higher than the target value.

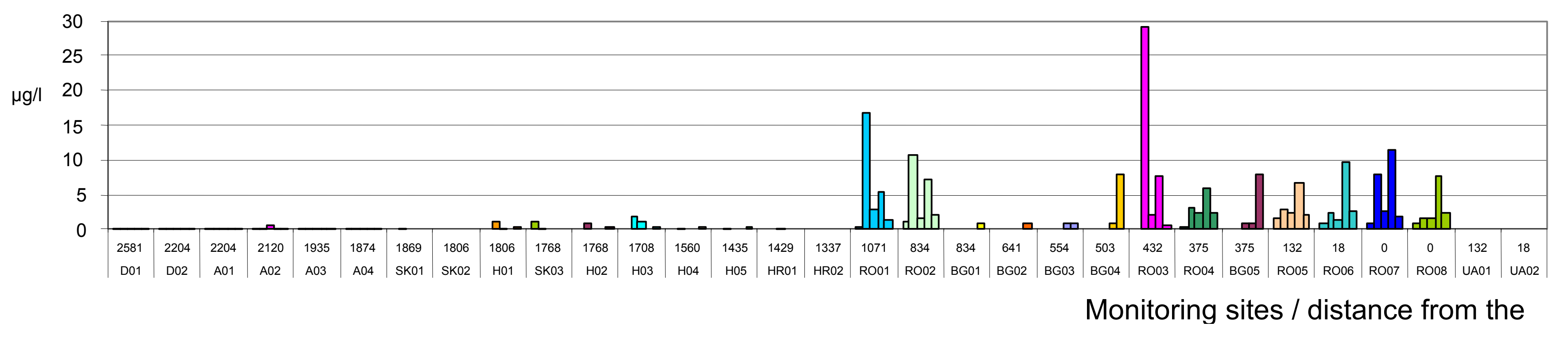

Fig. 8.1.3.17: Temporal trends of Cd – Danube River

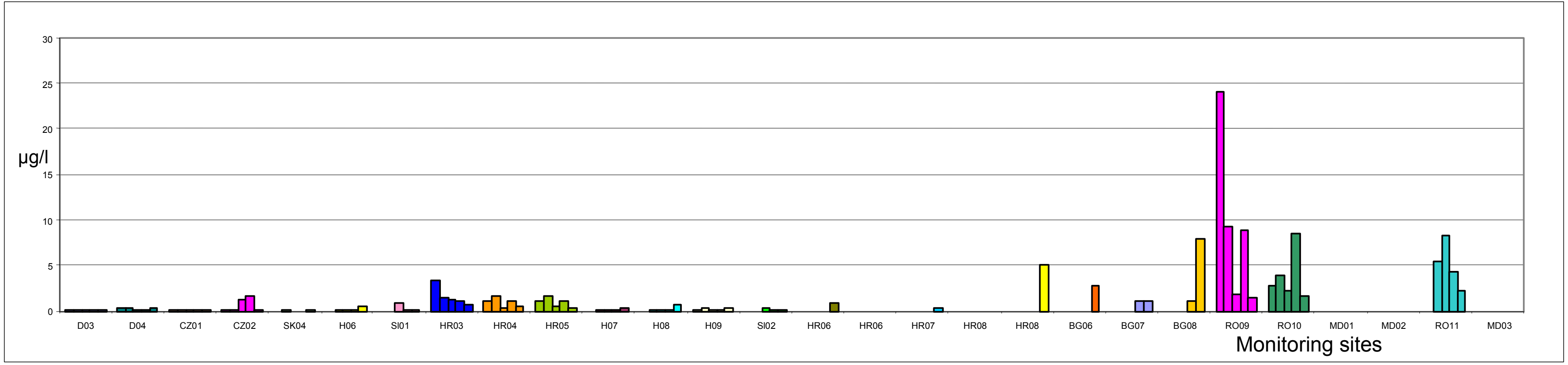

Fig. 8.1.3.18: Temporal trends of Cd – Tributaries

Chromium

There are two kinds of chromium with different effects upon environment: chromium (III) and chromium (VI). If the first one is an essential nutrient for humans, the second one is dangerous to health. Both forms can enter the environment through both natural sources and human activities. The main activities that increase the chromium (III) content are steel and leather manufacturing; for chromium (VI) chemical, textile manufacturing, electro-painting and other industrial applications of this form. In water, chromium is adsorbed on sediment and becomes immobile. That is why only a small part of chromium that ends up in water eventually dissolves.

In TNMN Programme, chromium is measured as total chromium (III + VI).

The distribution of monitoring sites according to the Classification System in the DRB for chromium is shown in **Fig. 8.1.3.19**.

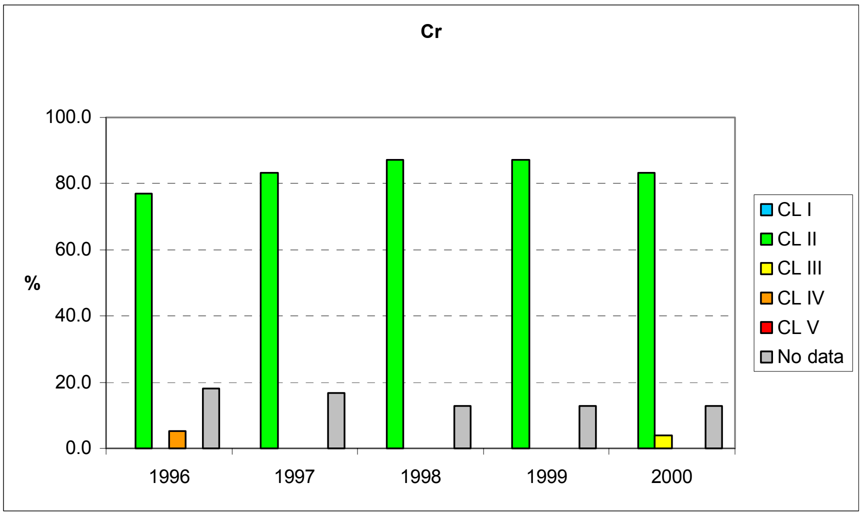

Fig. 8.1.3.19: Distribution of monitoring sites (%) according to the Quality Classification System in the DRB for **Cr**

Based on data reported from 78 monitoring sites (out of the assessment is 25 monitoring sites from Phase I List of Monitoring Sites, in which no measurements had been done in 1996-2000), the following remarks can be done:

- during 1997 – 2000, more than 80% of the monitoring points belong to Class II;
- very few monitoring sites are within Class III and IV (less than 6 %).

The spatial pattern for chromium concentrations along the Danube River is shown in **Fig. 8.1.3.20a** and **8.1.3.20b**:

Excepting the first and the last monitoring site from the upper section - Danube-Neu-Ulm (km 2581, D01) and Danube-Wolfsthal (km 1874, A04) - where chromium is detectable in very low concentrations, all the other monitoring sites reported data below the declared detection limit.

In the middle section, even though the spatial pattern shows significantly higher values according to the Hungarian data, no value from this stretch exceeds the target value for chromium (50 µg/l). Maximum values are around 20 µg/l there.

In the first part of the lower Danube, an increasing is observed between Danube-Bazias (km 1071, RO01) and Danube-Pristol/Novo Selo (km 834, RO02), followed by a decreasing profile down to Danube-us. Russe (km 503, BG04). Along this part of the river, no value is above the target limit.

In the second part of the lower section, chromium concentrations increase from Danube-Chiciu/Silistra (km 375, RO04) down to the Danube Delta. Three values exceed the quality target there: 82.00 µg/l at Danube-us. Arges (km 432, RO03), 79.45 µg/l at Danube-Sulina/ Sulina arm (km 0, RO07) and 97.00 at Danube-Sf. Gheorghe/Sf. Gheorghe arm (km 0, RO08), all characterising year 1996.

The spatial distribution of chromium concentrations for selected tributaries is shown in **Fig. 8.1.3.21a** and **8.1.3.21b**: even if higher values appear on tributaries located in the lower section of the Danube - the Arges-Conf. Danube (RO09), the Siret-Conf. Danube Sendreni (RO10) and Prut-Conf. Danube Giurgiulesti (RO11) - no chromium concentration is above the target limit.

The temporal trend for chromium is shown in **Fig. 8.1.3.22** for the Danube River and in **Fig. 8.1.3.23** for selected tributaries:

- in the upper and partially in the middle Danube, the general trend is a relative stationary state during the studied years; however, a slight decreasing tendency from 1996 to 2000 can be mentioned at Danube-Neu-Ulm (km 2581, D01);
- Hungarian sites located in the middle Danube, are characterized by higher chromium concentration values in 1999 and 2000;
- in the lower Danube, a decreasing decreasing tendency from 1998 to 2000 in Danube-Bazias (km 1071, RO01) and Danube-Sulina-Sulina arm (km 0, RO07) is observed;
- from tributaries in the upper Danube, in Morava-Lanzhot (CZ01) and Dyje-Pohansko (CZ02), a slight decreasing trend from 1996 to 2000 is present;
- a relatively common decreasing trend is visible at three monitoring sites located on the Drava tributary: the Drava-Varazdin (HR03), Drava-Botovo (HR04) and Drava-D. Miholjac (HR05);
- for the Arges-Conf. Danube (RO09), Siret (RO10) and Prut-Conf.Danube-Giurgiulest (RO11) also a decreasing tendency is observed.

In the frame of JDS maximum concentration of chromium was 7 µg/l. This value was exceeded frequently inTNMN, even reaching values higher by one order.

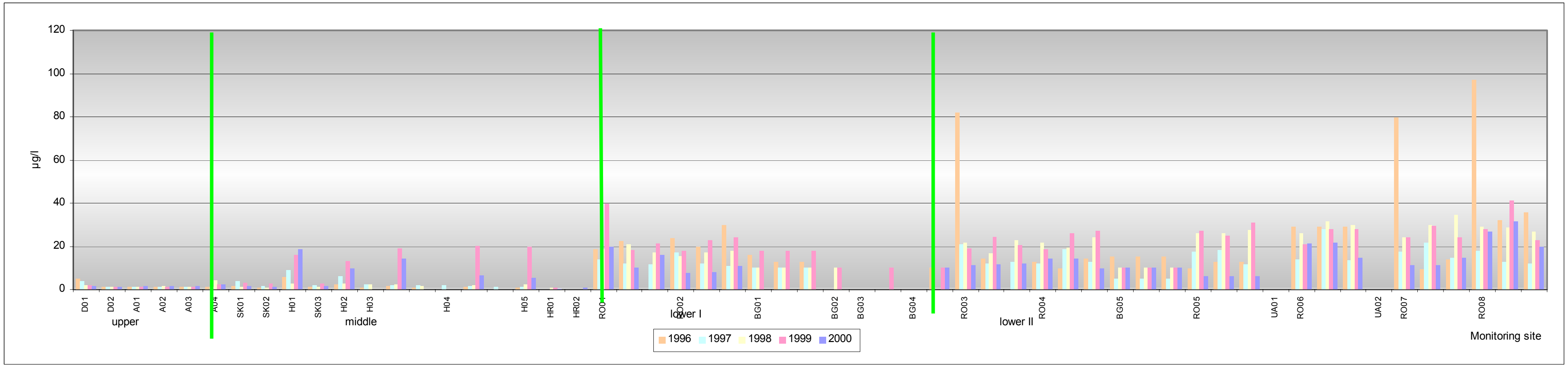

Fig. 8.1.3.20a: Spatial variation of Cr – Danube River

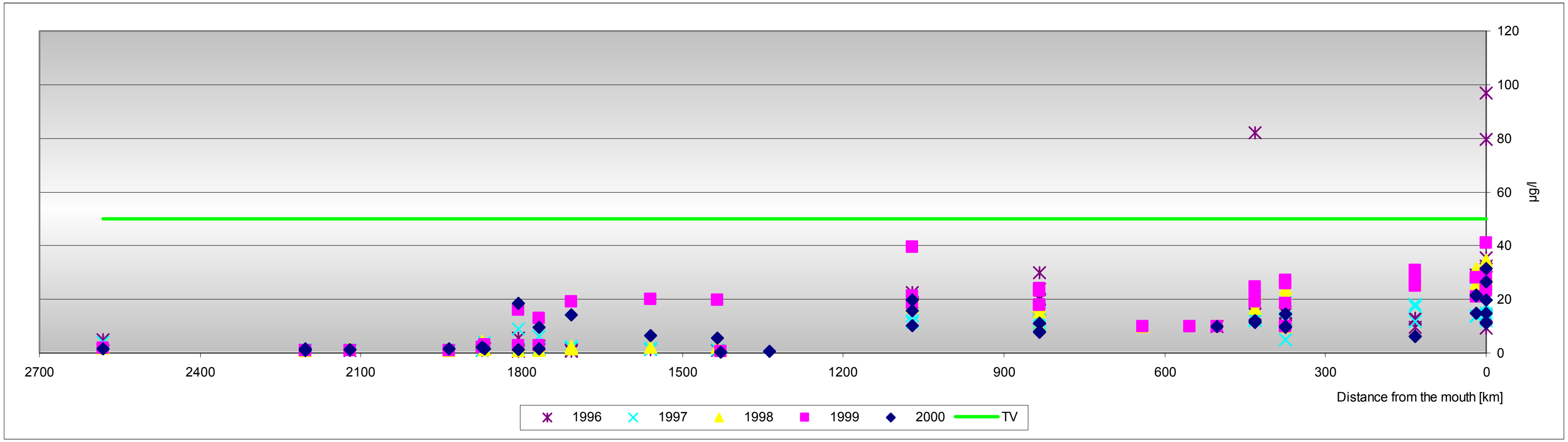

Fig. 8.1.3.20b: Spatial variation of Cr – Danube River

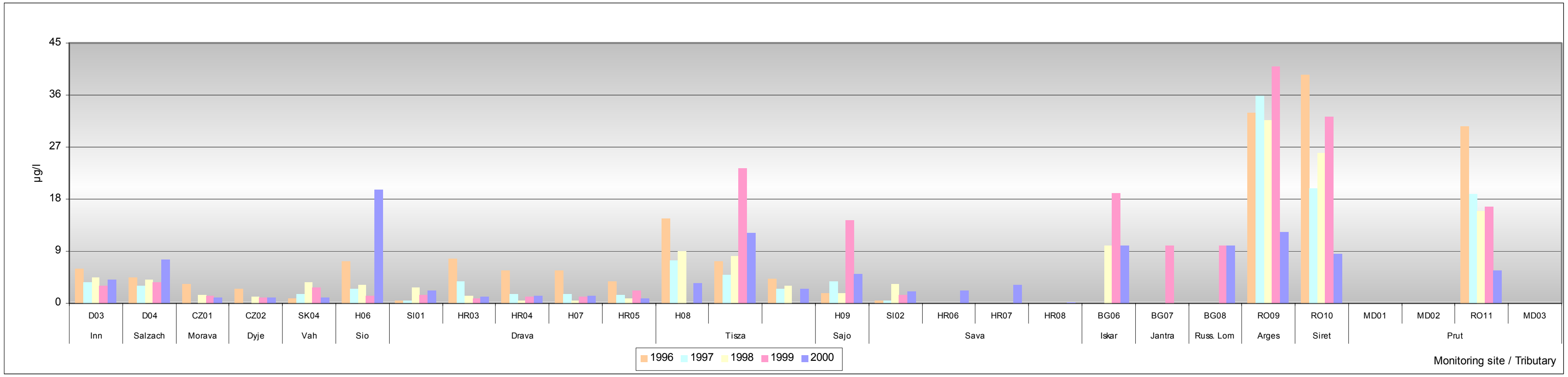

Fig. 8.1.3.21a: Spatial variation of Cr – Tributaries

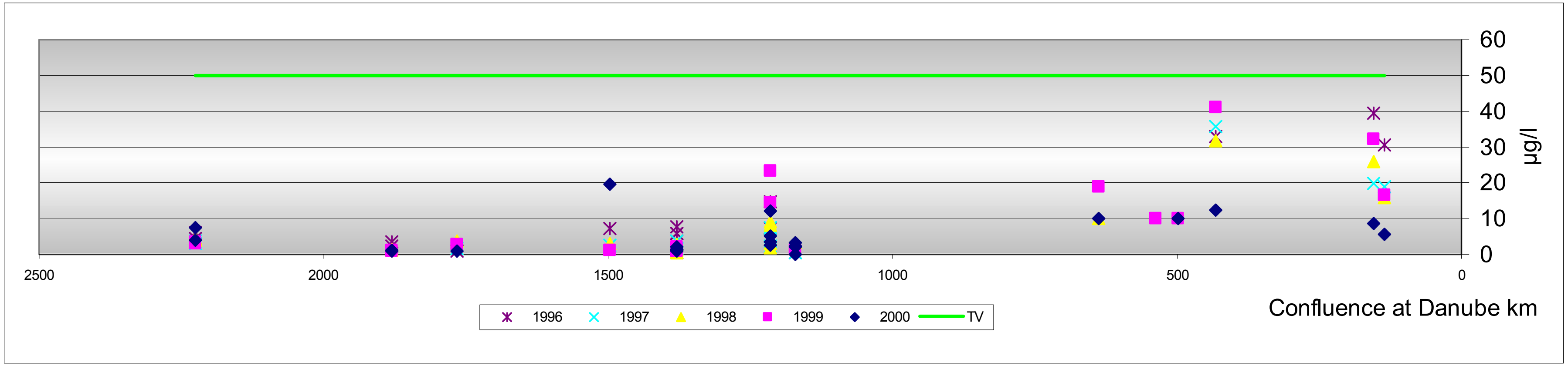

Fig. 8.1.3.21b: Spatial variation of Cr – Tributaries

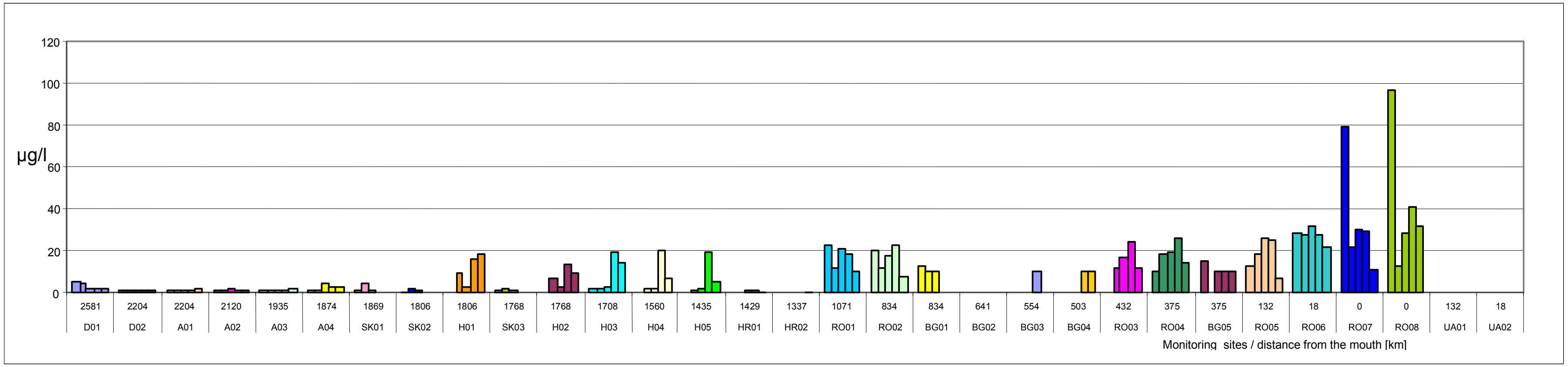

Fig. 8.1.3.22: Temporal trends of Cr – Danube River

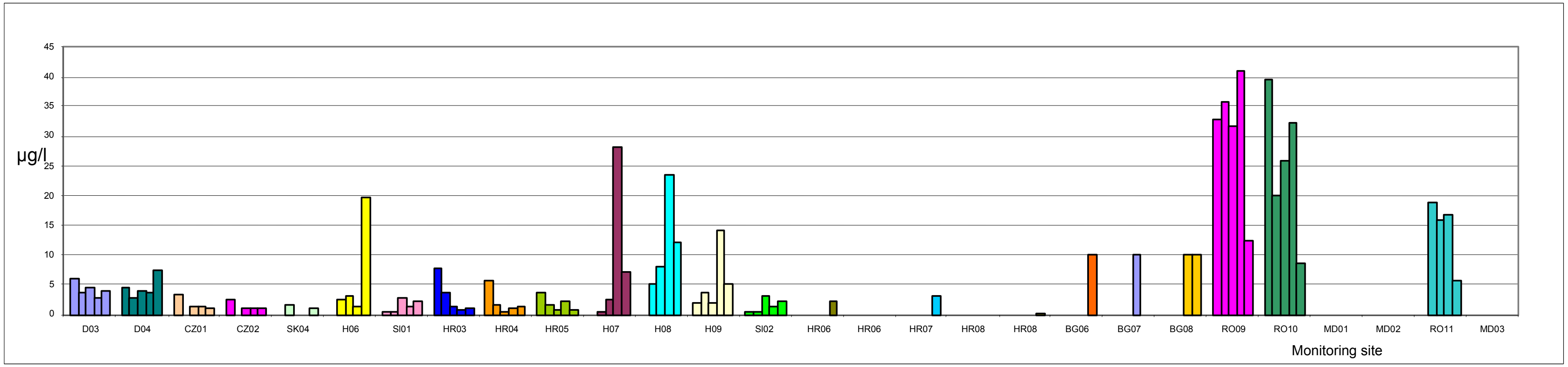

Fig. 8.1.3.23: Temporal trends of Cr – Tributaries

Copper

Copper is a very common substance that occurs naturally in the environment. Examples of natural sources are wind-blown dust, decaying vegetation, forest fires and sea spray. Humans widely use copper, because it is applied in industry and agriculture. That is why copper is often found near mines, industrial settings, landfills and waste disposals. In surface water, copper can be transported along great distances, either adsorbed on particles or as free ions. In catchments with no human inputs, the copper concentration is generally lower than 2 to 5 µg/l (*The Dobris Assessment, 1991*).

The distribution of monitoring sites according to the Classification System in the DRB for copper is shown in **Fig. 8.1.3.24**:

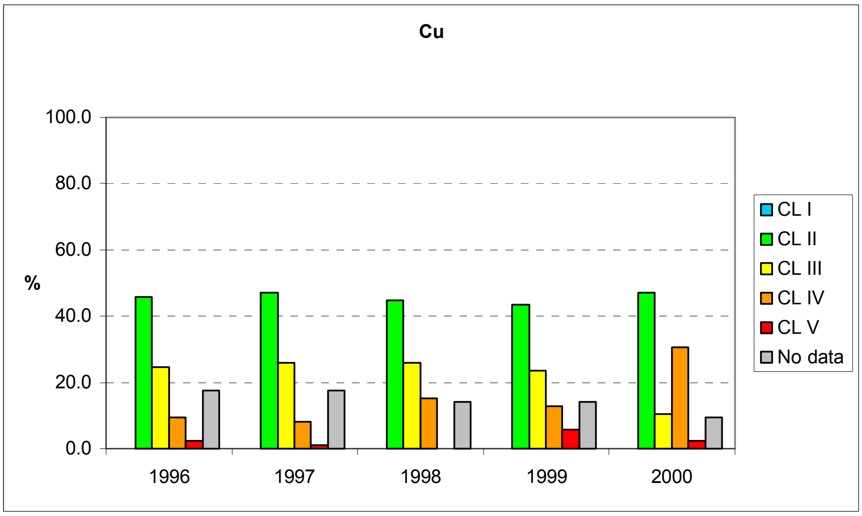

Fig. 8.1.3.24: Distribution of monitoring sites (%) according to the Quality Classification System in the DRB for **Cu**

Based on data reported from 85 monitoring sites (out of the assessment is 18 monitoring sites from Phase I List of Monitoring Sites, in which no measurements had been done in 1996-2000), the following remarks can be done:

- a relative uniform temporal distribution appears for Class II (more than 40% of monitoring sites) each year;
- percentage of sites within Class III decreases from 1996 to 2000, but percentage within Class IV increases in the same period;
- a small part of sites belongs to Class V (the maximum percentage is recorded in 1999 – 5.9%);

The spatial pattern for copper concentrations along the Danube River is shown in **Fig. 8.1.3.25a** and **8.1.3.25b**:

In the upper part of the Danube River, the distribution of the copper c90 values is uniform, with the maximum value hardly reaching half of the target value for this heavy metal (20 µg/l).
In the middle stretch, excepting only one value, the same spatial pattern as in the upper section is present. Exception occurs at Danube-Medve/Medvedov (km 1806, H01), where the copper concentration exceeds more than two times the quality target in 1996.

In the lower section, the first part is characterized by an elevated profile between Danube-Bazias (km 1071, RO01) and Danube-Pristol/Novo Selo (km 834, RO02). Differences between the reported data from Romania and Bulgaria at the same cross section are still noticeable. Downstream km 834, a decreasing spatial pattern is present, even if two high values appear at Danube-ds. Svishtov (km 554, BG03) and at Danube-us. Russe (km 503, BG04): 117.0 µg/l and 138.20 µg/l, respectively, in 1997.

In the second part of the lower Danube, copper concentrations begin to increase along the entire stretch. Thus, the maximum values appear at Danube-Silistra/Chiciu (km 375, BG05), ranging between 162.10 and 213.10 µg/l. It has to be mentioned that in the lower section, during 1996 – 2000, 139 values exceed the target value.

The spatial pattern for selected tributaries is shown in **Fig. 8.1.3.26a** and **8.1.3.26b**:

- copper concentrations have a relatively uniform distribution in tributaries located in the upper and in the middle sections, with two exceptions: the Salzach-Laufen (D04) with one value exceeding the target limit and the Tisza-Tiszasziget (H08) with 4 values above this limit
- as regarding the tributaries from the lower Danube, six of them are characterized by values above 20µg/l.

The temporal distribution for copper concentrations is shown in **Fig. 8.1.3.27** for the Danube River and in **Fig. 8.1.3.28** for tributaries. The following can be concluded:

- in the upper Danube, an increasing tendency is observed in Danube-Wolfsthal (km 1874, A04), for the rest of monitoring sites a relatively steady state is present excluding Danube Neu-Ulm (D01), being the site with higher variability of copper content in comparison with other sites in this section;
- in the middle Danube, a slight decreasing trend appears from Danube-Bratislava (km 1869, SK01) down to Danube-Komarno/Komarom (km 1768, SK03). In Danube-Hercegszanto (km 1435, H05) a slight increasing in time is present;
- in the first part of the lower Danube, the temporal trends are different from one site to another: Danube-Bazias (km 1071, RO01) is characterized by an increasing tendency, similarly as Danube-Chiciu-Silistra (RO04) and Danube – Vilkov-Chilia Arm/Kilia Arm (RO06). A decrease is observed in Danube-Novo Selo/Pristol (BG01);
- in the second part of the lower section, an increasing trend from 1996 to 2000 is observed in Danube-Chiciu/Silistra (km 375, RO04) and Danube-Vilkov-Chilia arm/Kilia arm (km 18, RO06); Monitoring sites like Danube-Ds.Svishtov (km 554, BG03), Danube-Us.Russe (km 503, BG04), Danube-Silistrta/Chiciu (km 375, BG05) and Danube-Sf.Gheorghe/Sf.Gheorghe arm (km 0, RO08) show high yearly variability without indication general tendency of development in time;
- for tributaries from the upper section, excepting the Salzach-Laufen (D04), where the maximum copper value appears in 1998, a relatively constant temporal profile is valid;
- for tributaries located in the middle Danube, different trends are present: a decreasing in Drava River, an increasing in Tisza-Tiszasziget (H08) and Sajo-Sajopuspoki (H09);
- for tributaries from the lower Danube, a decreasing trend is observed in Arges-Conf. Danube (RO09) and from 1997 in Siret-Conf. Danube Sendreni (RO10) and increase in Russenski Lom (BG08). For the rest of the tributaries in this section, the existing data cannot provide a clear temporal tendency.

Similarly to other heavy metals, in accordance to JDS results copper was found in much lower concentrations in the Danube River. In the frame of TNMN, concentrations are much higher.

Generally, concentrations of copper increase significantly along the Danube. Also in case of tributaries, those located in the lower part of Danube River Basin are characteristic by higher concentrations.

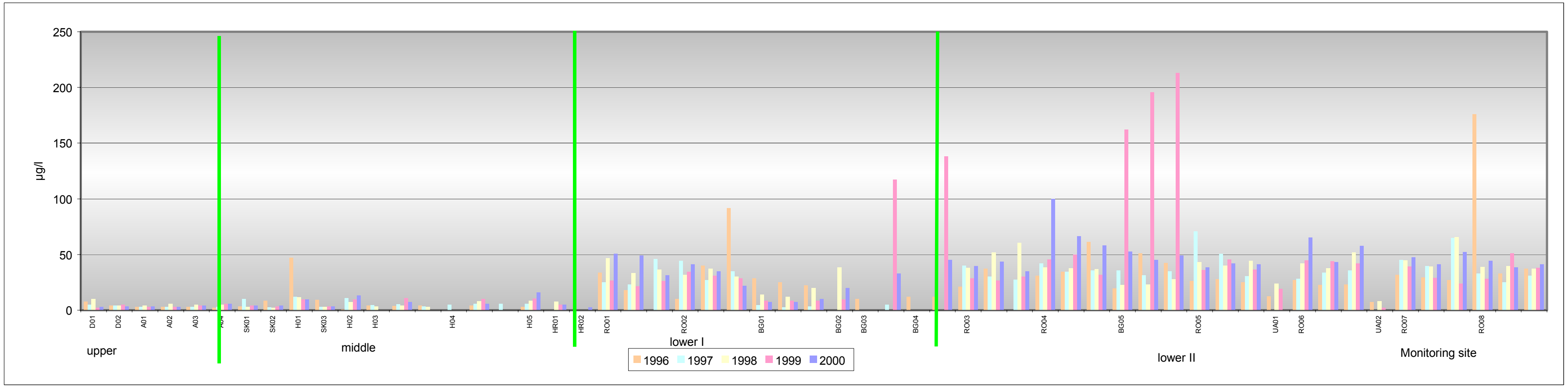

Fig. 8.1.3.25a: Spatial variation of Cu – Danube River

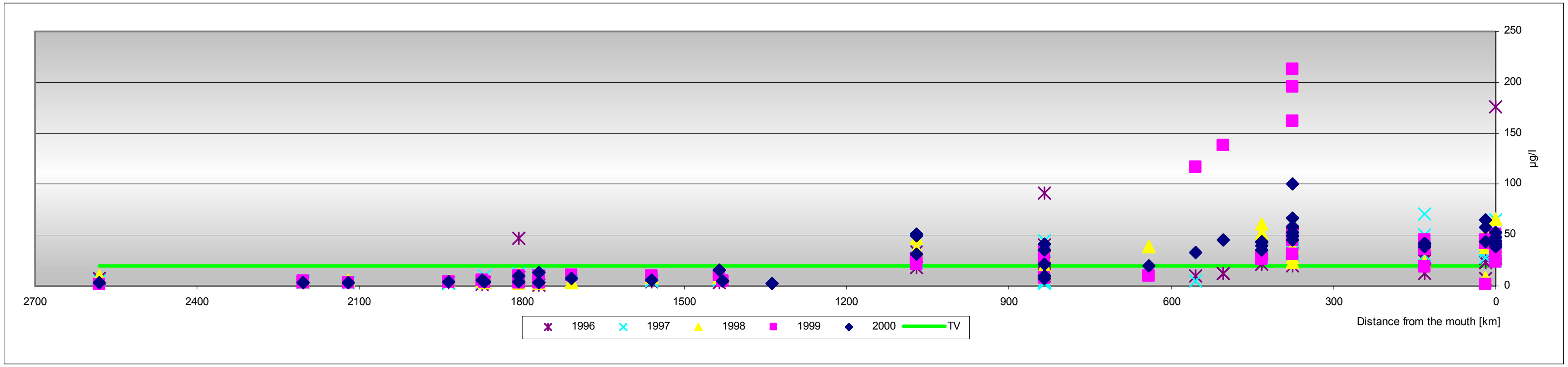

Fig. 8.1.3.25b: Spatial variation of Cu – Danube River

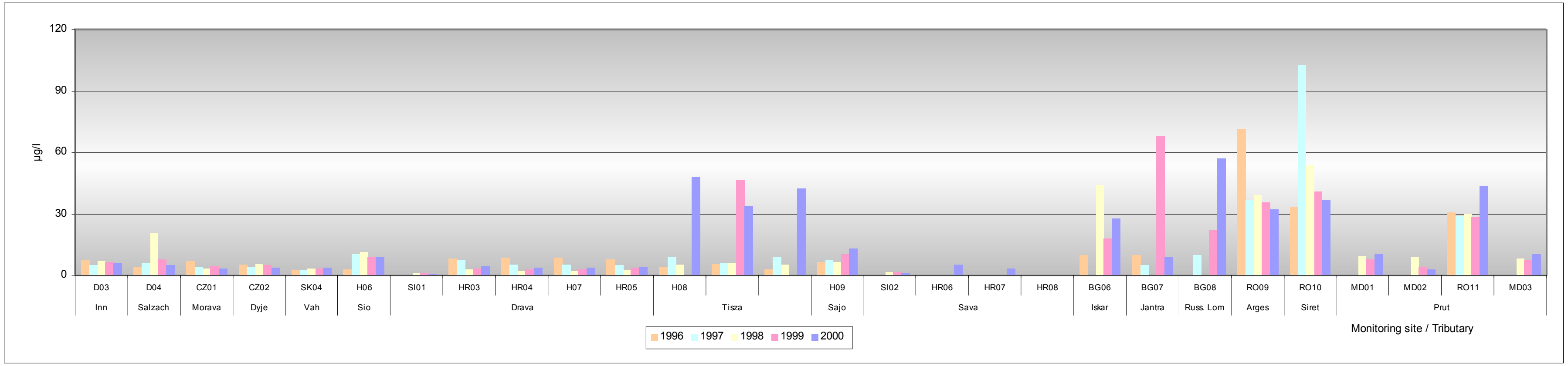

Fig. 8.1.3.26a: Spatial variation of Cu – Tributaries

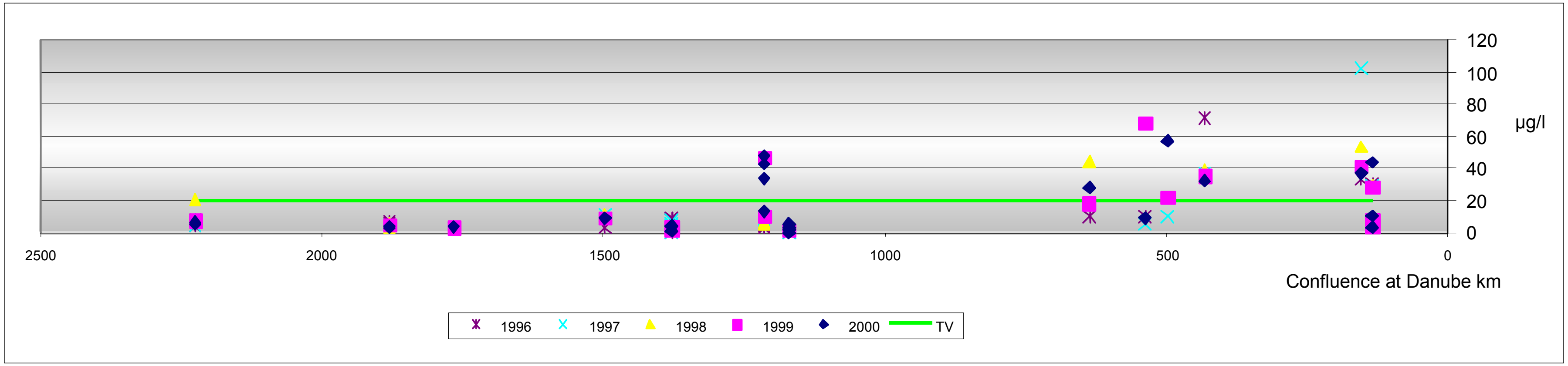

Fig. 8.1.3.26b: Spatial variation of Cu – Tributaries

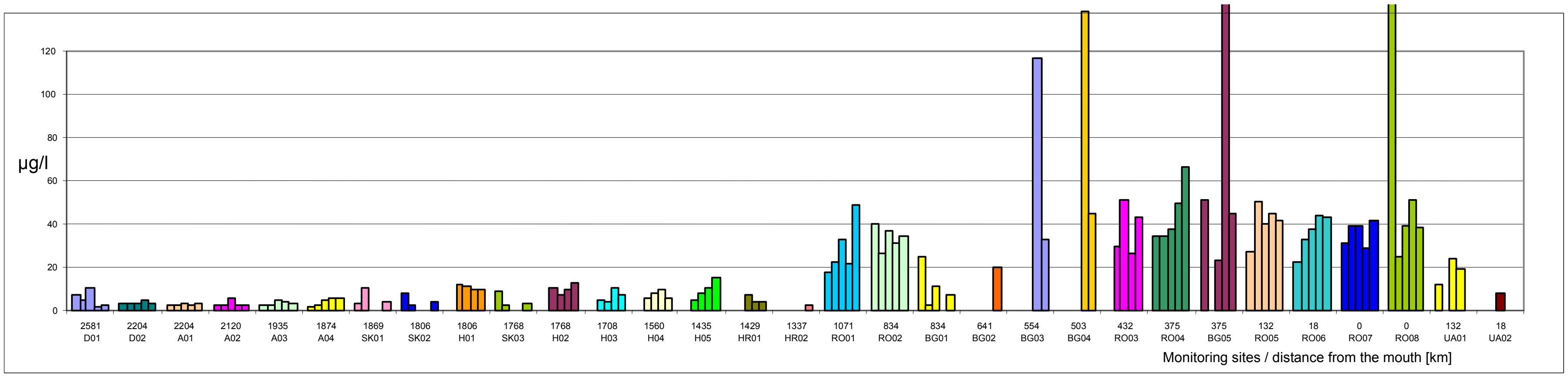

Fig. 8.1.3.27: Temporal trends of Cu – Danube River

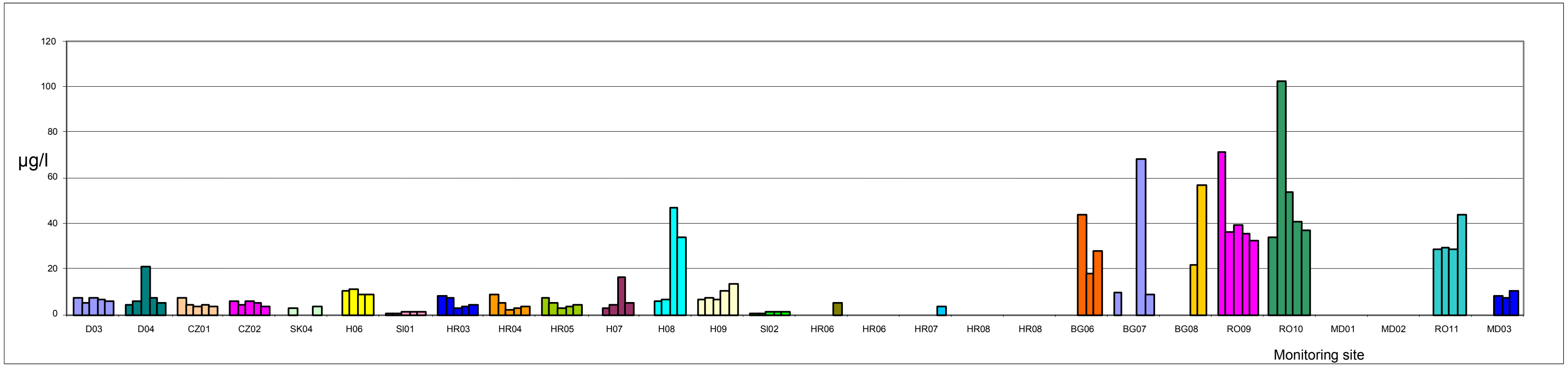

Fig. 8.1.3.28: Temporal trends of Cu – Tributaries

Lead

Lead is a particularly dangerous chemical. Most lead concentrations that are found in the environment are a result of human activities. Due to the application of lead in gasoline, through burning in car engines, lead salts (chlorine, bromines and oxides) enter the environment: the larger particles drop to ground immediately and pollute soils and surface waters, the smaller particles are transported long distances through air and fall back by raining. In water and soils lead can also end up through corrosion of leaded pipelines in a water transporting system and through corrosion of leaded paints (more likely to happen when the water is slightly acidic).

The distribution of monitoring sites according to the Classification System in the DRB for lead is shown in **Fig. 8.1.3.29**:

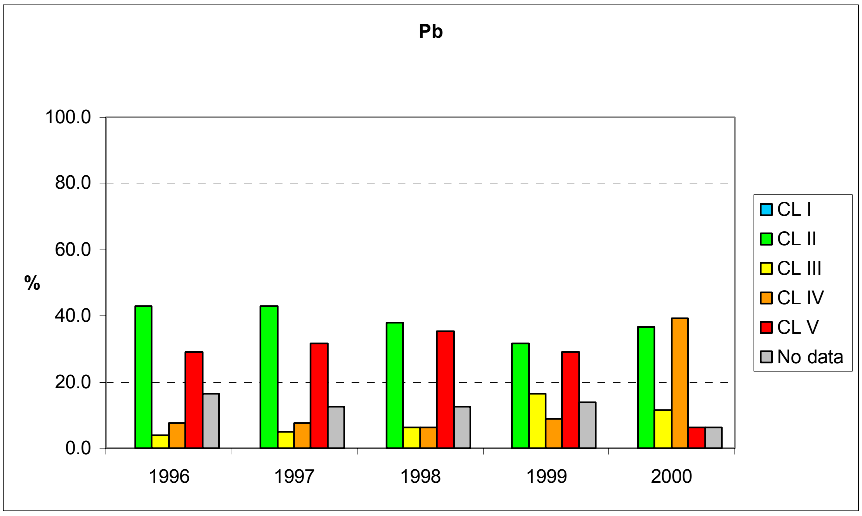

Fig. 8.1.3.29: Distribution of monitoring sites (%) according to the Quality Classification System in the DRB for **Pb**

Based on data reported from 79 monitoring sites (out of the assessment is 24 monitoring sites from Phase I List of Monitoring Sites, in which no measurements had been done in 1996-2000), the following remarks can be done:

- the highest percentage of sites within Class II is observed in years 1996-1999;
- year 2000 is the only one in which with percentage of sites corresponding to Class IV (39 %) exceed percentage of sites in Class II (37 %);
- the number of sites within Class III increases from 1996 to 1999, followed by a decreasing in
- lead is actually the only heavy metal which is represented by high percentage in Class V - even more than 30 % of the monitoring points in 1998), but this situation became better in 2000 (with 6.3 % of monitoring sites);

The spatial pattern of lead concentrations along the Danube River is illustrated in **Fig. 8.1.3.30a** and **8.1.3.30b**.

Similarly to the already discussed heavy metals, lead concentrations in the upper section present a uniform distribution, all values are below the target limit (5 µg/l).

This profile is valid also for the middle stretch; excepting one value – 17.45 µg/l at Danube-Dunafoldvar (km 1560, HO4) - all the others are below 5µg/l.

Spatial variation of lead concentration is totally different in the first part of the lower Danube. There is dramatic increase of lead concentrations from the beginning of this section and maximum is detected between Danube-Bazias (km 1071, RO01) – Danube-Pristol/Novo Selo (km 834, RO02); along this stretch, excepting the value from 2000, all the others are above two times target value. Here are also the highest values along the Danube River, the lead c90 value reaches up to 82.00 µg/l. Downstream this location, the existing data shows a decreasing spatial pattern.

The second part of the lower Danube is also characterised by rather high lead concentrations, especially at Danube-Chiciu/Silistra (km 375, RO04), where according to Romanian data the lead c90 value reaches up to 57.30 µg/l.
Concerning the exceeding of the target value, along the entire lower stretch, 136 values are above this limit. Most of the values are actually characteristic to Quality Class V.

The spatial distribution of lead concentrations in the selected tributaries is shown in **Fig. 8.1.3.31a** and **8.1.3.31b**. It can be seen that 55 values exceed the target value. Target limit for lead is exceeded in majority of monitoring sites. The highest concentrations are observed in the tributaries of the lower part of river basin. Maximum c90 values had been observed in Arges (RO09), Siret (RO10) and Prut (RO11), reaching values 91.00 µg/l in Arges-Conf. Danube (RO09); 88.71 µg/l in Siret-Conf. Danube Sendreni (RO10) and 49.70 µg/l in Prut-Conf. Danube Giurgiulesti (RO11).

The temporal distribution of lead c90 values along the Danube River is shown in **Fig. 8.1.3.32** and in **Fig. 8.1.3.33** for selected tributaries. It can be concluded that:

- in the upper and middle Danube, a relative constant values in evaluated period are present, excepting the monitoring site located at Danube-Dunafoldvar (km1560, H04), where an increasing tendency appears from 1997 to 2000;
- in the lower Danube, decreasing from 1998 is observed in all Romanian monitoring sites from Danube-Bazias (km 1071, RO01), down to Danube-Sf. Gheorghe/Sf. Gheorghe arm (km 0, RO08). In cross section RO02/BG01 and RO04/BG05, in accordance to existing Bulgarian data, the trend is somehow opposite - increasing from 1996 to 2000;
- as far as concerns the temporal changes in selected tributaries, the following has been observed:
    - increasing from 1997 to 2000 in Salzach-Laufen (D04);
    - decreasing in Drava-Varazdin (HR03), Drava-Botovo (HR04) and Drava-D. Miholjac (HR05);
    - decreasing in Arges-Conf. Danube (RO09), Siret-Conf. Danube Sendreni (RO10) and Prut-Conf. Danube Giurgiulesti (RO11).

The spatial pattern of lead is the same as was in case of other heavy metals, with generally several-times higher values in lower part of river basin, which is valid for both – Danube River itself and monitored tributaries. JDS results are much lower, TNMN data indicate values characterising lead content in lower Danube part sometimes even higher by one order.

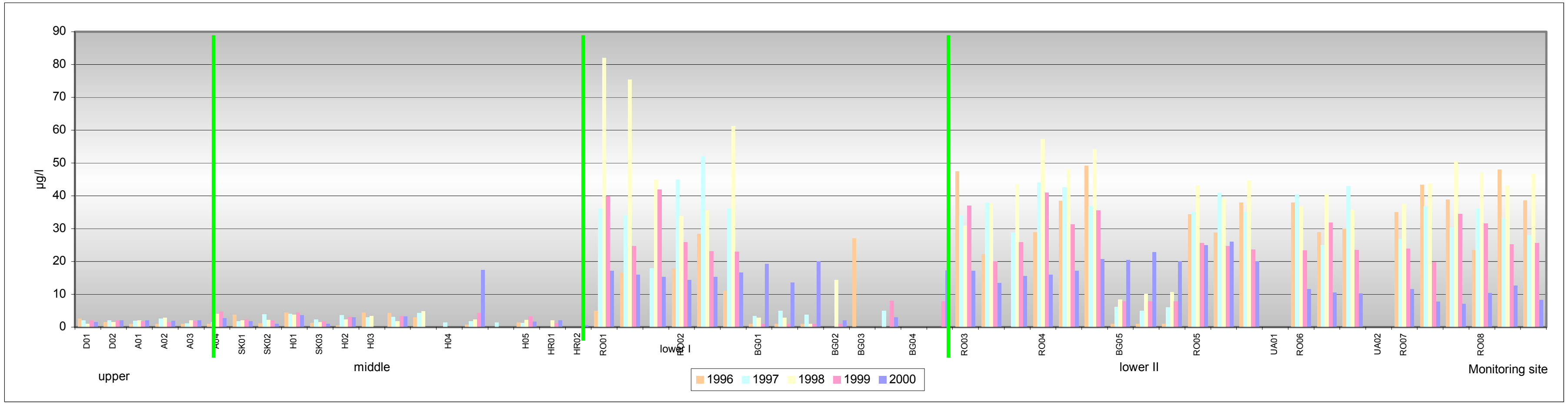

Fig. 8.1.3.30a: Spatial variation of Pb – Danube River

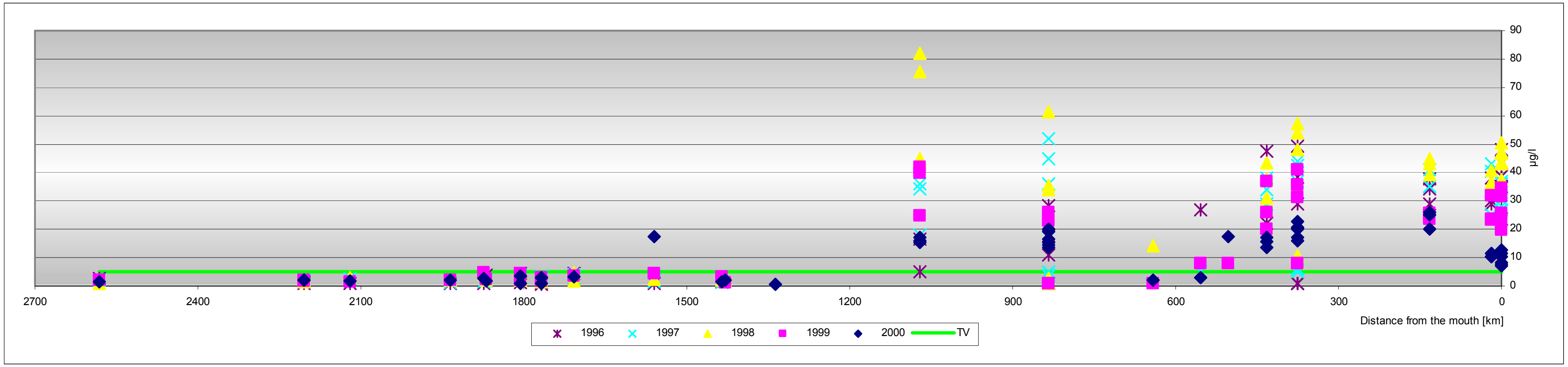

Fig. 8.1.3.30b: Spatial variation of Pb – Danube River

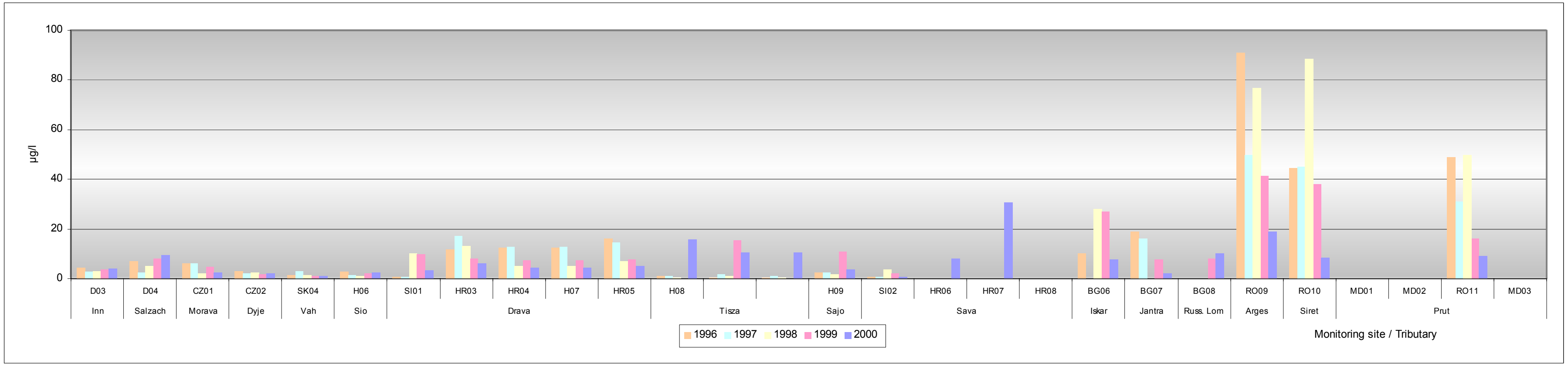

Fig. 8.1.3.31a: Spatial variation of Pb – Tributaries

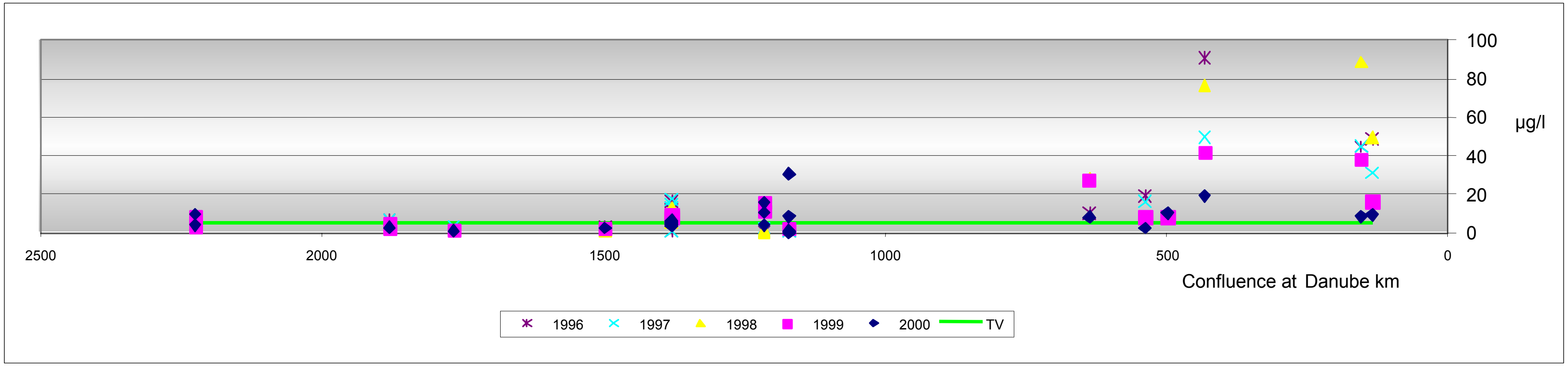

Fig. 8.1.3.31b: Spatial variation of Pb – Tributaries

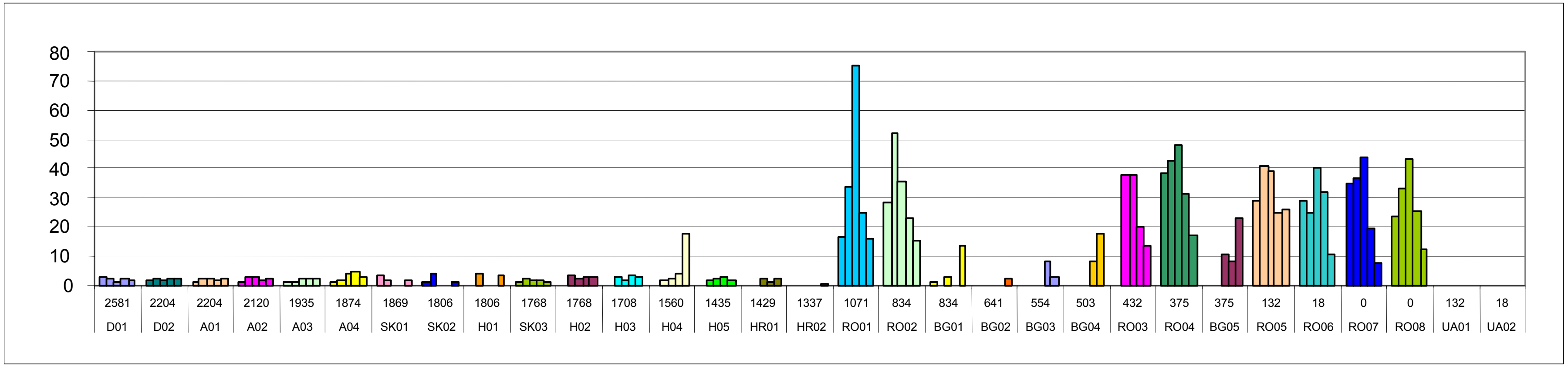

Fig. 8.1.3.32: Temporal trends of Pb – Danube River

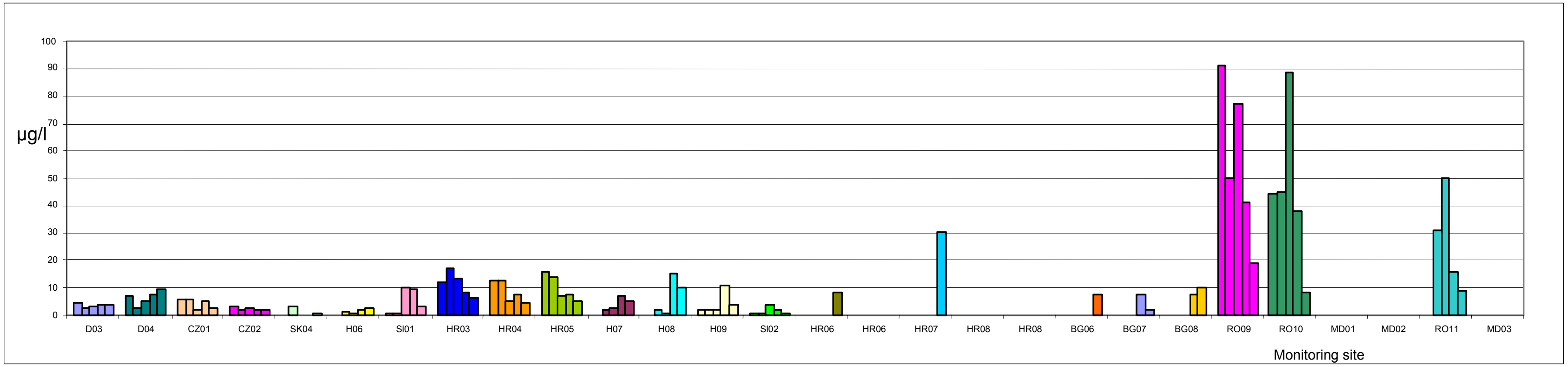

Fig. 8.1.3.33: Temporal trends of Pb – Tributaries

Mercury

Mercury is a metal that occurs naturally in the environment. It can be found as mercury salts or as organic mercury compounds. It enters the environment as a result of normal breakdown of minerals and exposure to wind and water. From human activities, mercury is released into air through fossil fuel combustion, mining, smelting and solid waste combustion. Some forms of human activities release mercury directly into soil or water, for instance the application of agricultural fertilizers and industrial waste water discharges. All mercury released into environment will eventually end up in soil and surface water. Acidic surface waters can contain significant amounts of mercury: when the pH values are between 5.00 and 7.00, the mercury concentrations in water increase due to mobilization of mercury in the ground. Once it reaches the surface water, microorganism can convert it into methyl mercury, a very dangerous organic compound.

The distribution of monitoring sites according to the Classification System in the DRB for mercury is shown in **Fig. 8.1.3.34**:

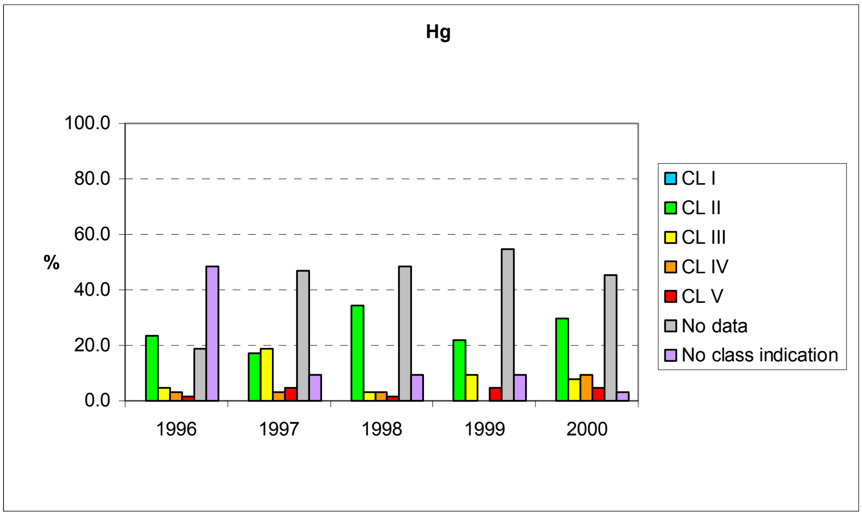

Fig. 8.1.3.34: Distribution of monitoring sites (%) according to the Quality Classification System in the DRB for **Hg**

Based on data reported from 64 monitoring sites (out of the assessment is 49 monitoring sites from Phase I List of Monitoring Sites, in which no measurements had been done in 1996-2000), the following remarks can be done:

- almost 50 % of the monitoring sites (in 1996) have no quality class indication, because the limit of detection is higher than the limit value for Class II. In years 1997-2000 sites with “no class” indication is low because data have not been provided from majority of these sites (and therefore percentage of sites with “no data” from the basic set of 64 monitoring sites is so high in 1997-2000) (see also Annex 1)
- in four of the five studied years, maximum percentage of sites correspond to Class II. In 1997, maximum belongs to Class III;
- the number of sites corresponding Class IV is uniform during 1996-1998 (3.1%), absent in 1999 but increases in 2000 at 9.4 %;
- the number of sites within Class V is below 5 % during the evaluated period;

The spatial pattern for mercury concentrations along the Danube River is shown in **Fig. 8.1.3.35a** and **8.1.3.35b**.

Mercury c90 values are between 0.100 – 0.416 µg/l in the upper section, being undetectable at Danube-Neu Ulm (km 2581, D01) and Danube-Jochentein (km 2204, D02). Mercury is the only heavy metal in case of which the upper Danube section contains 16 values above the target limit.

Although mercury was mostly undetected at monitoring sites from the middle stretch, still 14 values are above the quality target. The maximum value (0.82 µg/l) appears at Danube-Dunafoldvar (km 1560, H04).

Entire lower section of the Danube has no suitable data for assessment.[1]

The spatial pattern of mercury concentrations for selected tributaries is illustrated in Fig. **8.1.3.36a** and **8.1.3.36b**. All four tributaries from the upper section show mercury values exceeding the target value. Those from the middle stretch also show values above 0.1 µg/l. It has to be mentioned that in the case of the Drava-Ormoz (SL01) and the Sava-Jesenice (SL02) the represented values (0.5 µg/) are actually the limit of detection, so mercury is undetected at those sites. The maximum mercury concentration (1.54 µg/) appears on the Sava-ds. Zupanja (HR08). Concerning the tributaries from the lower Danube section, no mercury data are suitable for assessment[1].

The temporal distribution of mercury concentrations along the Danube River is shown in **Fig. 8.1.3.37** and in **Fig. 8.1.3.38** for selected tributaries. It can be concluded that:

- no tendency of development can be observed in the monitoring sites from the upper and middle Danube section;
- for selected tributaries, slight increase in Inn-Kirchdorf (D03) and Dyje (CZ02) and slight decrease in Morava-Lanzhot (CZ01) is observed.

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[1] the reported data for Romanian monitoring sites are excluded from assessment because all data are equal to 3.00µg/l, identical with the reported limit of detection

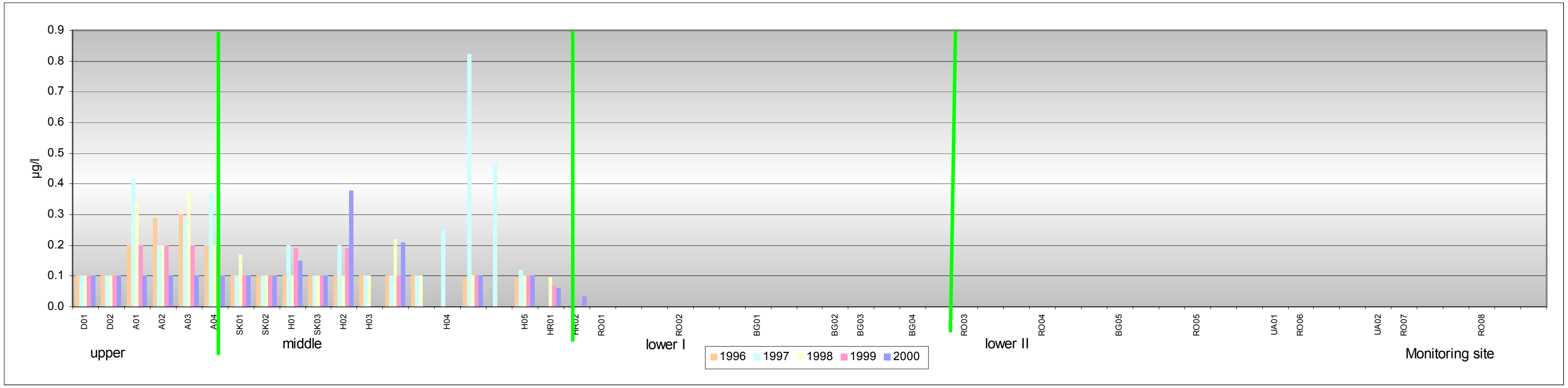

Fig. 8.1.3.35a: Spatial variation of Hg – Danube River

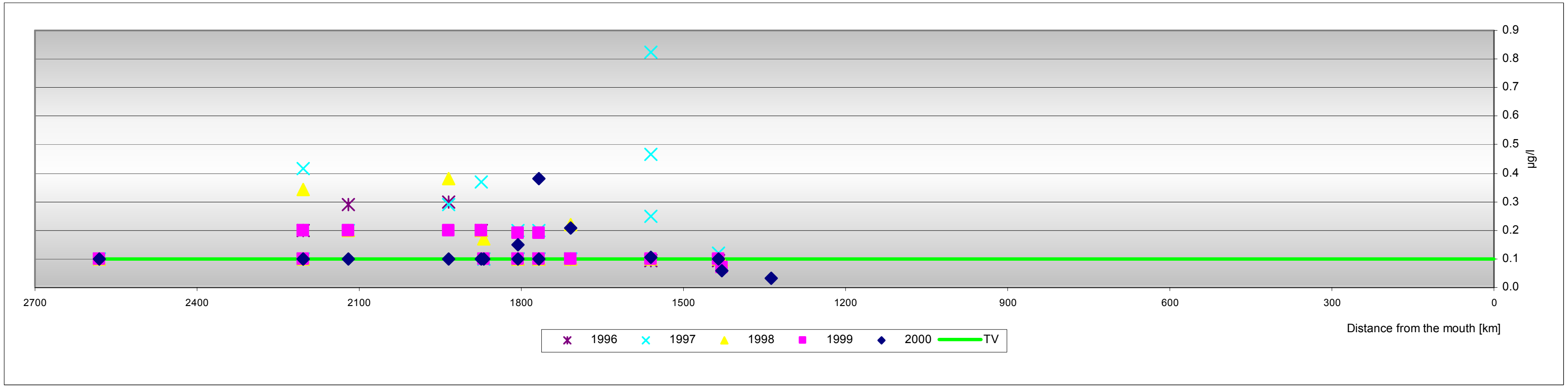

Fig. 8.1.3.35b: Spatial variation of Hg – Danube River

Note: In locations A01, A02, A03, A04 (96-99), RO01, RO02, RO03, RO04, RO05, RO06, RO07, RO08 (96) the values in the graph represent limits of detection that are higher than the target value.

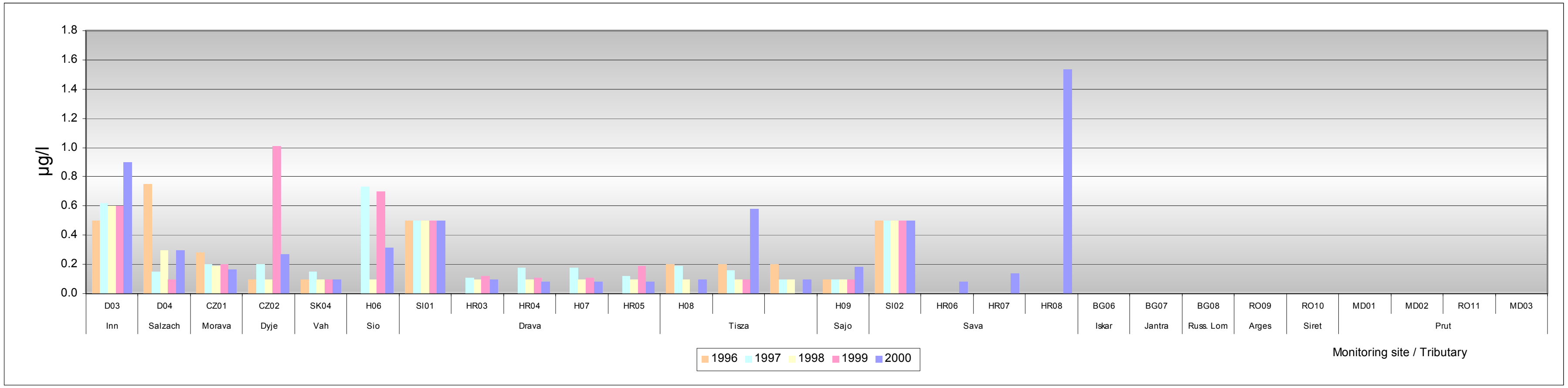

Fig. 8.1.3.36a: Spatial variation of Hg – Tributaries

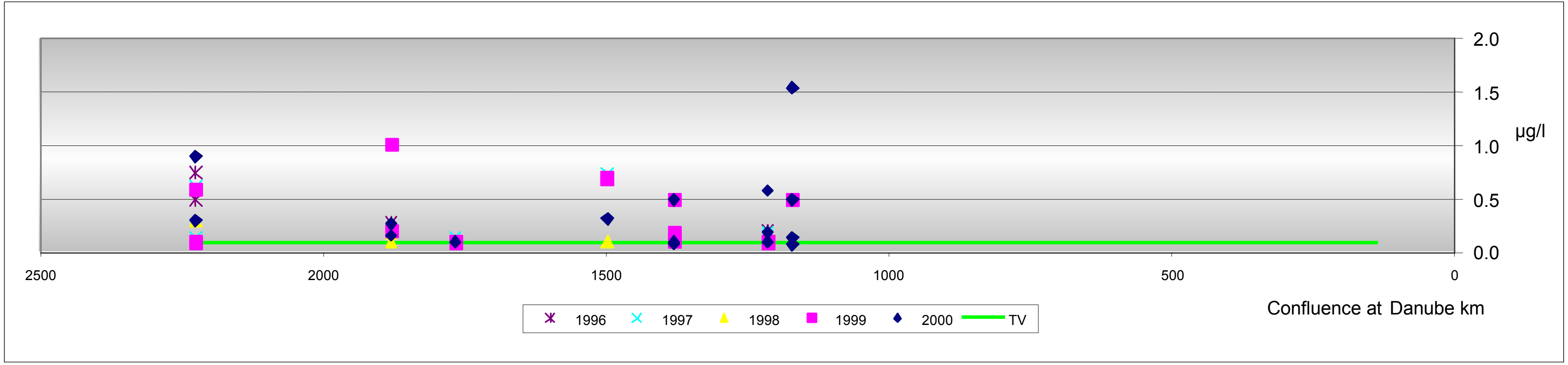

Fig. 8.1.3.36b: Spatial variation of Hg – Tributaries

Note: In locations SL01, SL02 (96-00), RO09, RO10, RO11 (96) the values in the graph represent limits of detection that are higher than the target value.

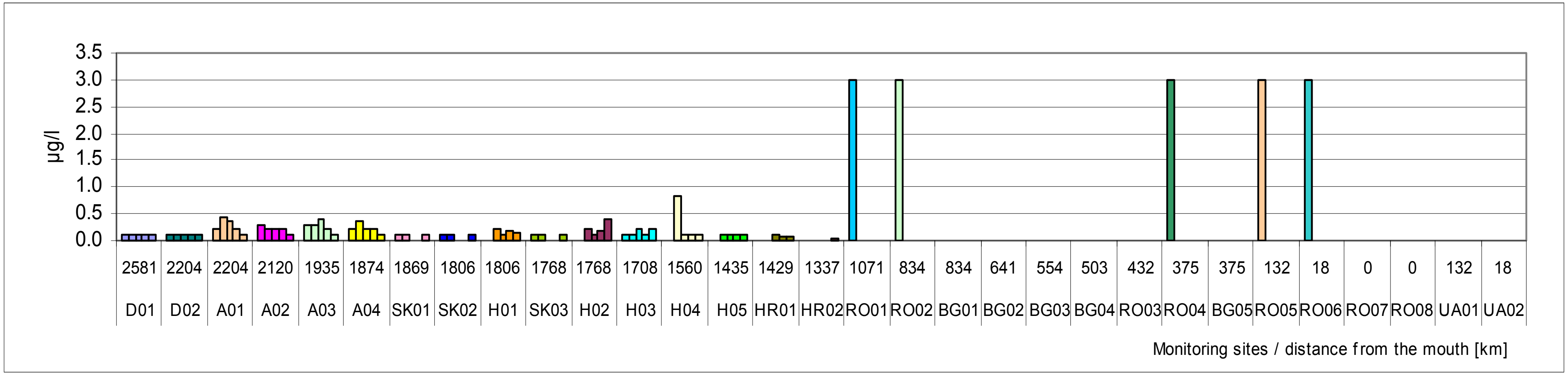

Fig. 8.1.3.37: Temporal trends of Hg – Danube River

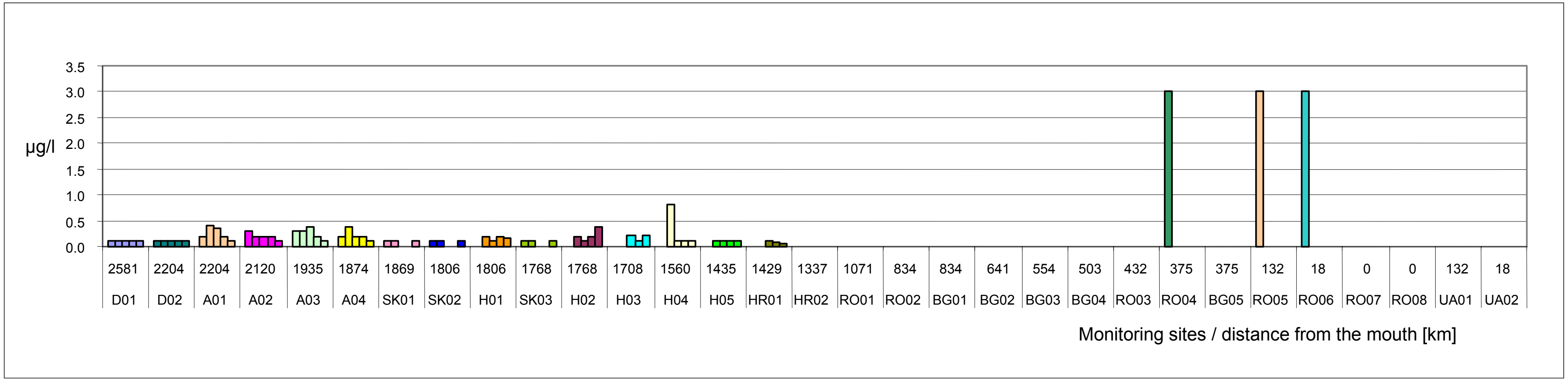

Fig. 8.1.3.38: Temporal trends of Hg – Tributaries

Nickel

The distribution of monitoring sites according to the Classification System in the DRB for nickel is shown in **Fig. 8.1.3.39**:

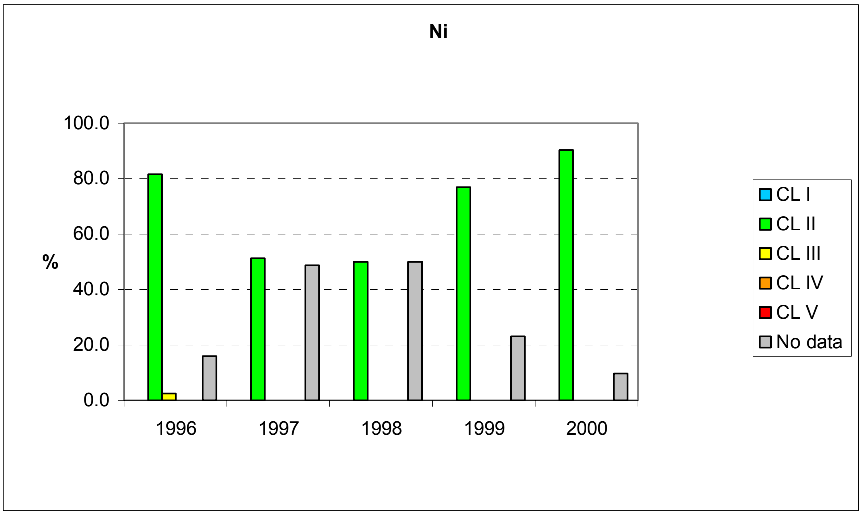

Fig. 8.1.3.39: Distribution of monitoring sites (%) according to the Quality Classification System in the DRB for **Ni**

Based on data reported least in one year by 82 monitoring sites (out of the assessment is 21 monitoring sites from Phase I List of Monitoring Sites, in which no measurements had been done in 1996-2000), it can be concluded that nickel seems to be the heavy metal for which the Danube River and its tributaries have “the best” quality, taking into account target value given by Class II of TNMN classification scheme. Monitoring sites correspond to Class II and Class III is represented only in 1996 by 2.4 % of monitoring sites.

The spatial distribution of nickel concentrations along the Danube River is shown in **Fig. 8.1.3.40a** and **8.1.3.40b**.

In the upper Danube, a slight increasing spatial profile is present from Danube-Jochenstein (km 2204, D02) to Danube-Wolfsthal (km 1874, A04), but no nickel concentration is above the target limit for this heavy metal (50 µg/l).

In the middle Danube, also an increasing pattern is present along Danube-Bratislava (km 1869, SK01) to Danube-Szob (km 1708, H03), followed by a decreasing down to Danube-Borovo (km 1337, HR02). Even the maximum value for this stretch (16.21 µg/l) is well below the target limit.

Along the first part of the lower Danube section, nickel concentrations are higher than in the middle stretch, reaching c90 value 28.10 µg/l at Danube-Pristol/Novo Selo (km 834, RO02). However, no value exceeds the quality target.

The second part of the lower Danube section shows several nickel concentrations higher than in the first section. Three monitoring sites - Danube-us. Arges (km 432, RO03), Danube-Chiciu/ Silistra (km 375, RO04) and Danube-Vilkov/Chilia arm/Kilia arm - present values above 30 µg/l, The target limit is not exceeded.

The spatial profile of nickel concentrations in the selected tributaries is shown in **Fig. 8.1.3.41a** and **8.1.3.41b**. It can be seen that, excepting one value recorded on the Salzach-Laufen (D04), the tributaries from the upper and middle Danube are characterized by low nickel concentrations, with no value above the target limit. For those located in the lower Danube, 2 values are above 50µg/l: on the Arges-Conf. Danube (RO09) and Siret-Conf. Danube Sendreni (RO10).

The temporal trends for nickel concentrations are shown in **Fig. 8.1.3.42** for the Danube River and in **Fig. 8.1.3.43** for selected tributaries:

- increasing tendency is observed in Hungarian section of the Danube River, from Danube-Komarom/Komarno (km1768, H02) down to Danube-Hercegszanto (km 1435, H05);
- in the lower part of Danube River interpretation is rather difficult, because whilst in Romanian sites maximum values have been observed at the beginning of the evaluated period – in 1996, in Bulgarian ones at the end of this period – in 2000
- from selected tributaries decreasing from 1996 to 2000 in Salzach-Laufen (D04) and Drava-Varazdin (HR03) is observed;
- for interpretation of tributaries in the lower part, the data available are not sufficient.

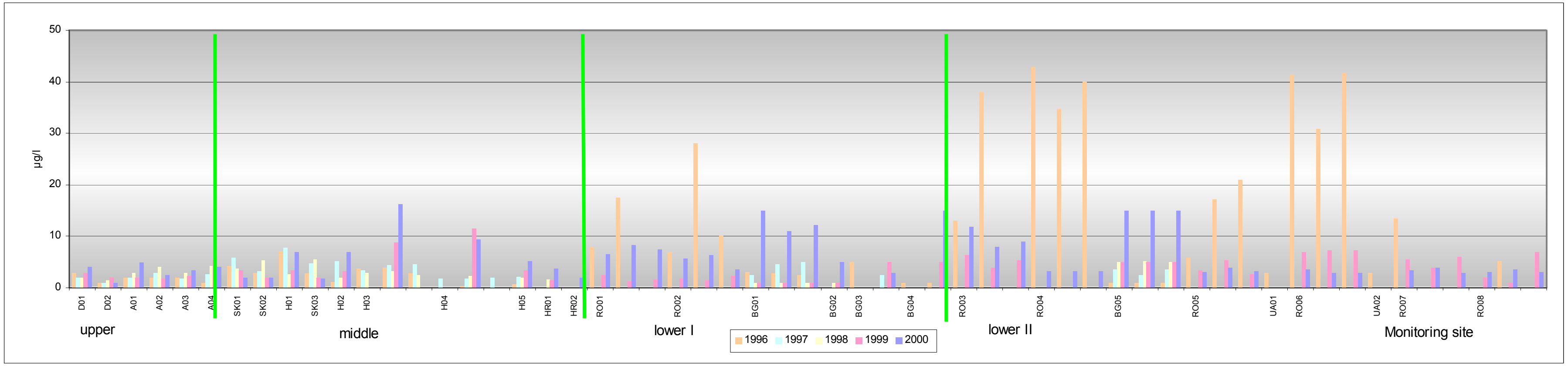

Fig. 8.1.3.40a: Spatial variation of Ni – Danube River

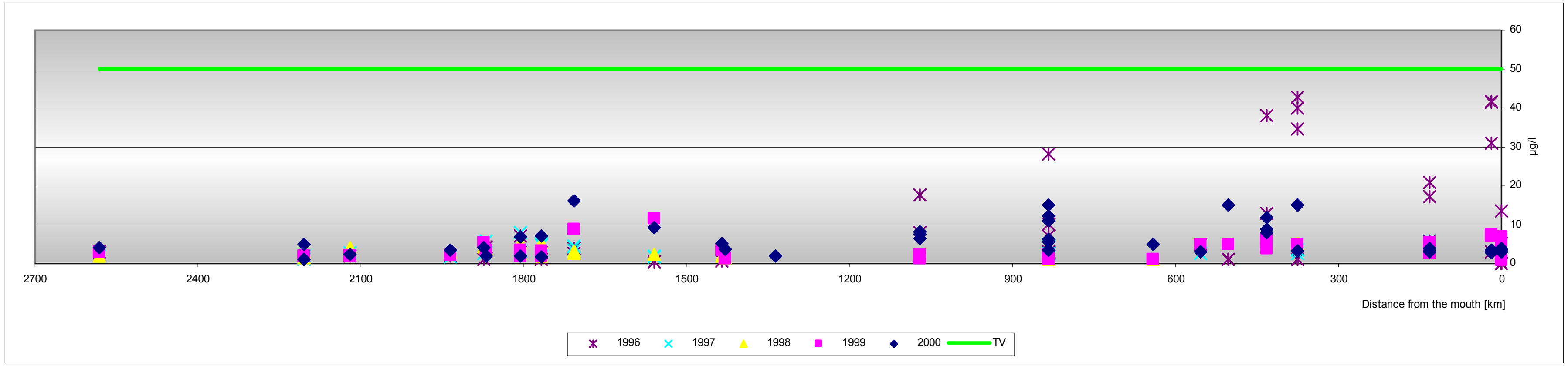

Fig. 8.1.3.40b: Spatial variation of Ni – Danube River

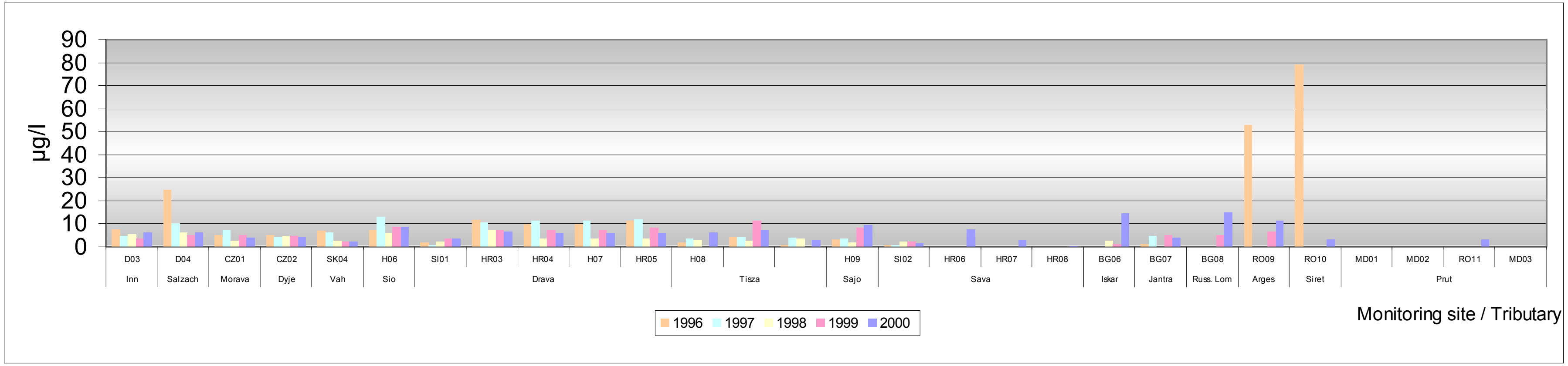

Fig. 8.1.3.41a: Spatial variation of Ni – Tributaries

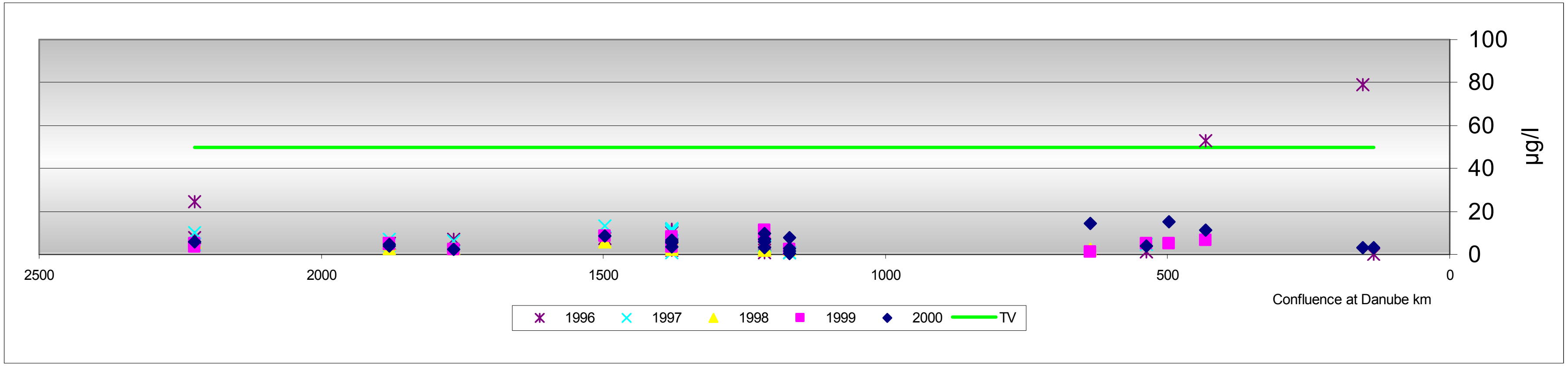

Fig. 8.1.3.41b: Spatial variation of Ni – Tributaries

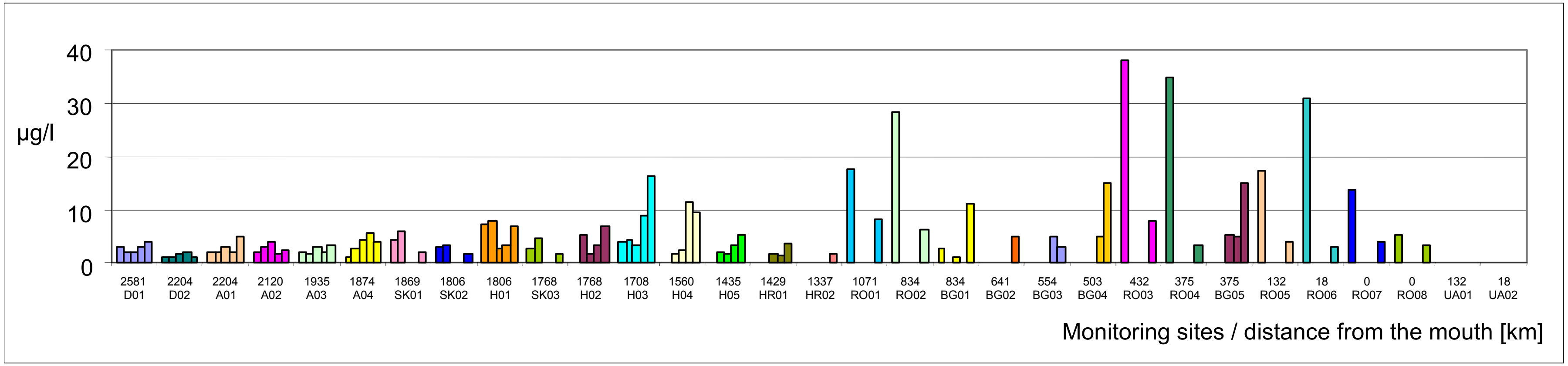

Fig. 8.1.3.42: Temporal trends of Ni – Danube River

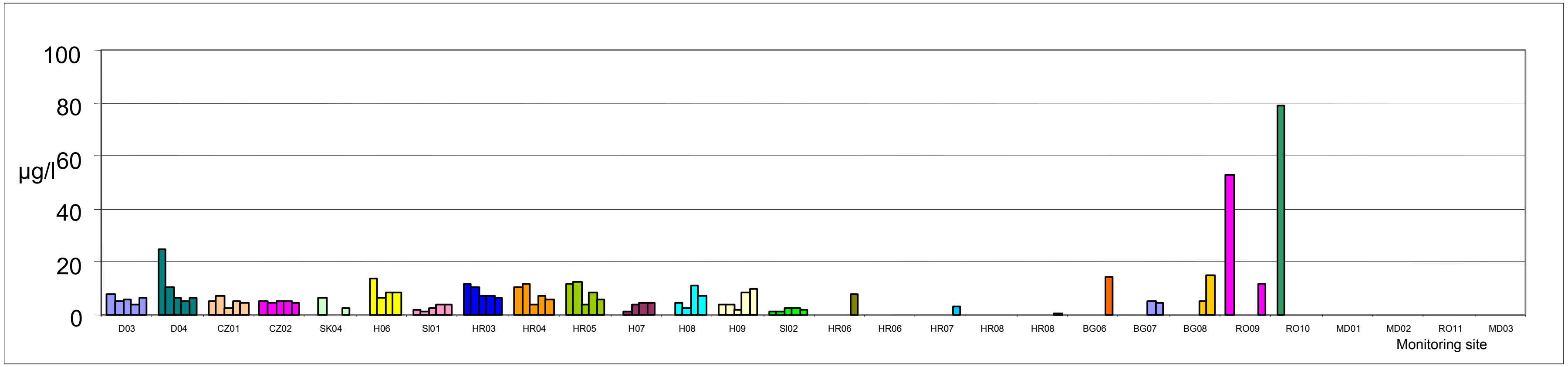

Fig. 8.1.3.43: Temporal trends of Ni – Tributaries

Zinc

Zinc occurs naturally in air, water and soil. Similar to copper, zinc is widely used in human activities. Mining of other different metals results in zinc discharging in the environment. In natural water, unaffected by anthropogenic influence, zinc concentration is usually below 5 µg/l (*The Dobris Assessment, 1991*). Due to the fact that its toxicity is generally higher in water with a low mineral content, the Council Directive 78/659/EEC concerning water standards for fish recommends that Zn levels to be below 300 µg//l in water with a hardness of 100 mg/l $CaCO_3$, but below 30 µg//l in water with a hardness of 10 mg/l $CaCO_3$. Within the Danube River Basin, Water Quality Classification System sets 100 µg/l as target value for zinc.

The distribution of monitoring sites according to the Classification System in the DRB for zinc is shown in **Fig. 8.1.3.44**:

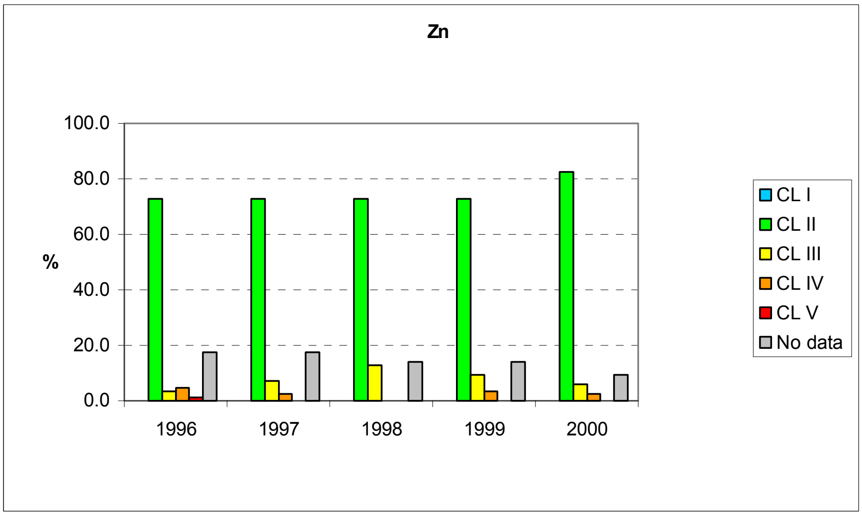

Fig. 8.1.3.44: Distribution of monitoring sites (%) according to the Quality Classification System in the DRB for **Zn**

Based on data reported from 85 monitoring sites (out of the assessment is 18 monitoring sites from Phase I List of Monitoring Sites, in which no measurements had been done in 1996-2000), the following remarks can be done:

- a relatively positive distribution is present, with more than 70 % of the monitoring sites within Class II during 1996 – 1999 and more than 80 % in 2000;
- Class III is represented by the maximum percentage in 1998 (12.9 %);
- percentage of sites corresponding to Class IV and Class V is low, less than 10 %.

The spatial distribution of zinc concentrations along the Danube River is shown in **Fig. 8.1.3.45a** and **8.1.3.45b**.

In the upper section, zinc concentration has an uneven spatial distribution: at first two monitoring sites – Danube-Neu Ulm (km 2581, D01) and Danube-Jochenstein (km 2204, D02) - excepting one value, this metal is undetectable, the limit of detection being here 10 µg/l. The rest of sites from this stretch are characterized by higher zinc concentrations, but no value is above the target limit.

In the middle stretch, the spatial distribution shows a maximum profile at Danube-Szob (km 1708 H03), where only one value exceeds the target limit. It has to be mentioned that at the cross sections from this stretch (SK02/H01 and SK03/H02), the Hungarian data shows higher concentrations. Downstream of Danube-Szob (H03) zinc content decreases, all c90 values are below 70 µg/l.

In the first part of the lower Danube, the spatial distribution presents a significantly higher values than in the middle stretch, with 11 values exceeding the target value. The maximum - 302.0 µg/l - appears at Danube-ds. Svishtov (km 554, BG03).

The second part of the lower Danube is also characterized by high zinc concentrations. At Danube-us. Arges (km 432, RO03) three values are more than two times higher than the target limit. For this part, the total number of zinc values above this limit is 14.

The spatial distribution for selected tributaries is shown in **Fig. 8.1.3.46a** and **8.1.3.46b**. Taking the target limit as a criterion for assessment the zinc concentration levels in tributaries, the following remarks can be done:

- in upper stretch, no c90 value is above the target value;
- in the middle stretch, above the target value are concentrations characterising Tisza-Tiszasziget (H08) and Sajo-Sajopuspoki (H09);
- in the lower stretch, the Iskar-Orechovitza (BG06), Russenski Lom-Basarbovo (BG08), Arges-Conf. Danube (RO09), Siret-Conf. Danube Sendreni (RO10) and Prut-Conf. Danube Giurgiulesti (RO11) are the tributaries with zinc content exceeding target value.

The temporal trends for zinc concentrations are shown in **Fig. 8.1.3.47** for the Danube River and in **Fig. 8.1.3.48** for selected tributaries:

- in the upper Danube, at the monitoring sites where zinc is detectable, the temporal profile shows that higher values are recorded in 1998 and/or 1999;
- in the middle Danube, an increasing is observed in Danube-Dunafoldvar (km 1560, H04) and Danube-Herceszanto (km 1435, H05); decreasing in Danube-Bratislava (km 1869, SK01), and Danube-Komarno/Komarom (km 1768, SK03);
- sites in the lower Danube are characteristic with rather high variability, but decrease can be observed in Danube-Chiciu/Silistra (km 375, RO04), Danube-Reni-Chilia/Kilia Arm (km 132, RO05) and taking into account high value in 1997, also in Danube-Sulina-Sulina Arm (km 0, RO07) temporal changes are going in a positive direction.
- tributaries from the upper Danube do not show significant temporal variations, only on Dyje-Pohansko (CZ02) a decreasing trend is visible;
- in the middle Danube, increasing tendency is observed in Sio-Szekszard-Palank (H06) and Drava-Ormoz (SL01) and decreasing tendency in the rest on monitoring sites on Drava River and in Sajo-Sajopuspoki (H09);
- for Romanian tributaries located in the lower Danube – the Arges-Conf. Danube (RO09), Siret-Conf. Danube Sendreni (RO10) and Prut-Conf. Danube Giurgiulesti (RO11) the general trend is decreasing, while for Iskar (BG06) and Russenski Lom (BG08) there is an increase in evaluated period.

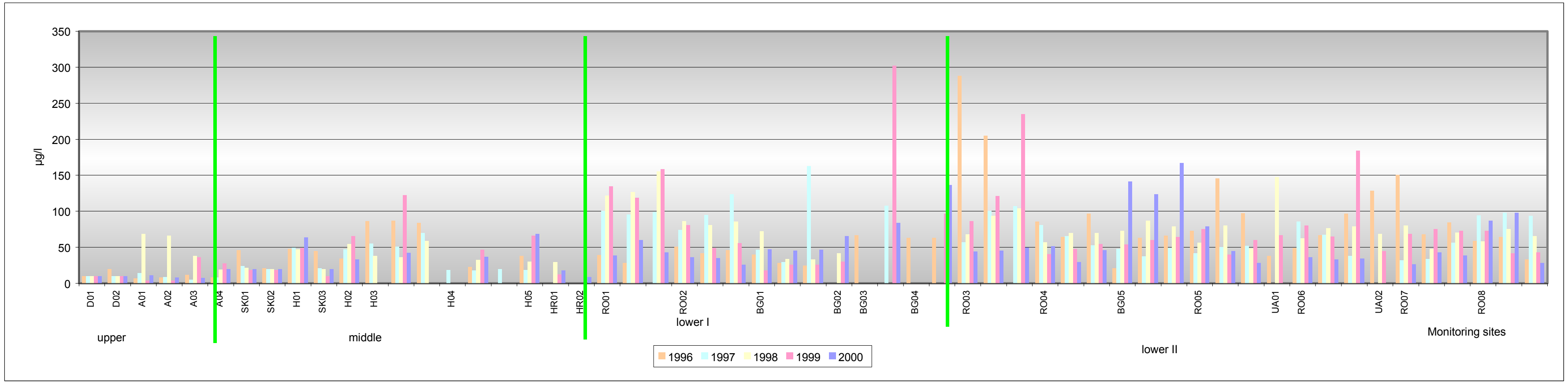

Fig. 8.1.3.45a: Spatial variation of Zn – Danube River

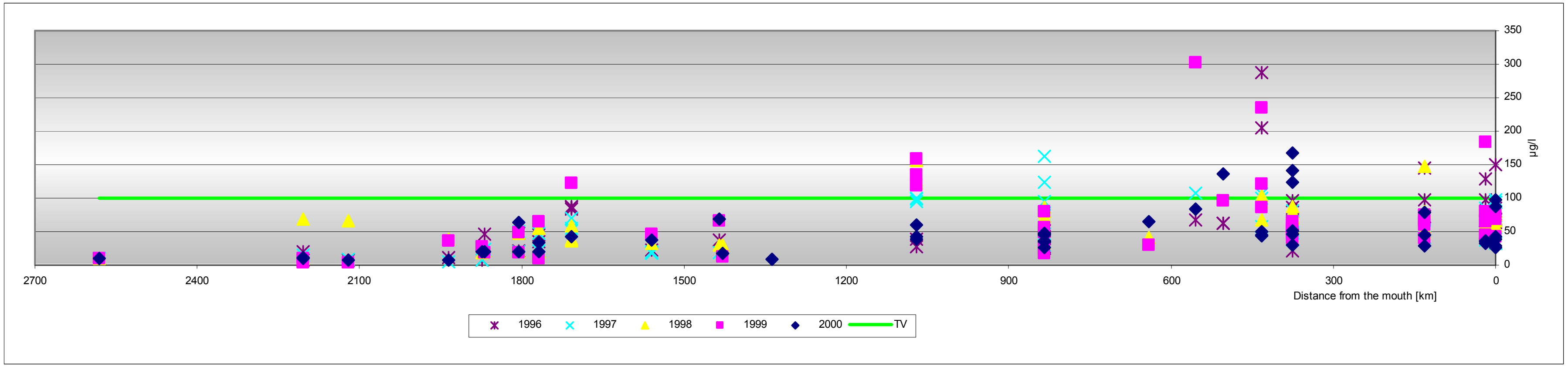

Fig. 8.1.3.45b: Spatial variation of Zn – Danube River

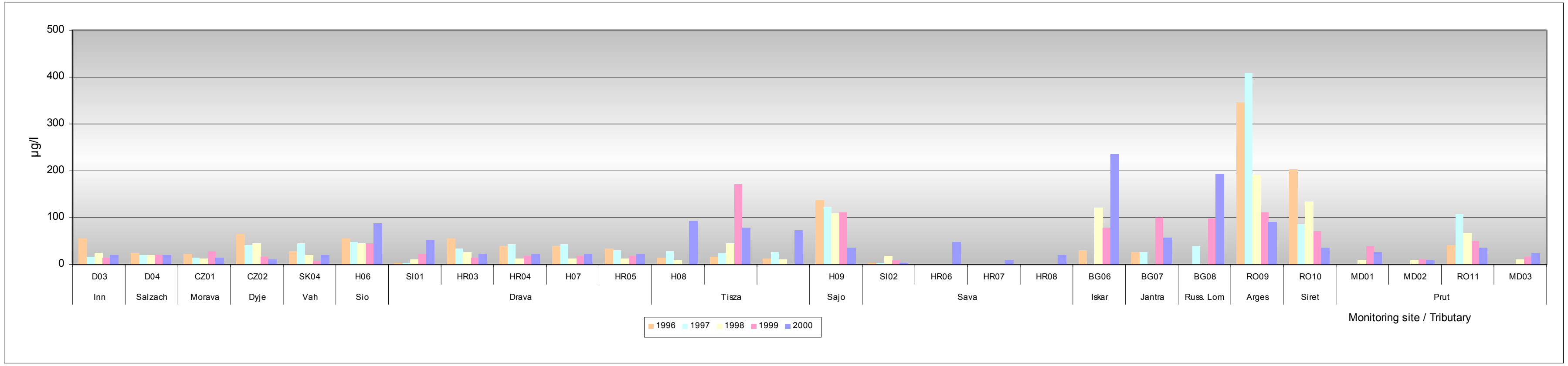

Fig. 8.1.3.46a: Spatial variation of Zn – Tributaries

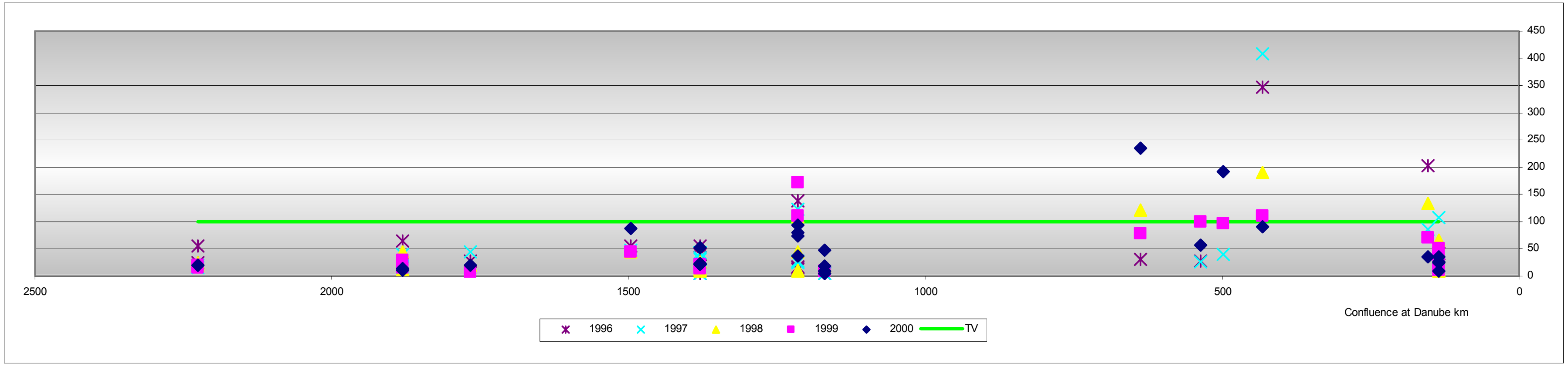

Fig. 8.1.3.46b: Spatial variation of Zn – Tributaries

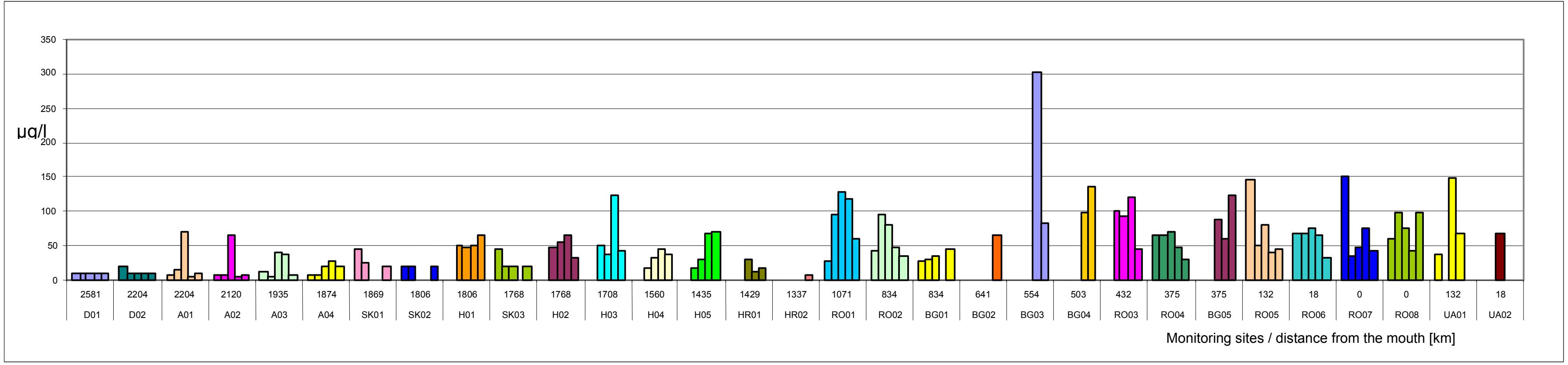

Fig. 8.1.3.47: Temporal trends of Zn – Danube River

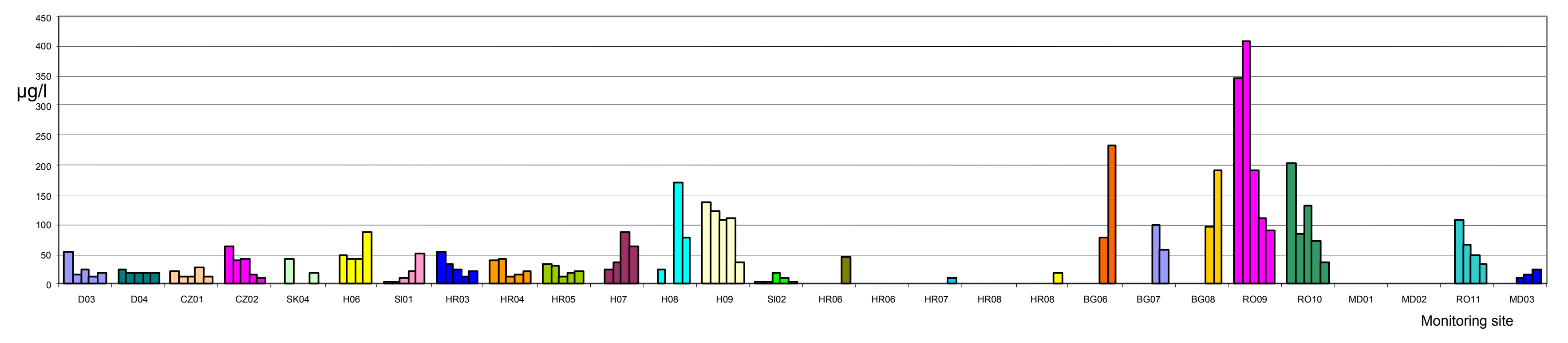

Fig. 8.1.3.48: Temporal trends of Zn – Tributaries

Arsenic, cadmium, chromium, copper, lead, mercury, nickel and zinc in filtered water samples (dissolved forms)

For heavy metals in the filtered water samples (dissolved forms), data are available from 1998 to 2000 only. The monitoring sites for which dissolved forms data are available are located in the upper and in the middle section of the Danube River, the same situation being valid also for the tributaries.

Based on existing data, the **Fig. 8.1.3.49** illustrates the percentage of monitoring sites, which exceed the target limits - for both dissolved and total forms, and for entire studied period (1996 – 2000).

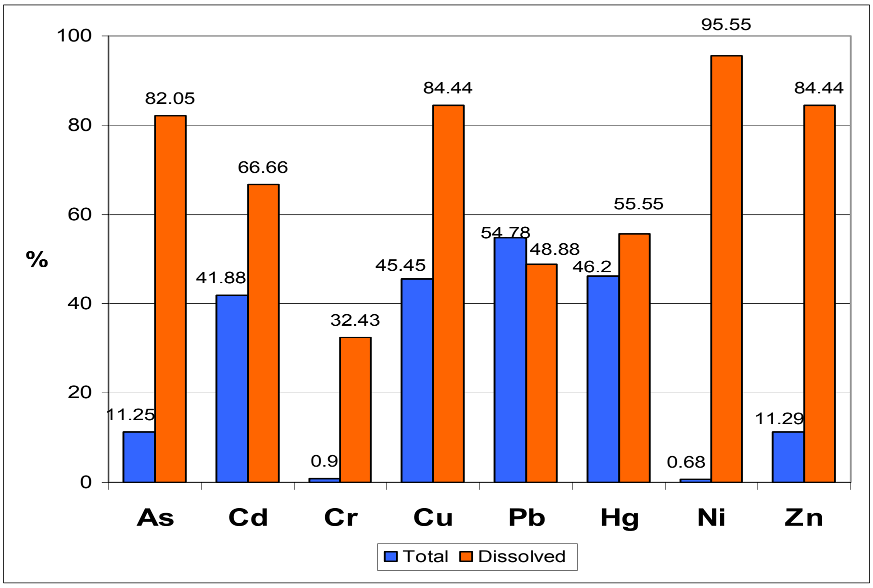

Fig. 8.1.3.49: Total percentage of monitoring sites exceeding target values in period 1996-00

As it can be seen from the figure above, the highest differences between percentages of exceedance based on analysis of total samples and dissolved fraction belong to nickel, chromium, arsenic and zinc, dissolved fractions having much higher percentage of exceedance.

As an overview on heavy metals concentration levels in the Danube River and its main tributaries, the Table 8.1.3.1 shows a comparison of TNMN data for several investigated heavy metals with literature data on river water background concentration, quality targets of other river monitoring networks and of those from water quality classification of MLIM Expert Group Proposal.

Table 8.1.3.1: Comparison of heavy metals concentration in the Danube River and its tributaries with various concentration levels (the concentration ranges are valid for total heavy metals forms)

Metal	**Upper Danube**	**Middle Danube**	**Lower Danube**	**Tributaries**	**Background level [2]**	**Target Value [3] (diss.)**	**Target Value [4] (Total / diss.)**
	Range concentration (min – max) µg/l				**µg/l**		
As	1.00 – 3.27	0.10 – 4.84	0.30 – 11.02	1.00 – 79.36	-	?	5 / 1
Cd	0.10 – 0.66	0.02 – 2.25	0.14 – 29.10	0.02 – 24.18	0.009 – 0.036	0.072	1 / 0.1
Cr	1.00 – 5.00	0.43 – 20.17	5.00 – 97.00	0.10 – 41.00	1.3 – 5.0	3.1	50 / 2

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[2] LAWA Guide

[3] Joint Danube Survey – Technical Report, 2002

[4] MLIM Expert Group Proposal on Water Quality Classification in Danube River Basin

Metal	Upper Danube	Middle Danube	Lower Danube	Tributaries	Background level [2]	Target Value [3] (diss.)	Target Value [4] (Total / diss.)
	Range concentration (min – max) µg/l				**µg/l**		
Cu	2.00 – 10.20	0.73 – 46.98	2.00 – 213.1	0.02 – 102.5	0.5 – 2.0	3	20 / 2
Pb	1.00 – 4.70	0.55 – 17.45	1.00 – 82.00	0.05 – 91.00	0.4 – 1.7	3.4	5 / 1
Hg	0.10 – 0.42	0.03 – 0.82	-	0.08 – 1.54	0.005 – 0.020	0.04	0.1 / 0.1
Ni	1.00 – 5.40	0.39 – 16.21	0.05 – 42.90	0.05 – 79.00	0.6 – 2.2	1.8	50 / 1
Zn	3.90 – 69.00	9.05 – 122.9	18.0 – 288.0	4.0 – 409.0	1.8 – 7.0	7	100 / 5

8.1.4. Oxygen Regime

The natural organic matter occurring in water originates mainly from soil erosion and decomposition of dead plants and animals; it is relatively insoluble and slowly decomposed. Organic matter evolved from various human activities represent one of the most important pollutants discharged into a rivers; it is generally soluble and rapidly divided and decomposed. Since the decomposition of this matter is carried out by microorganisms and requires consumption of oxygen, the assessment of oxygen regime indicators is of a major importance. Hence, the variation of dissolved oxygen in terms of concentration (DO), biochemical oxygen demand (BOD_5) and chemical oxygen demand – both COD-Mn and COD-Cr was taken into account:

Dissolved oxygen

The actual amount of oxygen present is an important water quality parameter. As a general rule, the less of oxygen dissolved in water the worse is the water quality. Therefore, for oxygen low values, described in this report by 10 %-iles, have to be examined. In general the concentration of dissolved oxygen shows strong daily and seasonal variation. Monitoring results are therefore very much dependent on the time of sampling. In periods of high primary production and algae growth concentration may fluctuate for several milligrams per litre.

The distribution of monitoring sites according to the Classification System in the DRB for dissolved oxygen is shown in **Fig. 8.1.4.1**:

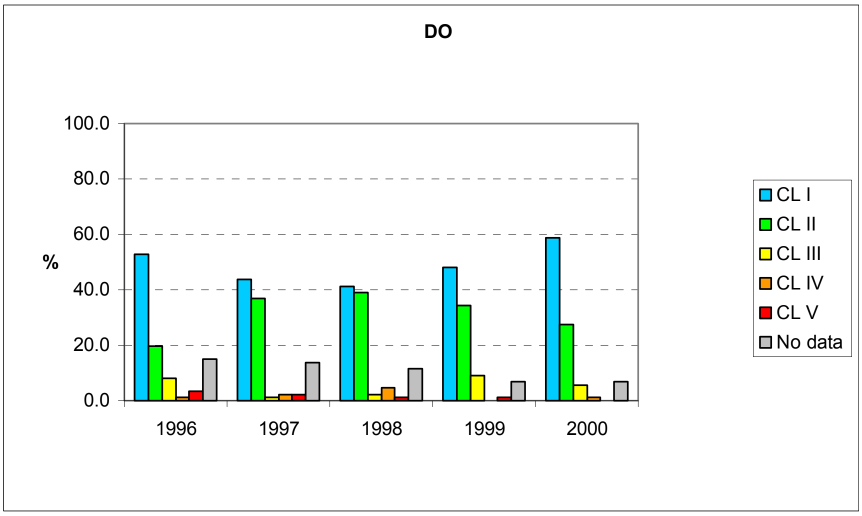


Fig. 8.1.4.1: Distribution of monitoring sites (%) according to the Quality Classification System in the DRB for **DO**

The quality assessment within the five-class system is made on the basis of data reported from 87 monitoring sites (out of the assessment is 16 monitoring sites from Phase I List of Monitoring Sites, in which no measurements had been done in 1996-2000) and the following remarks can be done in this respect:

- the number of monitoring sites within Class I decreases from 1996 to 1998 and then increases until 2000; values above 50% are present in 1996 and 2000 only;
- the monitoring sites within Class II show a maximum percentage in 1998 (when the percentage for Class I is minimum);
- the number within Class III is below 10% in all five years;
- Class IV does not appear in 1997; for the other years, all values are below 5% of the monitoring sites;
- the number of sites within Class V decreases continuously from 1996 to 1999, in 2000 being totally absent, which demonstrates the improving in water quality from the DO point of view;

The spatial pattern of dissolved oxygen concentrations for the Danube River is shown in **Fig, 8.1.4.2a** and **8.1.4.2.b**.

In the upper section, dissolved oxygen values increase from Danube-Neu Ulm (km 2581, D01) to Danube-Wien-Nussdorf (km 1935, A03). In this stretch, all concentrations are above 8.5 mg/l and no value is below the target limit for oxygen (6 mg/l).

In the middle stretch, oxygen concentrations are slightly lower then that from the upper one, but a uniform pattern is present along this stretch. The apparent "V" profile with minimum located at Danube-Medve/Medvedov (km 1806, H01) is caused by the lower Hungarian data in comparison with Slovak data in this cross section. It has to be mentioned that along this stretch no value is below the target limit.

In the first part of the lower section, oxygen c10 values clearly decrease from Danube-Bazias (km 1071, RO01) to Danube-Novo Selo/Pristol (km 834, BG01) by more than 2 mg/l, varying in the range 4.45 – 7.10 mg/l O_2; this situation can be mainly attributable to the Iron Gate Reservoir influence. From Danube- us. Iskar (km 641, BG02) to Danube-us. Russe (km 503, BG04), the dissolved oxygen regime is better, even if due to the lack of some data it is not possible to give a comprehensive picture.

The second part of the lower Danube shows a uniform spatial pattern of dissolved oxygen, the values vary within the range 5.72 – 8.80 mg/l O_2.

For the entire lower Danube, 19 values were below the target limit, with minimums in Danube-Novo Selo/Pristol (km 834, BG01); but especially in 1997-1998 there are remarkable differences in the results reported by Bulgaria and Romania in this river profile (BG01 and RO02) (see Fig. 8.1.4.2a).

The spatial distribution of dissolved oxygen concentrations in selected tributaries is illustrated in **Fig. 8.1.4.3a** and **8.1.4.3b**. It can be mentioned that oxygen content generally decreases, from those located in the upper to those from the lower part. For example, two tributaries from the upper Danube, the Inn-Kirchdorf (D03) and Salzach-Laufen (D04), have a dissolved oxygen concentration ranging between 9.9 – 10.5 mg/l O_2, while for a tributary located in the lower Danube, the Arges-Conf. Danube (RO09), this range is 2.50 – 6.20 mg/l O_2. Similarly, on the Siret-Conf. Danube Sendreni (RO10) and Prut-Conf. Danube Giugiulesti (RO11), rather low values are recorded (2.95 and 2.06 mg/l O_2, respectively).

As concerning the tributaries located in the middle section, the oxygen content is generally lower than in the Danube itself, the minimum values are recorded on the Sio-Szekszard-Palank (H06) and Sava-ds. Zupanja (HR08) – 5.13 and 5.52 mg/l O_2, respectively.

From selected tributaries, 11 values of dissolved oxygen are below the target limit most of them being in the lower Danube - the Arges-Conf. Danube (RO09), Siret-Conf. Danube Sendreni (RO10) and Prut-Conf. Danube Giugiulesti (RO11).

Regarding yearly variations of oxygen it can be concluded, that they do not exceed 1 mg/l at many monitoring sites. In particular the sites at the Danube River remain rather constant. As to the tributaries, Arges (RO09) and Siret (RO10) show the biggest differences between the years.

The temporal trends are illustrated in **Fig. 8.1.4.4** for the Danube River and in **Fig. 8.1.4.5** for selected tributaries. The following trends are visible:

- increasing tendencies were observed in Danube-Neu-Ulm (D01), Danube-Jochenstein (km 2204, D02), Danube-us. Arges (km 432, RO03), Danube-Chiciu/Silistra (km 375, RO04) and Danube-us. Iskar-Bajkal (km 641, BG02);
- slight decreasing tendencies are in Danube-Borovo (km 1337, HR02) and Danube-Pristol/Novo Selo (km 834, RO02);
- the different tendencies at the cross sections at km 834 (RO02/BG01) and km 375 (RO04/BG05) has to be mentioned, the reason of which could be a lower frequencies of measurements in Bulgaria;
- in selected tributaries increasing tendencies were observed in Iskar-Orechovitza (BG06), Arges-Conf. Danube (RO09) and Siret-Conf. Danube Sendreni (RO10).

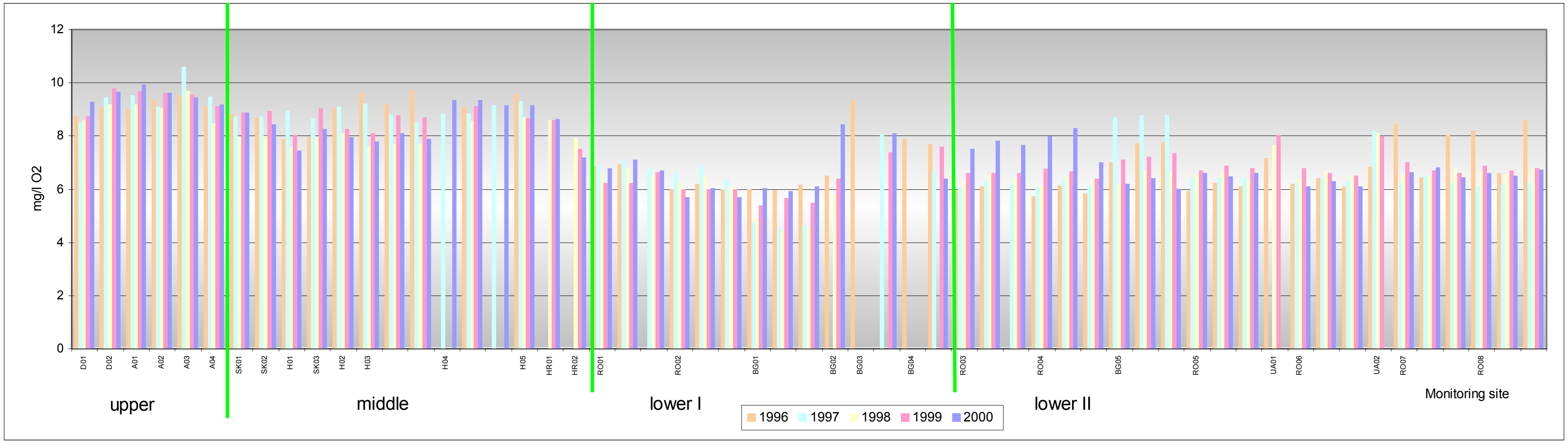


Fig. 8.1.4.2a: Spatial variation of DO – Danube River

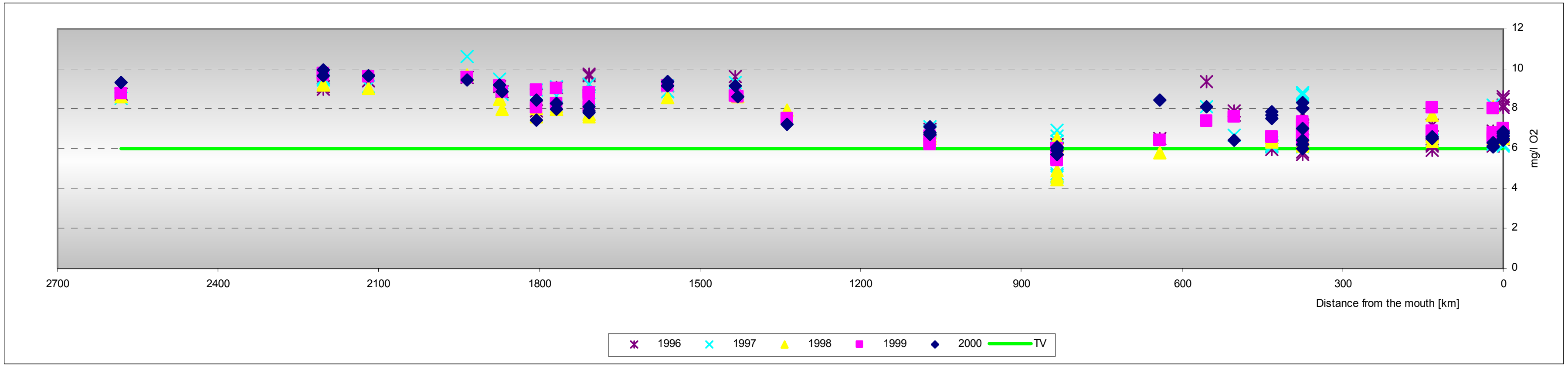


Fig. 8.1.4.2b: Spatial variation of DO – Danube River

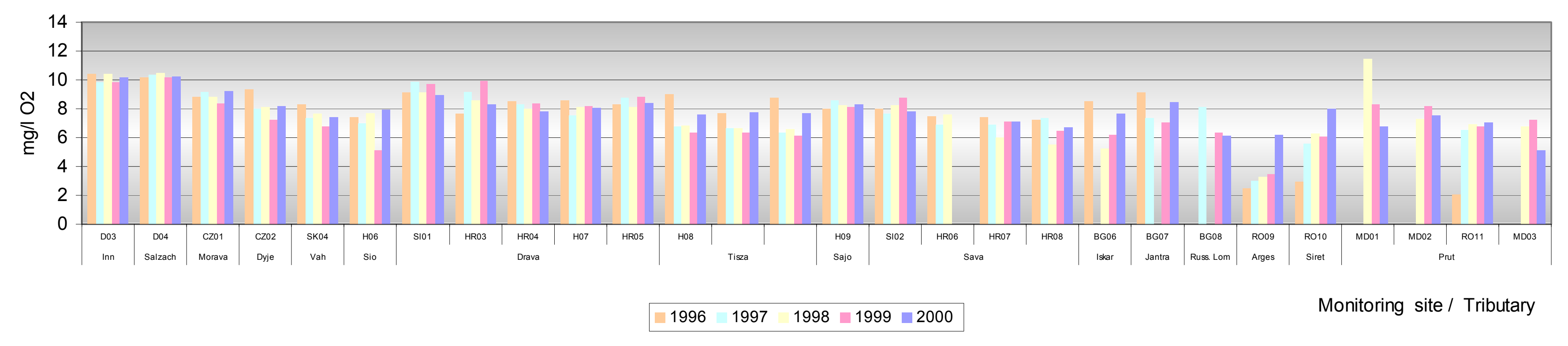


Fig. 8.1.4.3a: Spatial variation of DO – Tributaries

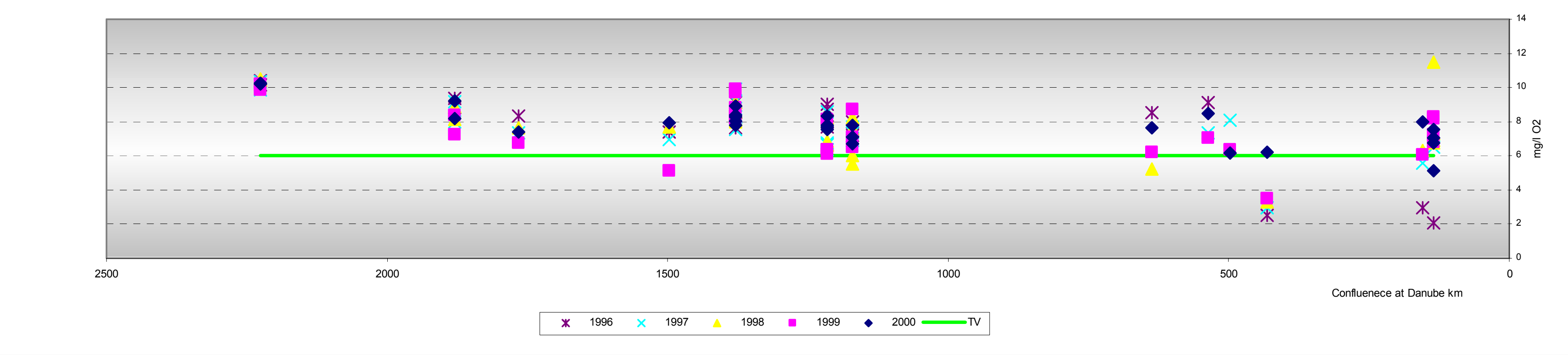


Fig. 8.1.4.3b: Spatial variation of DO – Tributaries

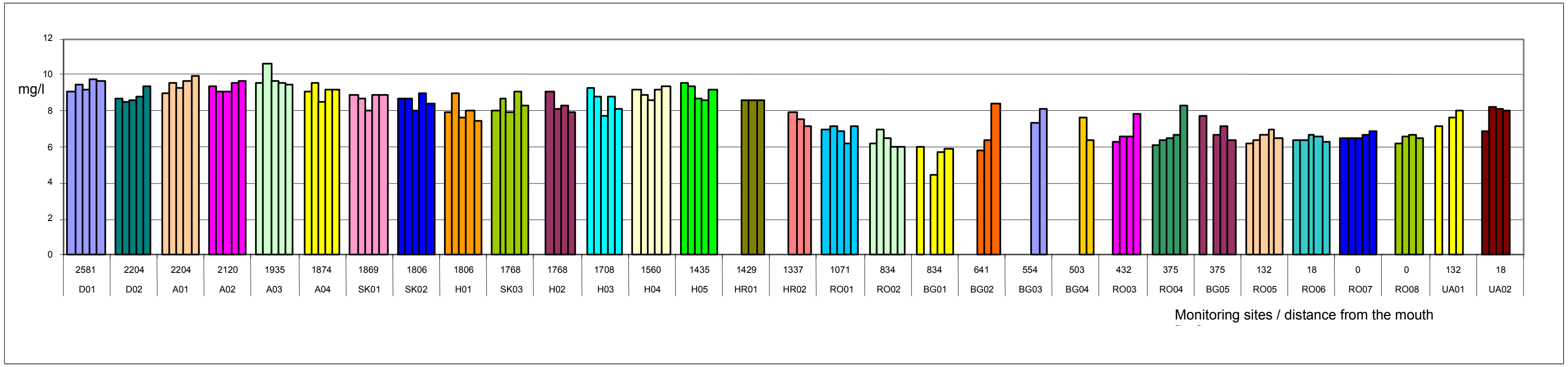


Fig. 8.1.4.4: Temporal trends of DO – Danube River

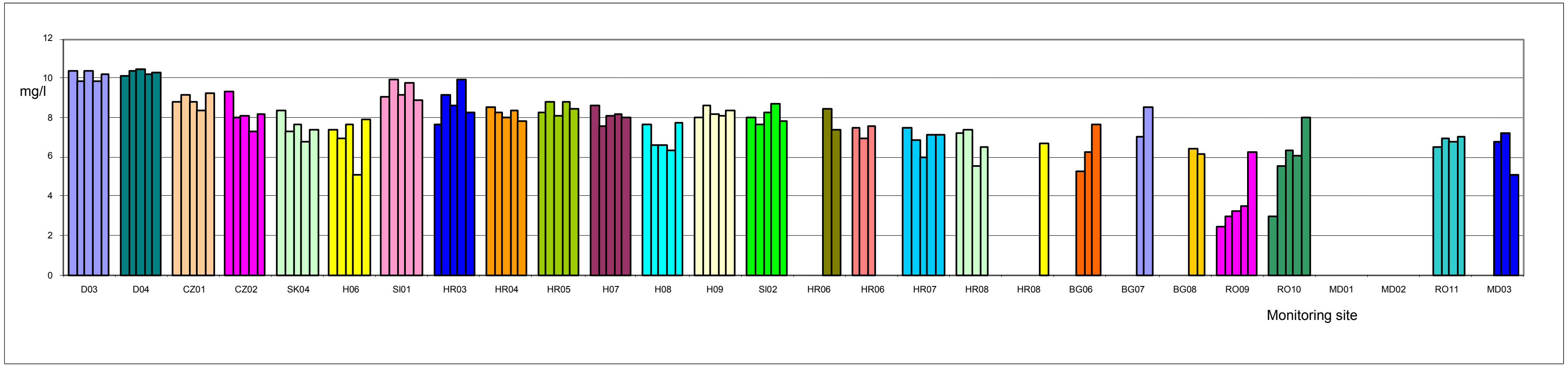


Fig. 8.1.4.5: Temporal trends of DO – Tributaries

In order to have a more comprehensive picture of the dissolved oxygen distribution along the Danube River within the five years time period (1996-2000), beside 10 percentiles both maximum and minimum concentration values were represented for each studied year, separately for the Danube River itself and selected tributaries - **Fig. 8.1.4.6 – 8.1.4.15.**

Table 8.1.4.1.summarizes some relevant data related to oxygen content distribution along the Danube and its tributaries:

Table 8.1.4.1: Ranges of maximum and minimum values for dissolved oxygen concentrations

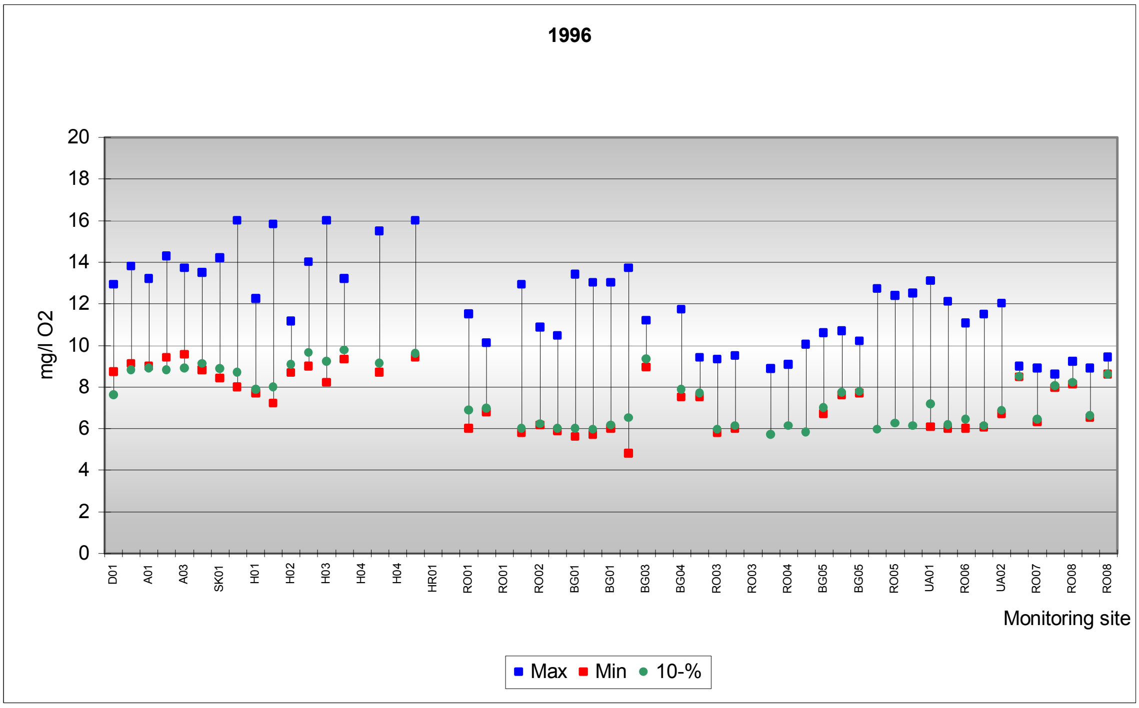
Year	Range of maximum values (mg/l O_2)		Range of minimum values (mg/l O_2)	
	Danube	**Tributaries**	**Danube**	**Tributaries**
1996	8.6 – 16.0	9.1 – 29.5	4.8 – 9.6	2.4 – 10.4
1997	8.3 – 18.3	8.1 – 15.2	3.9 – 9.4	2.3 – 9.9
1998	10.3 – 15.6	8.5 – 17.4	4.3 – 9.2	3.0 – 11.4
1999	8.8 – 15.3	6.4 – 15.3	4.5 – 9.5	2.9 – 9.8
2000	8.5 – 15.6	6.1 – 15.9	4.3 – 9.8	3.7 – 9.9

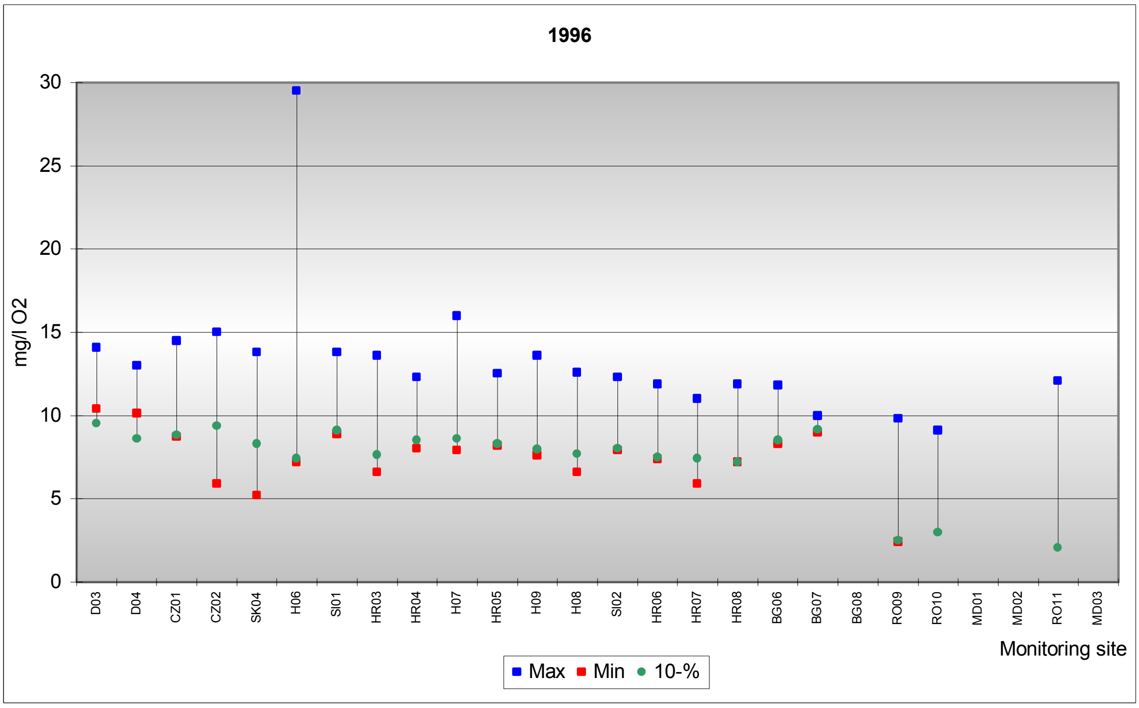
Based on the above mentioned figures and table, the following remarks can be done:

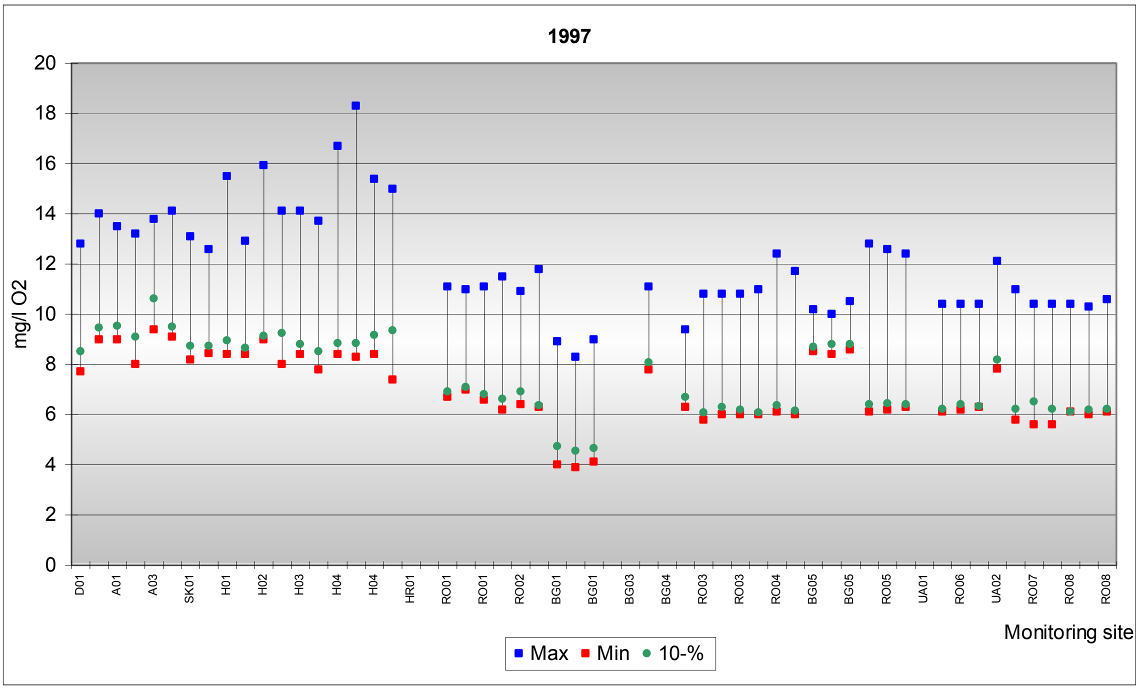
- apart from the extreme values, a relative constancy among the studied years for both minimum and maximum dissolved oxygen ranges is illustrated;
- a closer look should be given to the “top” of the maximum recorded values as well as to the “bottom” of the minimum ones.
    - the maximum-recorded value for the Danube River itself (18.3 mg/l O_2) appears in 1997, at Danube-Dunafoldvar (km 1560, H04);
    - the maximum-recorded value for tributaries (29.5 mg/l O_2) is present in 1996 on the Sio-Szekszard (H06). Other related data - pH = 8.72, BOD_5 = 9.5 mg/l O_2, N-NH_4 = 1.30 mg/l, N-NO_3 = 9.54 mg/l (*TNMN Data Base 1996 - 2000*) - indicate strong pollution by nutrients, allowing excessive growth of primary producers producing an oxygen. Also data obtained in the frame of JDS (*Joint Danube Survey – 2001*) indicated a high value of oxygen content for the Sio-Szekszard (H06) tributary – 18.9 mg/l O_2;
    - the minimum dissolved oxygen concentration on the Danube River (3.9 mg/l O_2) is present in 1997, at Danube-Novo Selo/Pristol (km 834, BG01), but is not in harmony with the observations from Romanian side at the same cross section (6.4 mg/l O_2);
    - the minimum dissolved oxygen concentration for selected tributaries (2.3 mg/l O_2) appears in 1997 and, as well as the most of the minimum recorded values, is specific to the Arges-Conf. Danube. This critical problem is mainly caused by the fact that this tributary regularly serves as recipient of untreated and not adequately treated waste water and its low dilution regime (discharge flows ranging within the range 34.9 – 102.0 m^3/s) cannot compensate these pollution inputs;
- some differentiations can be made among the oxygen contents in the studied years:
    - *1996,* as the first year of TNMN monitoring Programme, is characterized by a scattered profile of both minimum and maximum oxygen concentrations; apart from the above discussed value of 29.5 mg/l O_2, the maximum level of 16.0 mg/l O_2 is met at several monitoring point located on the main course of the Danube and on tributaries: Danube-Medvedov/Medve (km 1806, SK02) even if it doesn’t make a good correlation with the cross reported data (12.2 mg/l O_2 at H01), further in Danube-Szob (km 1708, H03), Danube-Hercegszanto (km 1435, H05) and on the alpine tributary, Drava-Dravaszabolcs (H07);

- *1997*: as it was already mentioned, the maximum recorded value appears at Danube-Dunafoldvar (km 1560, H04); the minimum values profile of the Danube is spatially uniform;
- *1998*: the maximum value (17.4 mg/l O_2) is recorded on the Sio-Szekszard -Palank (H06), but the other maximum concentrations do not exceed 16.0 mg/l O_2. Excepting one already mentioned value, all minimum ones are above 4.0 mg/l O_2;
- *1999* and *2000* present a uniform spatial distribution of maximum and minimum concentration values, ranging between 4.0 and 16.0 mg/l O_2, only one value being outside of this interval.

Fig. 8.1.4.6 – 8.1.4.15: Minimum, maximum and 10%-iles values for Dissolved Oxygen (Danube River and Tributaries)


1996


1996


1997
mg/l O2
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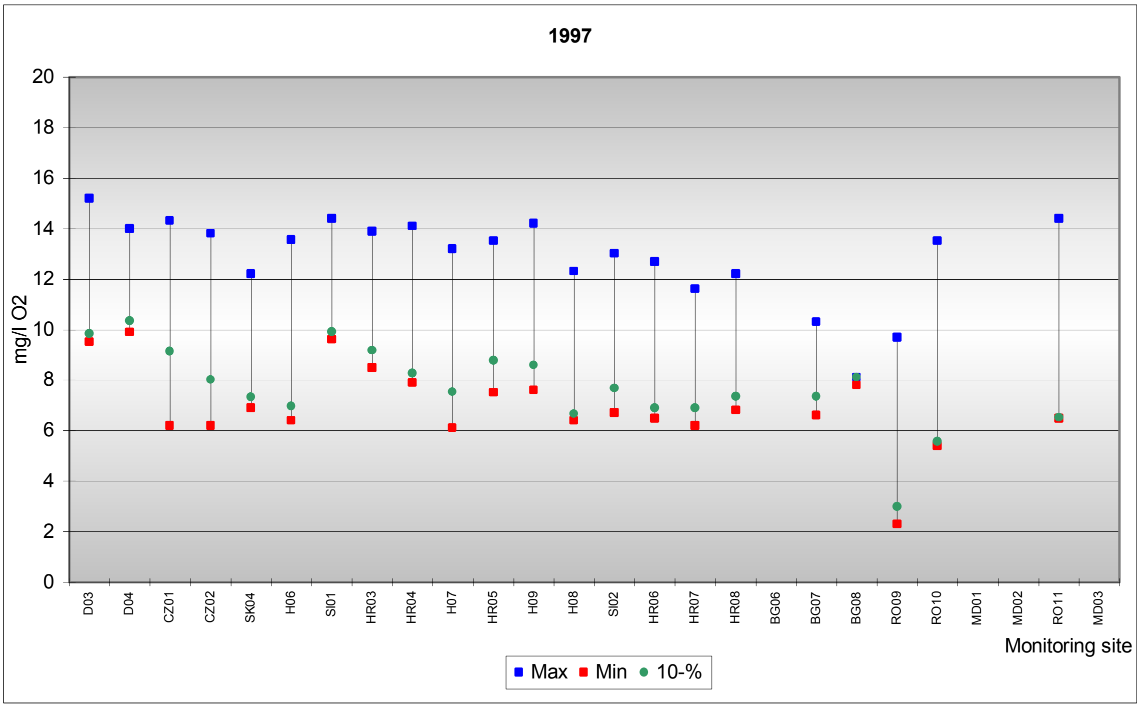
2
4
6
8
10
12
14
16
18
20
D01
A01
A03
SK01
H01
H02
H03
H04
H04
HR01
RO01
RO01
RO02
BG01
BG01
BG03
BG04
RO03
RO03
RO04
BG05
BG05
RO05
UA01
RO06
UA02
RO07
RO08
RO08
Monitoring site
Max
Min
10-%


1997
mg/l O2
0
2
4
6
8
10
12
14
16
18
20
D03
D04
CZ01
CZ02
SK04
H06
SI01
HR03
HR04
H07
HR05
H09
H08
SI02
HR06
HR07
HR08
BG06
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MD01
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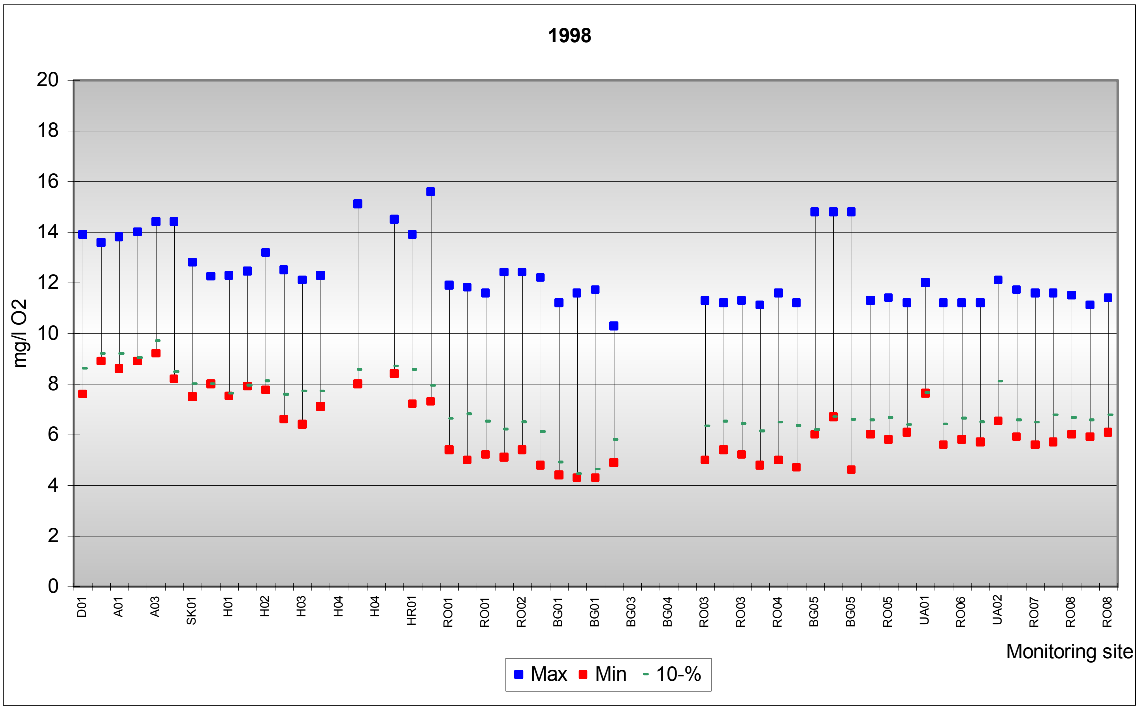
RO11
MD03
Monitoring site
Max
Min
10-%


1998
mg/l O2
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18
16
14
12
10
8
6
4
2
0
D01
A01
A03
SK01
H01
H02
H03
H04
H04
HR01
RO01
RO01
RO02
BG01
BG01
BG03
BG04
RO03
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BG05
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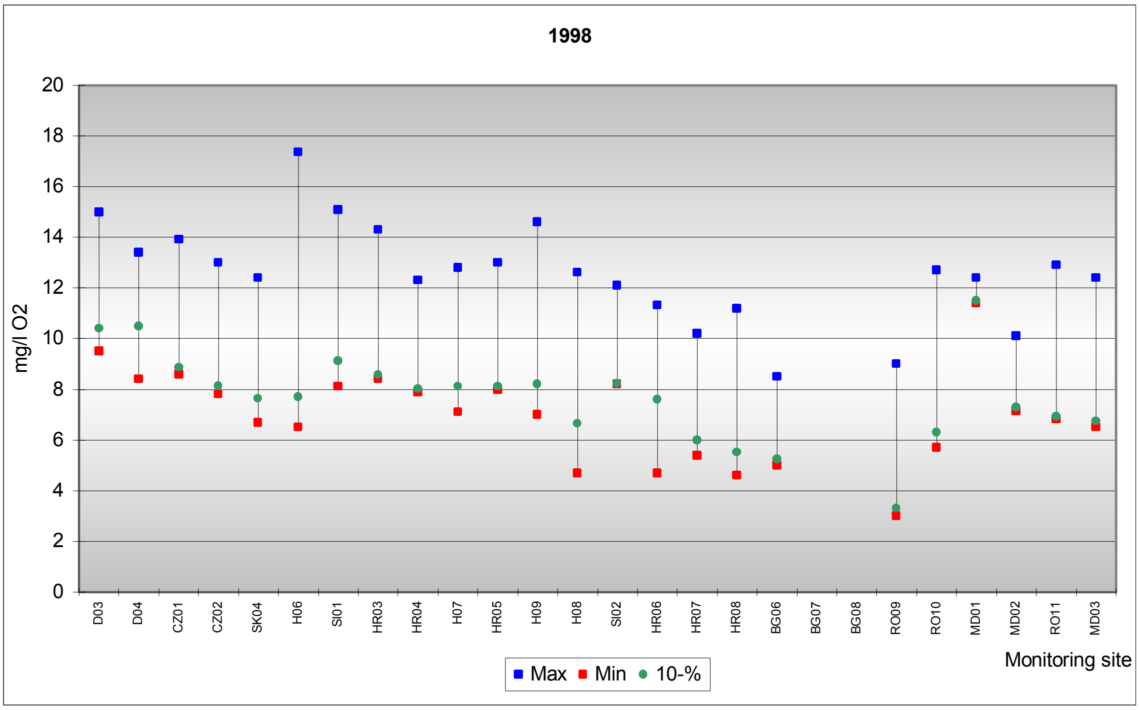
UA01
RO06
UA02
RO07
RO08
RO08
Monitoring site
Max
Min
10-%


1998
mg/l O2
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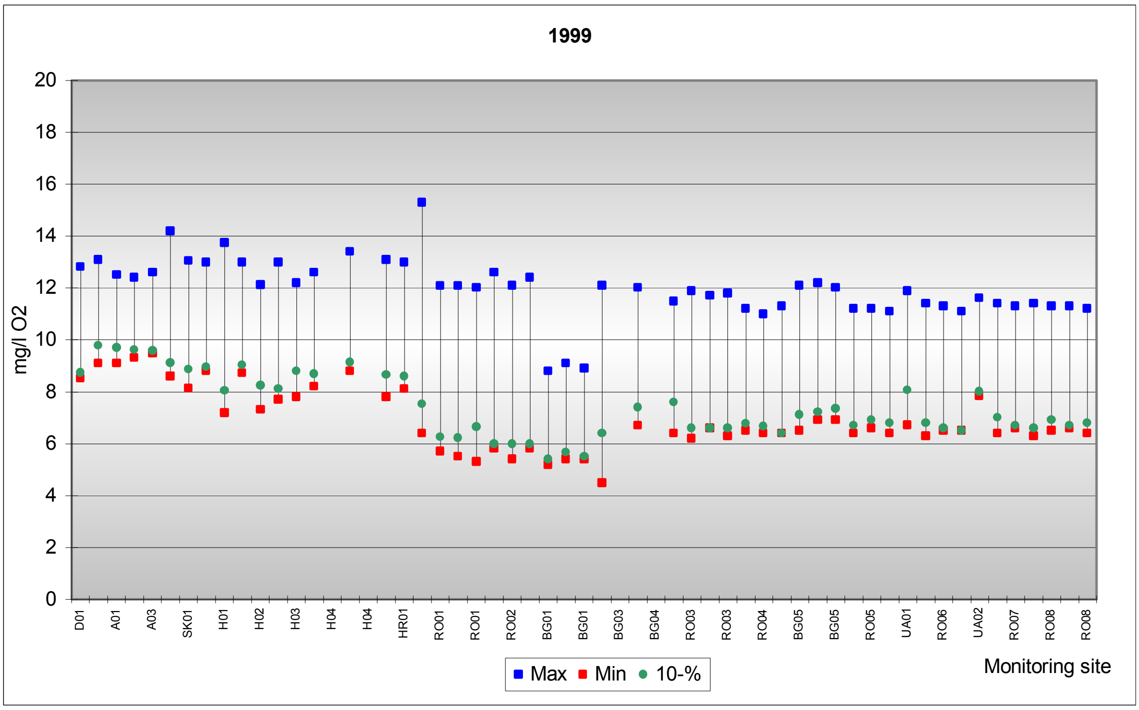
18
16
14
12
10
8
6
4
2
0
D03
D04
CZ01
CZ02
SK04
H06
SI01
HR03
HR04
H07
HR05
H09
H08
SI02
HR06
HR07
HR08
BG06
BG07
BG08
RO09
RO10
MD01
MD02
RO11
MD03
Monitoring site
Max
Min
10-%


1999
mg/l O2
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2
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6
8
10
12
14
16
18
20
D01
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A03
SK01
H01
H02
H03
H04
H04
HR01
RO01
RO01
RO02
BG01
BG01
BG03
BG04
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Max
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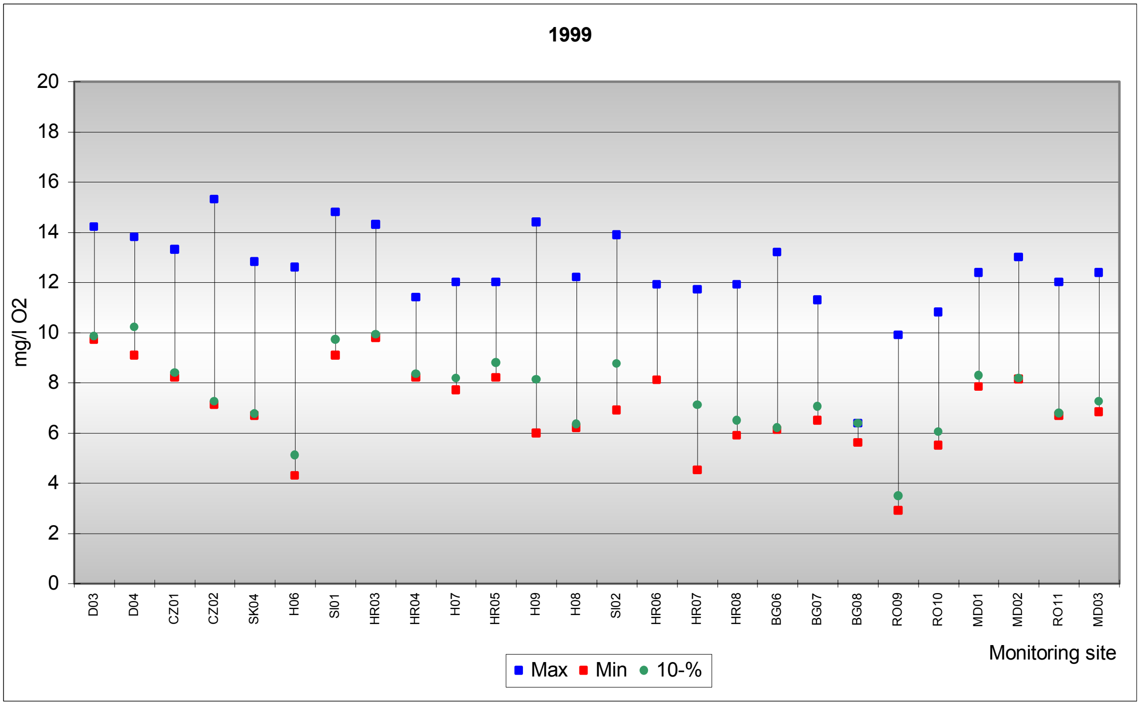
10-%
Monitoring site


1999
mg/l O2
0
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4
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10
12
14
16
18
20
D03
D04
CZ01
CZ02
SK04
H06
SI01
HR03
HR04
H07
HR05
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SI02
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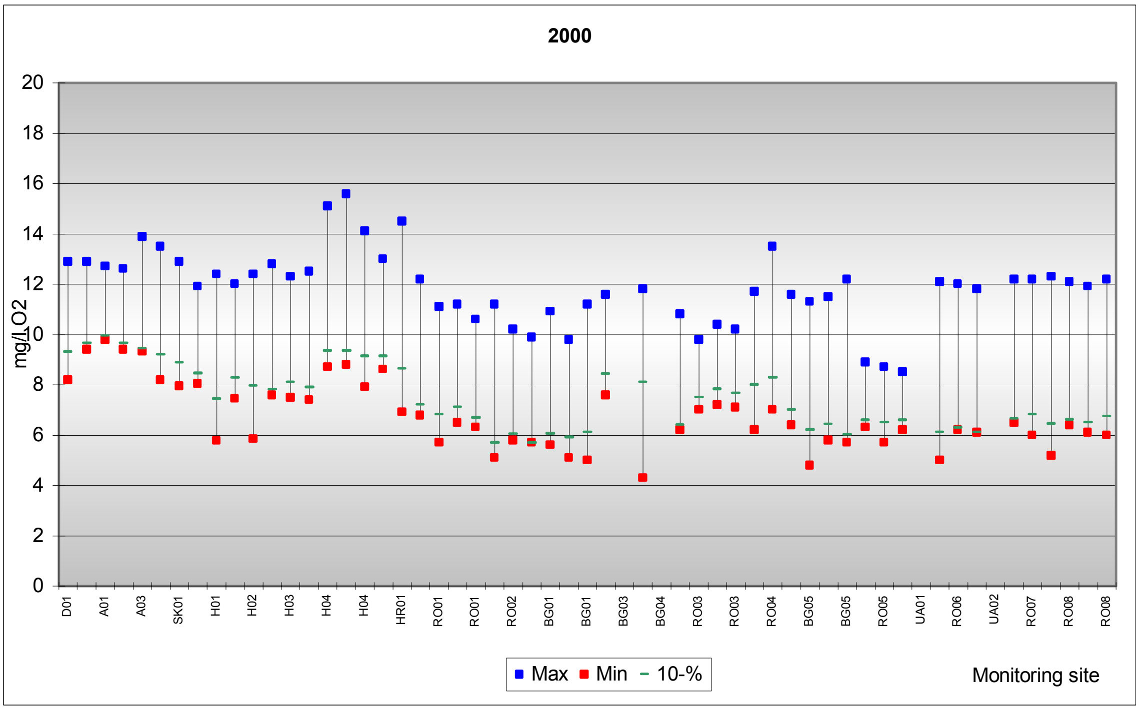
10-%
Monitoring site


2000
mg/l O2
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16
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D01
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SK01
H01
H02
H03
H04
H04
HR01
RO01
RO01
RO02
BG01
BG01
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UA01
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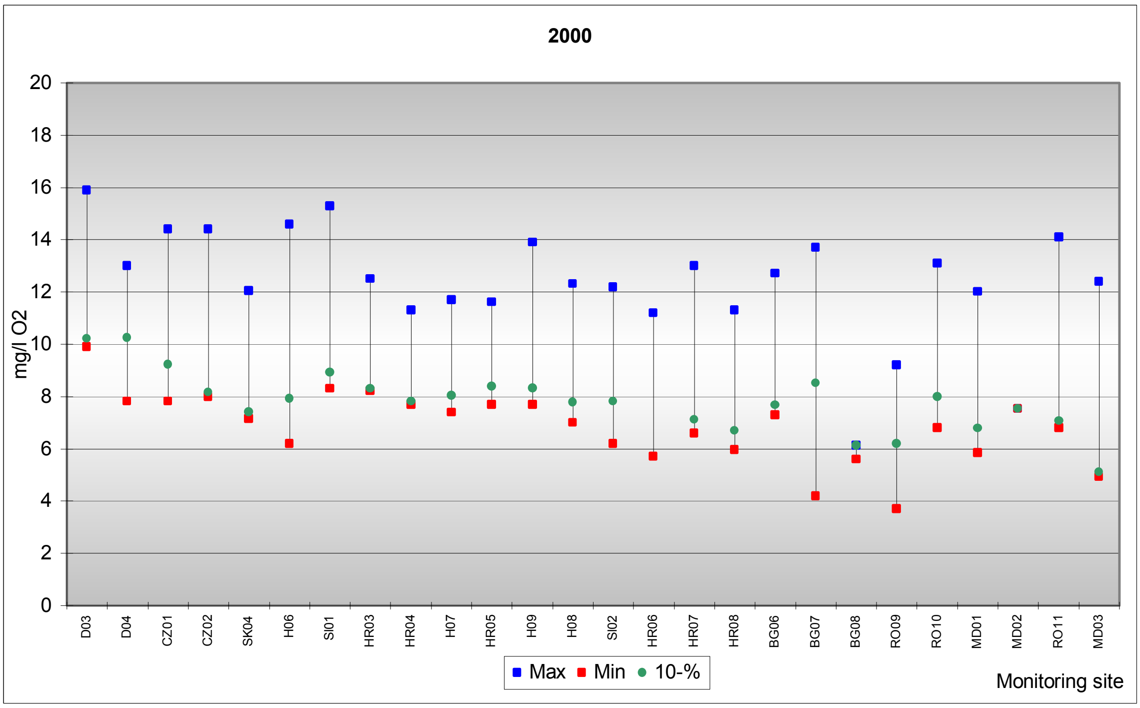
RO08
■ Max ■ Min – 10-%
Monitoring site


2000
mg/l O2
20
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16
14
12
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4
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D03
D04
CZ01
CZ02
SK04
H06
SI01
HR03
HR04
H07
HR05
H09
H08
SI02
HR06
HR07
HR08
BG06
BG07
BG08
RO09
RO10
MD01
MD02
RO11
MD03
■ Max ■ Min ● 10-%
Monitoring site

Biochemical and Chemical Oxygen Demand

Because microorganisms mediate the composition of organic matter and it is an oxygen consuming process, the amount of organic matter in a water body is measured in terms of biochemical and chemical oxygen demand. Thus, in order to evaluate the temporal variation of organic matter content in the longitudinal profile of the Danube River and in its selected tributaries, BOD_5, COD-Mn and COD-Cr are the determinands that were taken into account in this respect.

Biochemical Oxygen Demand (BOD_5)

The distribution of monitoring sites according to the Classification System in the DRB for **BOD_5** is shown in **Fig. 8.1.4.16**:

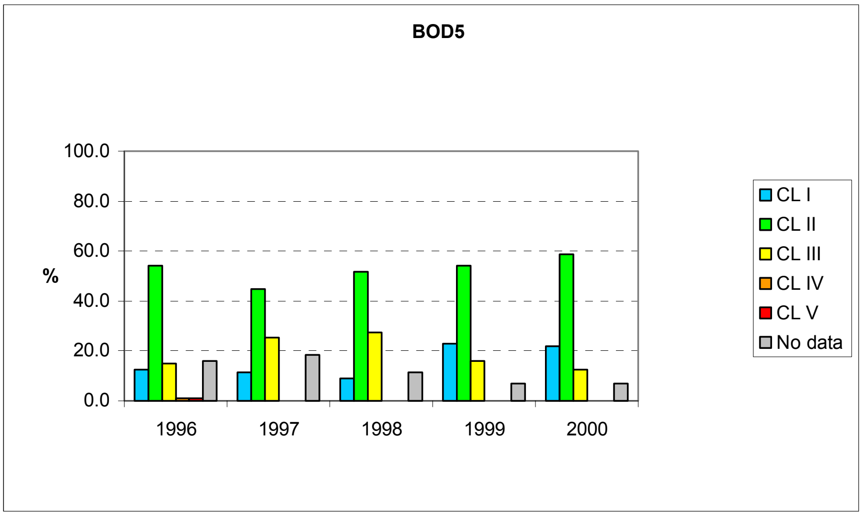

Fig. 8.1.4.16: Distribution of monitoring sites (%) according to the Quality Classification System in the DRB for **BOD_5**

The assessment is made based on data reported from 87 monitoring sites (out of the assessment is 16 monitoring sites from Phase I List of Monitoring Sites, in which no measurements had been done in 1996-2000):

- the percentage of monitoring sites within Class I is below 25% during the entire time period;
- the maximum percentages belong to Class II and the values within this quality class increase from 44.8 % in 1997 to 58.6 % in 2000;
- the number of sites within Class III increases from 1996 to 1998 up to 27.6 % and decrease until 2000 down to 12.6 %;
- Class IV and V are present in 1996, at 1.1 % of all monitoring sites only.

The spatial variation of BOD_5 values for the Danube River is illustrated in **Fig. 8.1.4.17a** and **8.1.4.17b**.

In the upper section of the Danube, BOD_5 values increase from Danube- Neu-Ulm (km 2581, D01) to Danube-Wolfsthal (km 1874, A04), excepting the monitoring site located at Danube-Wien –Nussdorf (km 1935, A03). It has to be mentioned that in the upper Danube two values are below 2 mg/l O_2, indicating no human activities impact (*The Dobris Assessment, 1991),* but two values are above the target limit for BOD_5.

In the middle stretch, a relative constancy (2.0 – 4.6 mg/l O_2) is visible from Danube-Bratislava (km 1869, SK01) to Danube-Szob (km 1708, H03). In this point - the confluence with the Ipoly tributary – values are within the interval 4.4 – 5.6 mg/l O_2. The spatial increasing pattern is valid also down to

Danube-Hercegszanto (km 1435, H05), where BOD_5 reaches 8.2 mg/l O_2, the maximum obtained value for the Danube River. For the middle stretch, 15 BOD_5 values are above the target limit, mainly located in the stretch from Danube-Szob (km 1708, H03) to Danube-Borovo (km 1337, HR02).

Longitudinal assessment in the first part of the lower Danube shows a different spatial variation of BOD_5 values, it depends on the cross section data at which the reference is made to: a uniform spatial profile if the Danube-Pristol/Novo Selo (km 834, RO02) data are taken into account and a spatial decreasing if the Danube- Novo Selo/Pristol (km 834, BG01) data are considered. (Actually, the differences between the data reported in 1997 are serious: from 6.1 mg/l O_2 in RO02 to 2.1 mg/l O_2 in BG01). Even if the interpretation is quite problematic, it can be estimated that a uniform level is valid for this stretch.

The second part presents a uniform spatial pattern from Danube-us. Arges (km 432, RO03) and the three arms of the delta, with BOD_5 values within the range 1.8 – 5.5 mg/l O_2.

Generally can be said that along the Danube the organic pollution expressed by BOD increases, reaching maximum values in the section from Danube-Dunafoldvar (rkm 1560, H04) to Danube-Pristol/Novo Selo (rkm834, RO02). Here is also the highest frequency of exceedance of target value recorded in 5-years evaluation period. In addition, in this section there is the highest year-to-year variability of values, reaching in some cases even more than 3 mg/l.

For selected tributaries, the BOD_5 values are illustrated in **Fig. 8.1.4.18a** and **8.1.4.18b**. The following remarks can be done:

- even if in the upper and in the middle Danube, the Morava-Lanzhot (CZ01), Dyje-Pohansko (CZ02) and Sio-Szekszard (H06) have values above the target limit, the general spatial pattern of BOD_5 values is decreasing down to Tisza tributary, with no big differences between the tributaries and the Danube itself;
- in the lower section, BOD_5 values are slightly higher for the right side tributaries - the Iskar-Orechovitza (BG06), Jantra-Karantzi (BG07) and Russenski Lom-Basarbovo (BG08), but the most critical problem occurs on the Arges-Conf. Danube (RO09), where an extreme value (60.5 mg/l O_2) is recorded in 1996;
- for all selected tributaries, 46 BOD_5 values exceed the target limit; most likely, the main reason for this exceeding is existence of significant point sources of pollution in some cases in combination with low flows.

The temporal trends of BOD_5 are illustrated in **Fig. 8.1.4.19** for the Danube River and in **Fig. 8.1.4.20** for tributaries. Several different trends can be noticed:

- decreasing from 1997 or 1998 to 2000 from Danube-Neu Ulm (km 2581, D01) to Danube-Abwinden-Asten (km 2120, A02), at the cross sections Danube-Medve/Medvedov/Medve (km 1806, SK02/H01) and Danube-Komarom/Komarno/Komarom (km 1768, SK03/H02), from Danube-Borovo (km 1337, HR02) to Danube-Bazias (km 1071, RO01), in Danube-Reni/Chilia arm/Kilia arm (km 132, RO05), Danube-Vilkov/Kilia arm/Chilia arm (km 18, UA02);
- increasing from 1996 to 1997 or 1998 followed by a decreasing until 2000 at Danube-Dunafoldvar (km 1560, H04), Danube-Hercegszanto (km 1435, H05) and from Danube-Chiciu/Silistra (RO04) to Danube-Sulina/Sulina arm (km 0, RO07);
- regarding tributaries, a decreasing trend for BOD_5 can be observed in Inn (D03), Salzach (D04), Dyje (CZ02), Vah (SK04) Drava (HR03, HR04,HR05, H07) and Arges (RO09), whilst the sites at Tisza River (H08) ad its tributary Sajo (H09) show a reverse behaviour.

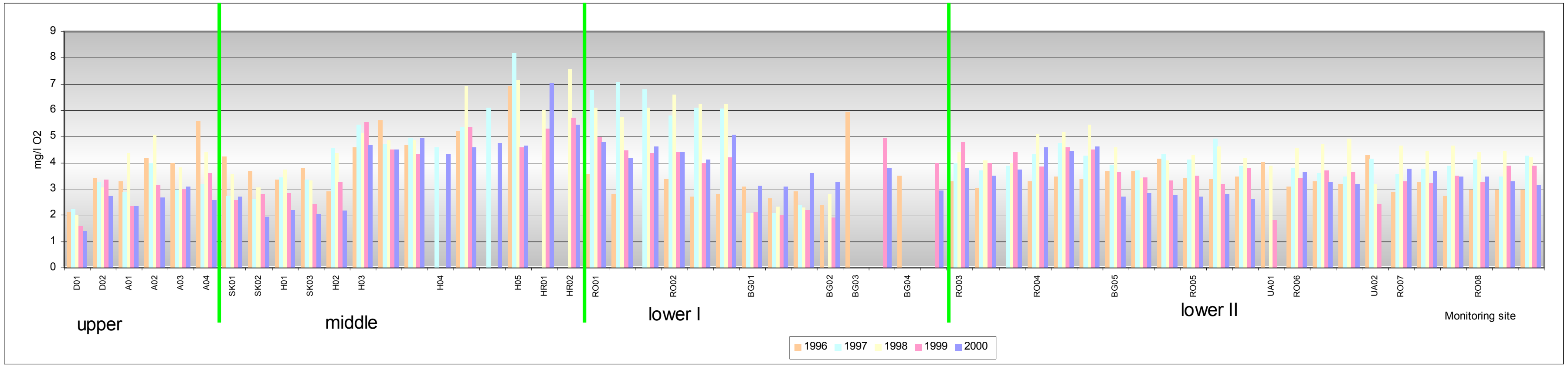

Fig. 8.1.4.17a: Spatial variation of BOD$_5$ – Danube River

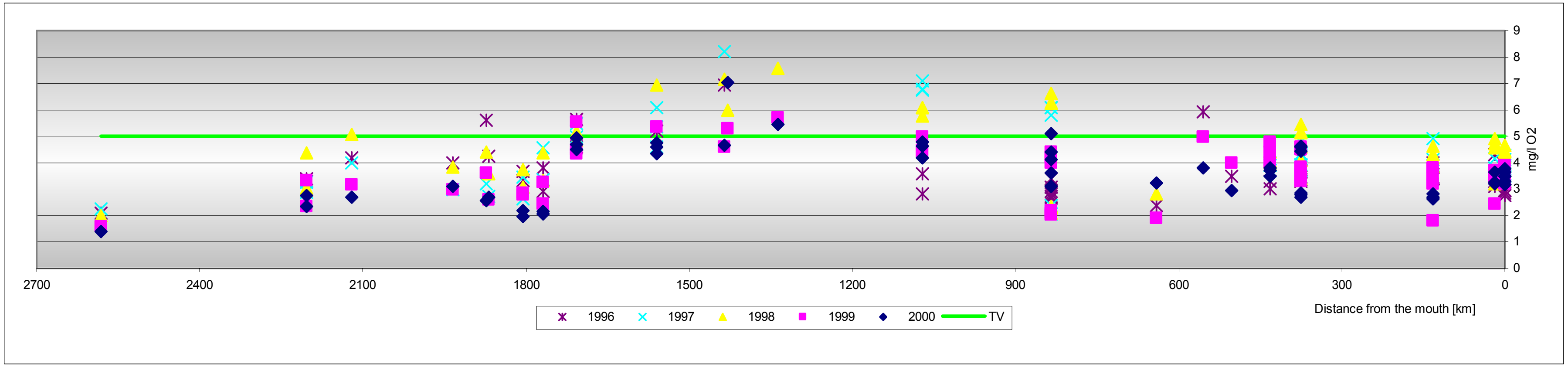

Fig. 8.1.4.17b: Spatial variation of BOD5 – Danube River

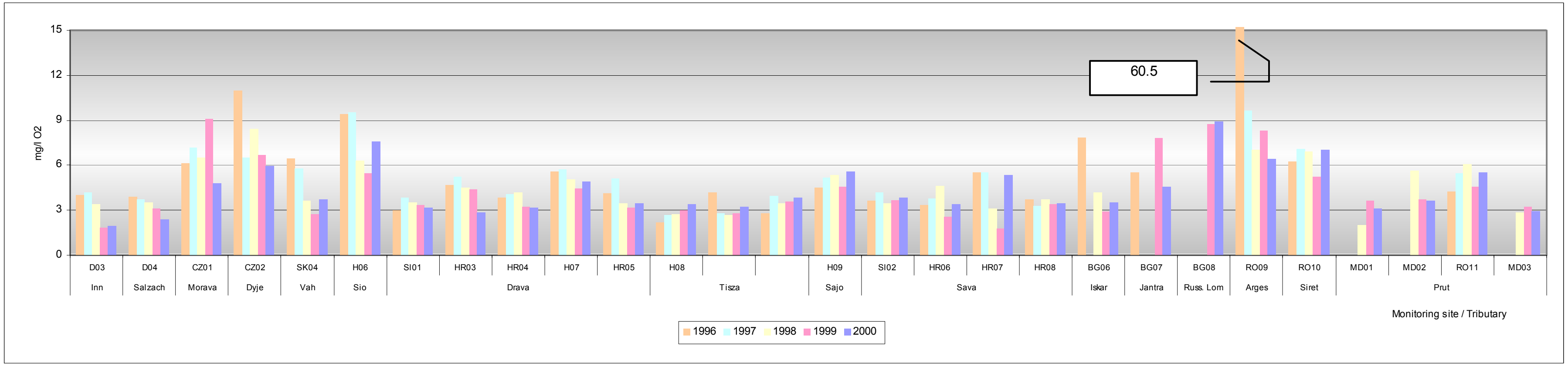

Fig. 8.1.4.18a: Spatial variation of BOD5 – Tributaries

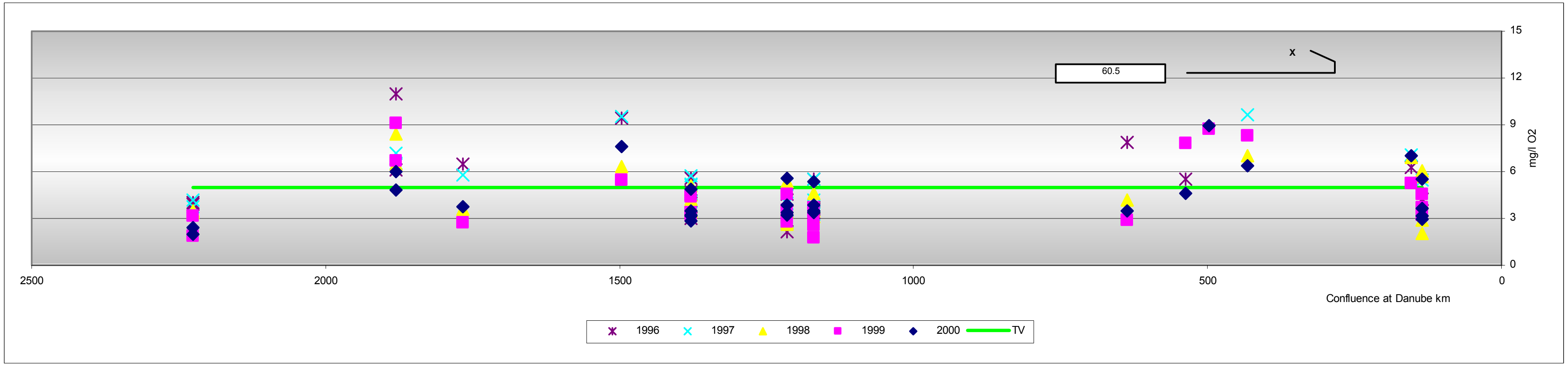

Fig. 8.1.4.18b: Spatial variation of BOD5 – Tributaries

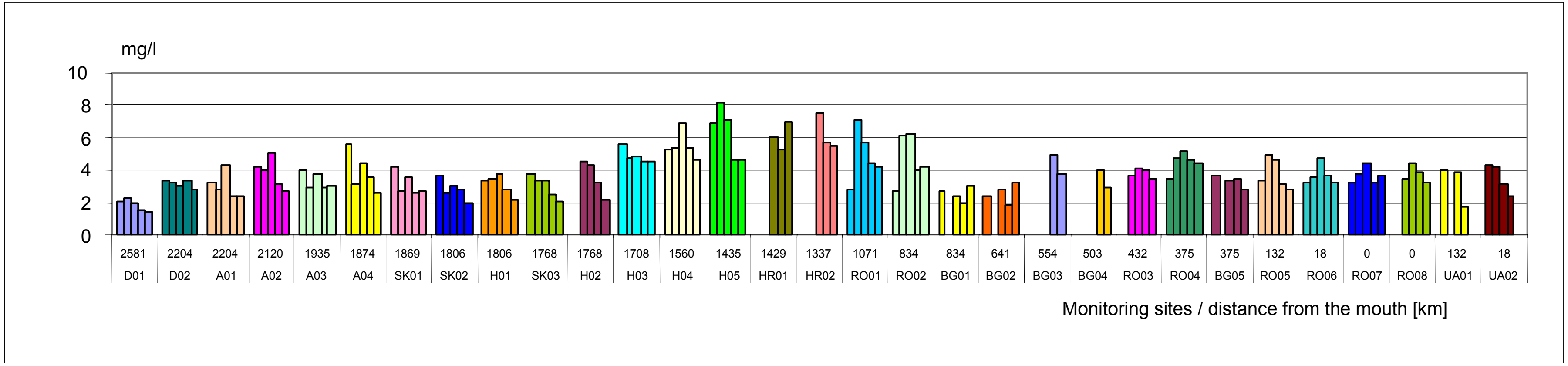

Fig. 8.1.4.19: Temporal trends of BOD5 – Danube River

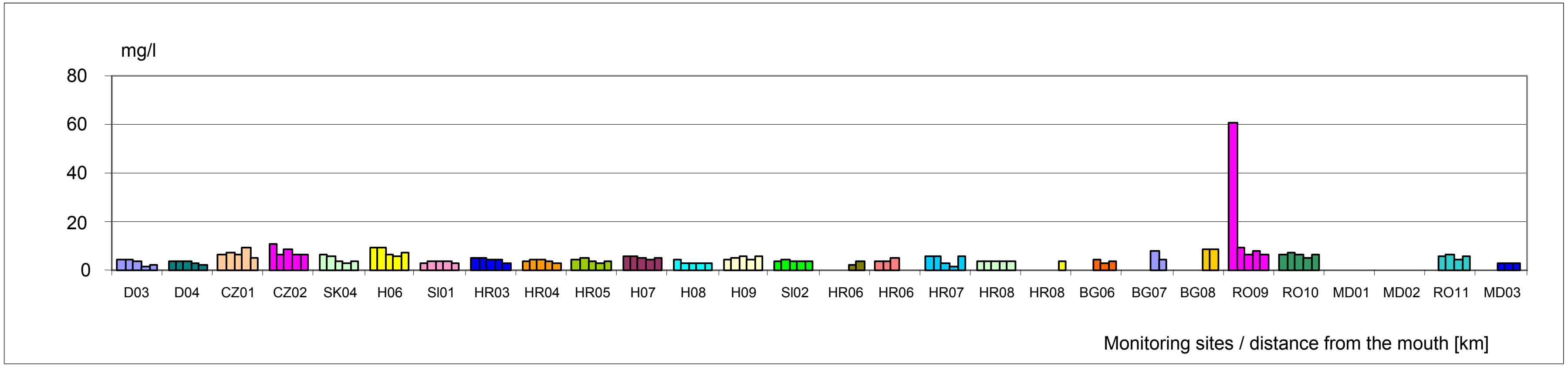

Fig. 8.1.4.20: Temporal trends of BOD5 – Tributaries

Chemical Oxygen Demand

COD-Mn and COD-Cr

The other two determinands that illustrate the presence of oxygen-consuming compounds in the water column are COD by $KMnO_4$ and $K_2Cr_2O_7$ methods.

The distribution of monitoring sites according to the Classification System in the DRB for **COD-Mn** is shown in **Fig. 8.1.4.21**:

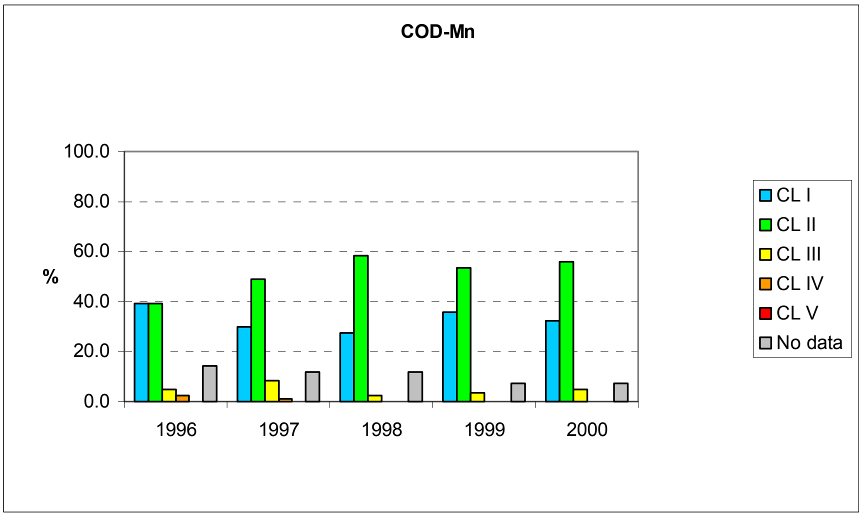

Fig. 8.1.4.21: Distribution of monitoring sites (%) according to the Quality Classification System in the DRB for **COD-Mn**

For COD-Mn, the assessment is made based on data reported from 84 monitoring sites (out of the assessment is 19 monitoring sites from Phase I List of Monitoring Sites, in which no measurements had been done in 1996-2000):

- Class I is represented by less than 40 % of all monitoring sites;
- excepting 1996, when the number of monitoring sites within Class I is identical to that specific to Class II (39.3%), for all the other studied years the maximum percentages belong to Class II, in the range of 48.8 % in 1997 –58.3 % in 1998;
- Class III is represented by low percentages in all five years, within the range from 2.4 % in 1998 – 8.3 % in 1997;
- Class IV appears only in 1996 and 1997 (at 2.4 % and 1.2 % of sites respectively);
- no monitoring site shows values within Class V;

The distribution of monitoring sites according to the Classification System in the DRB for **COD-Cr** is shown in **Fig. 8.1.4.26**:

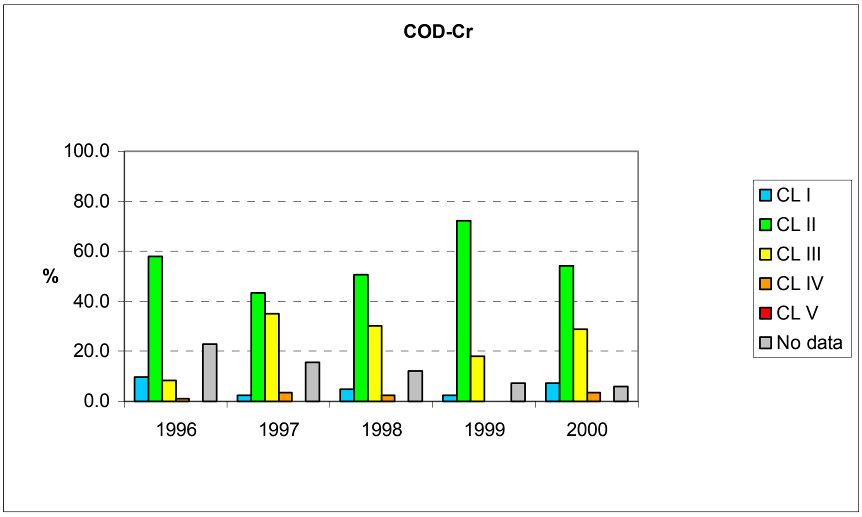

Fig. 8.1.4.26: Distribution of monitoring sites (%) according to the Quality Classification System in the DRB for **COD-Cr**

For COD-Cr, the assessment is made based on data reported from 83 monitoring sites (therefore, out of the assessment is 20 monitoring sites from Phase I List of Monitoring Sites, in which no measurements had been done in 1996-2000):

- Class I is represented by low number of sites, with a minimum of 2.4 % in 1997 and 1999 and a maximum of 9.6 % in 1996;
- the maximum percentages from all sites belong to Class II each year: in 1997 only, less than 50 % of the monitoring sites belong to this class, all the other values are above this level;
- Class III has an uneven distribution, with percentages within the range 8.4 % in 1996 up to 34.9 % in 1997;
- only few monitoring sites show values within Class IV, the maximum being 3.6 % in 1997 and 2000;
- similarly to COD-Mn, no monitoring site is described by COD-Cr values within Class V.

The spatial distributions of COD-Mn and COD-Cr values for the Danube River are shown in **Fig. 8.1.4.22a, 8.1.4.22b** and **Fig. 8.1.4.27a, 8.1.4.27b,** respectively.

In the upper section of the Danube River, both determinands present a uniform spatial pattern, with variation intervals of 1.8 – 6.1 mg/l O_2 for COD-Mn and 8.9 – 19.2 mg/l O_2 for COD-Cr. For monitoring sites located in this stretch, no value is above the target limits (10.0 mg/l O_2 for COD-Mn and 25.0 mg/l O_2 for COD-Cr).

Middle stretch is characterized by slightly higher values than the upper part for both determinands. But, unlike the COD-Mn for which no value is above the target limit in this stretch, for COD-Cr four values exceeded this limit.

For COD-Mn, the first part of the lower Danube is characterized by higher values than the middle stretch, within the range 2.8 – 9.6 mg/l O_2. A similar pattern as for BOD_5 is valid at the cross section from Danube-Pristol Novo Selo/Pristol (km 834, RO02/BG01), where again the differences between the recorded data by two countries are noticeable. For COD-Cr spatial pattern is uniform, with values within the range 11.5 – 23.9 mg/l O_2, only one value reaching 30.0 mg/l O_2 level.

The second part of the lower Danube shows a uniform line for COD-Mn. However, slightly increased values are noticed at Danube-Chiciu/Silistra (km 375, RO04), with values within the range 5.5 – 10 mg/l O_2. COD-Cr pattern is characterized by an increasing values from Danube-us. Arges (km 432, RO03) down to the three main arms of the Danube Delta. The maximum value (58.0 mg/l O_2) appears at Danube-Sulina/Sulina arm (km 0, RO07).

For the entire lower Danube, no COD-Mn value is above the target limit, but 51 values exceed this limit for COD-Cr – few of them in the middle section, but most of them in the lower Danube section. It also should be mentioned that yearly variation of COD-Mn and COD-Cr is much higher in the lower Danube section than in the upper and middle ones.

The spatial pattern of COD-Mn and COD-Cr values for selected tributaries are shown in **Fig.8.1.4.23a**, **8.1.4.23b** and **8.1.4.28a**, **8.1.4.28b** respectively. The following remarks can be done in this respect:

- in the upper section Morava-Lanzhot (CZ01) and Dyje-Pohansko (CZ02) are characterized by rather high values, in Dyje exceeding 10.0 mg/l in COD-Mn and 40.0 mg/l in COD-Cr;
- in the middle stretch Sio-Szekszard (H06) presents relatively higher values, with intervals of 14.7 – 16.5 mg/l O_2 for COD-Mn and 33.5 – 49.2 mg/l O_2 for COD-Cr, but still these are not extreme values for a tributary;
- in the first part of the lower Danube, only one tributary located in this section, the Jantra-Karantzi (BG07) shows higher organic matter content with values up to 33.8 mg/l and 90.4 mg/l using COD-Mn and COD-Cr, respectively;
- in the second part of the lower Danube stretch, concerning COD-Mn, three tributaries along this stretch – the Arges-Conf. Danube (RO09), Siret-Conf. Danube Sendreni (RO10) and Prut-Conf. Danube Giurgiulesti (RO11) - do not present extreme values for this determinand; COD-Cr values are above level 50.0 mg/l O_2 on the Siret-Conf. Danube Sendreni (RO10) and Prut-Conf. Danube Giurgiulesti (RO11), but they are not much different from the values recorded on the main delta arms;
- concerning the exceeding quality target for selected tributaries, 22 values are above this limit for COD-Mn and 46 for COD-Cr.

The temporal trends for the Danube River are illustrated in **Fig. 8.1.4.24** and **8.1.4.29**. For selected tributaries, the trends are shown in **Fig. 8.1.4.25** and **8.1.4.30**:

- for COD-Mn, the following temporal changes are observed for the Danube River and its tributaries:
    - slight increasing tendency in monitoring sites from Danube-Jochenstein (km 2204, D02) to Danube-Bratislava (km 1869, SK01);
    - most of the monitoring sites from the middle Danube are characterized by slight decreasing trend from 1996 to 2000;
    - in the lower Danube, most of the sites do not indicate any clear trend, high values were observed mainly in 1997 and 1998;
    - from tributaries, slight increasing trend is visible in Sajo-Sajopuspoki (H09); all the others are characterized either by stationary state or decreasing trends;
- for COD-Cr, the following was observed for the Danube River and its tributaries:
    - in the upper and middle Danube, most of the monitoring sites present a “V” temporal profile, with lower values in 1998 and 1999 or a decreasing trend;
    - concerning the sites located in the lower Danube, in its second part – downstream Danube-Chiciu/Silistra (rkm 375, RO04) – increasing was observed especially in sites measured by Romania, which was not confirmed by Bulgarian data in the same section RO04/BG05. Bulgarian data indicate decrease in period 1998-2000 there;
    - similarly to COD-Mn, slight increasing trend is observed in Sajo-Sajopuspoki (H09), but the general trend is decreasing from 1996 to 2000; it has to be mentioned that for three tributaries located in the lower Danube, the Arges-Conf. Danube (RO09), Siret-Conf. Danube Sendreni (RO10) and Prut-Conf. Danube Giurgiulesti (RO11), very high values are recorded in 1997 and 1998.

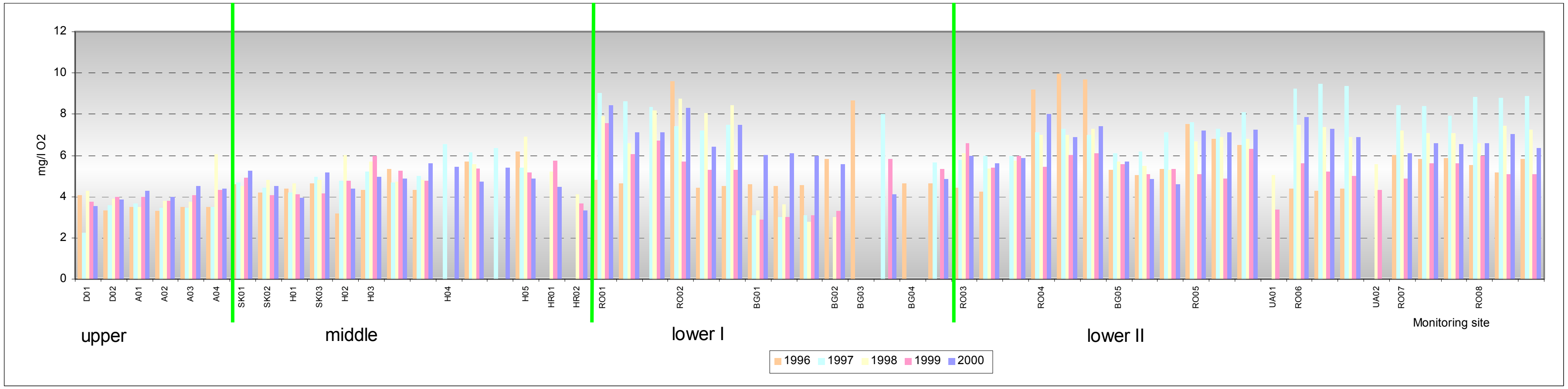

Fig. 8.1.4.22a: Spatial variation of COD-Mn – Danube River

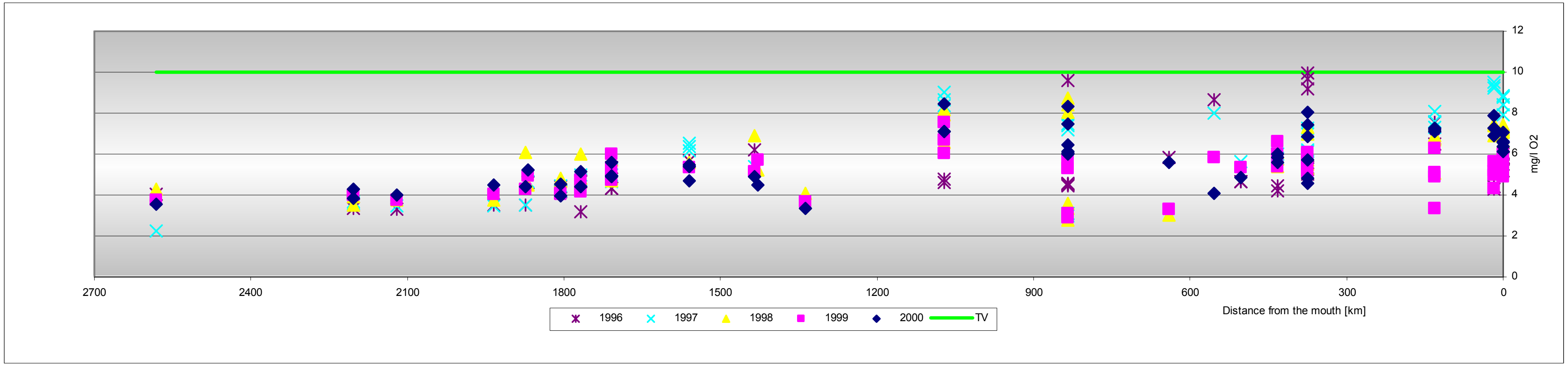

Fig. 8.1.4.22b: Spatial variation of COD-Mn – Danube River

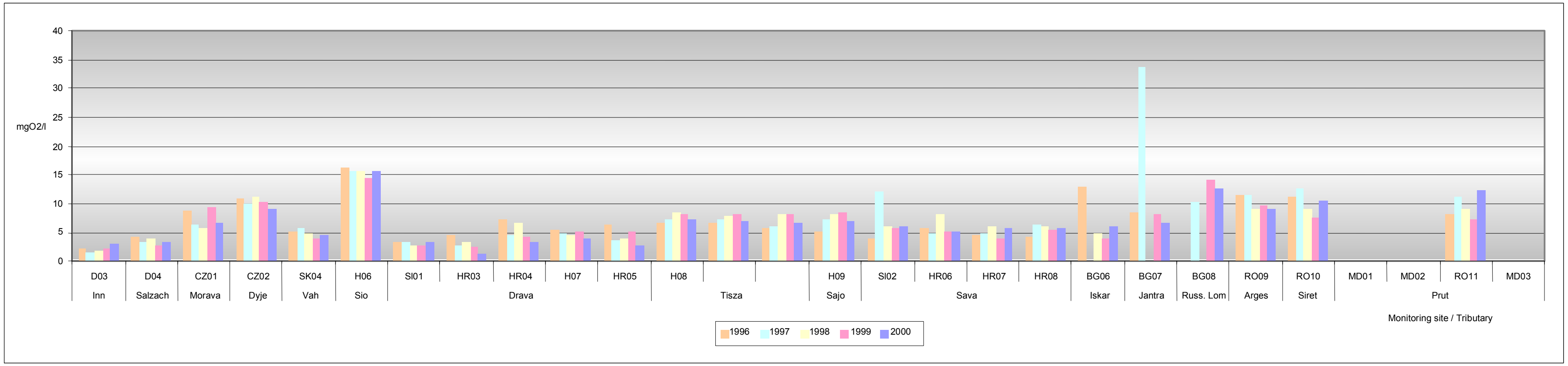

Fig. 8.1.4.23a: Spatial variation of COD-Mn - Tributaries

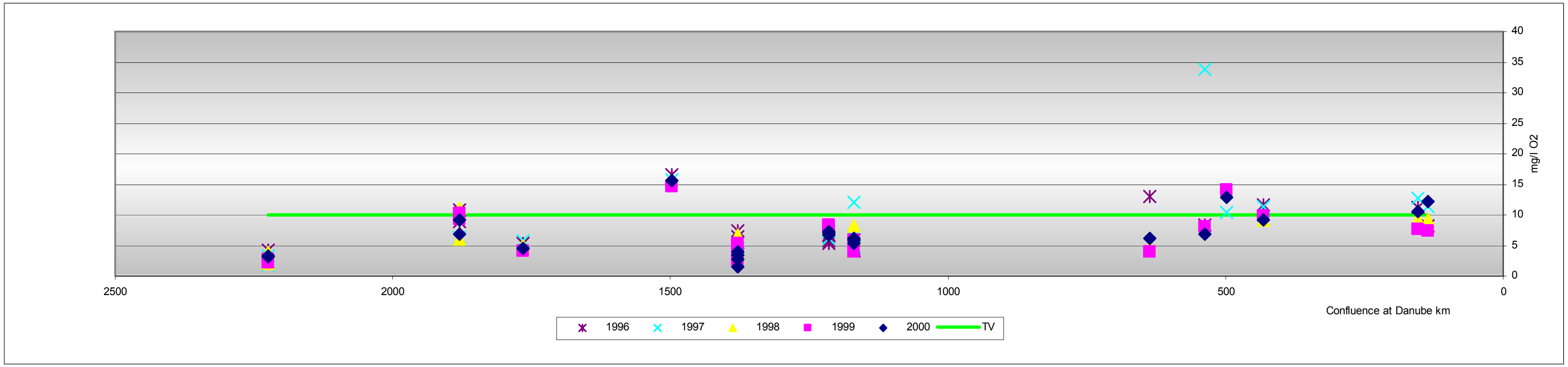

Fig. 8.1.4.23b: Spatial variation of COD-Mn - Tributaries

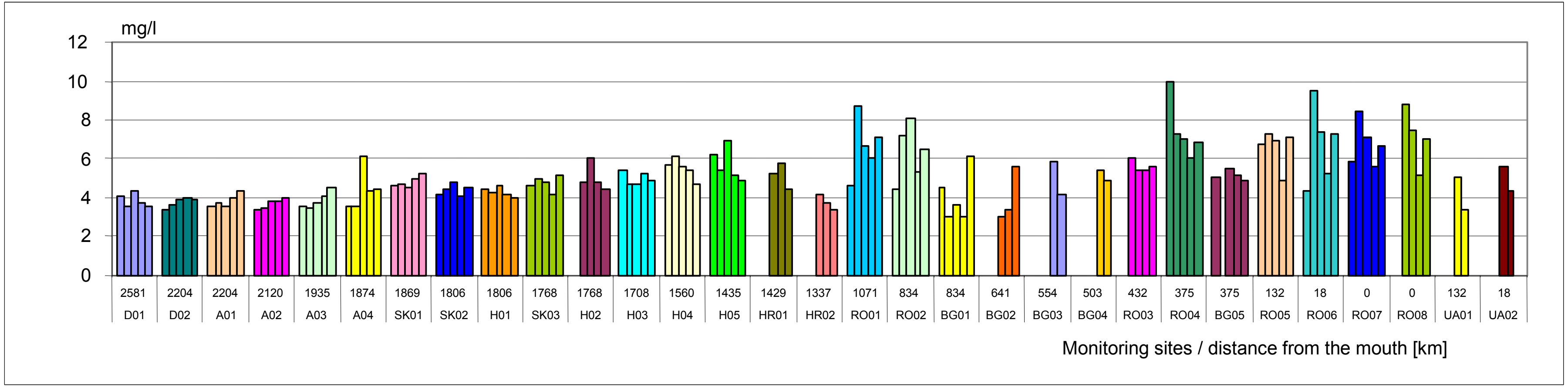

Fig. 8.1.4.24: Temporal trends of COD-Mn – Danube River

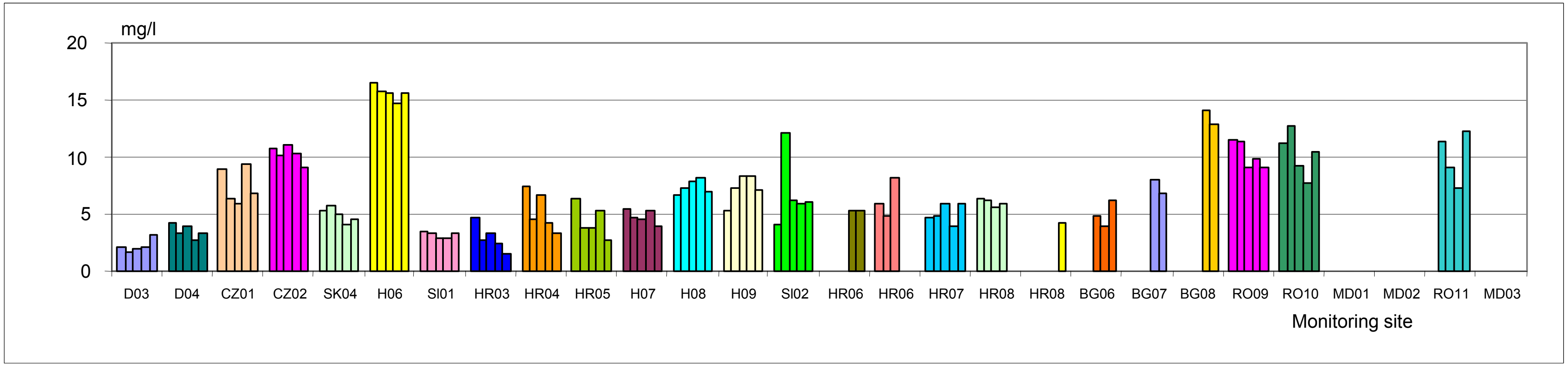

Fig. 8.1.4.25: Temporal trends of COD-Mn – Tributaries

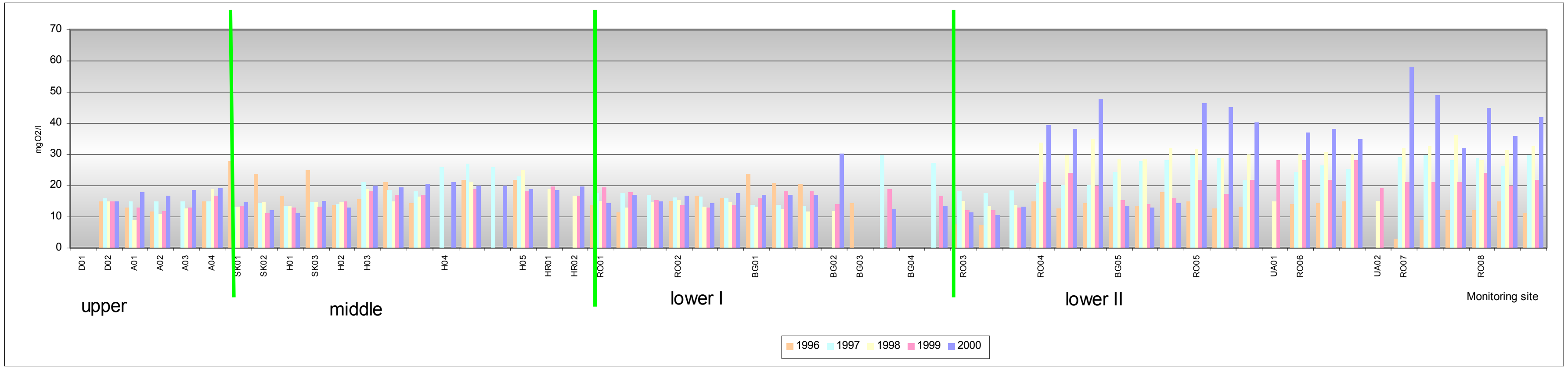

Fig. 8.1.4.27a: Spatial variation of COD-Cr – Danube River

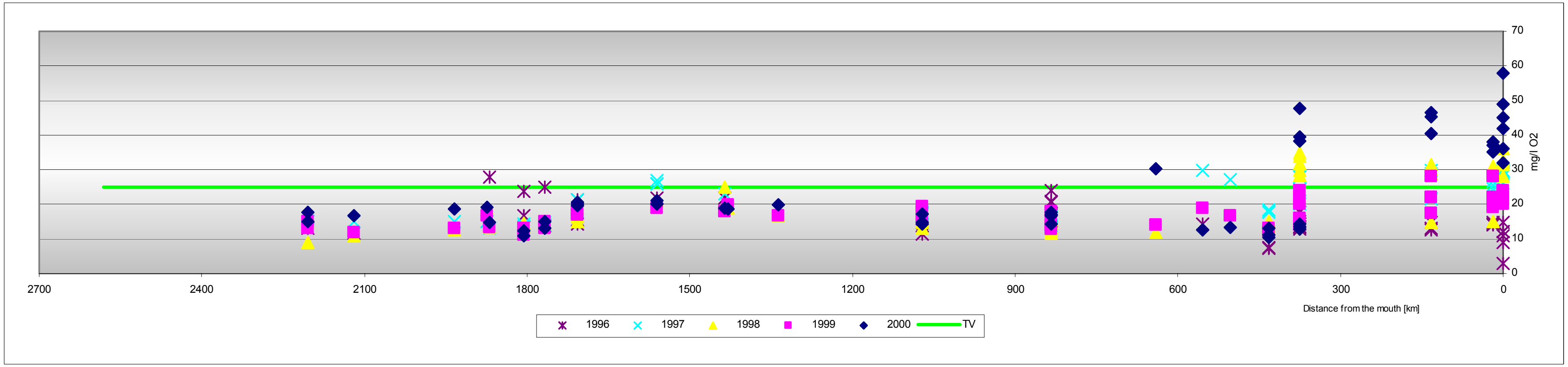

Fig. 8.1.4.27b: Spatial variation of COD-Cr – Danube River

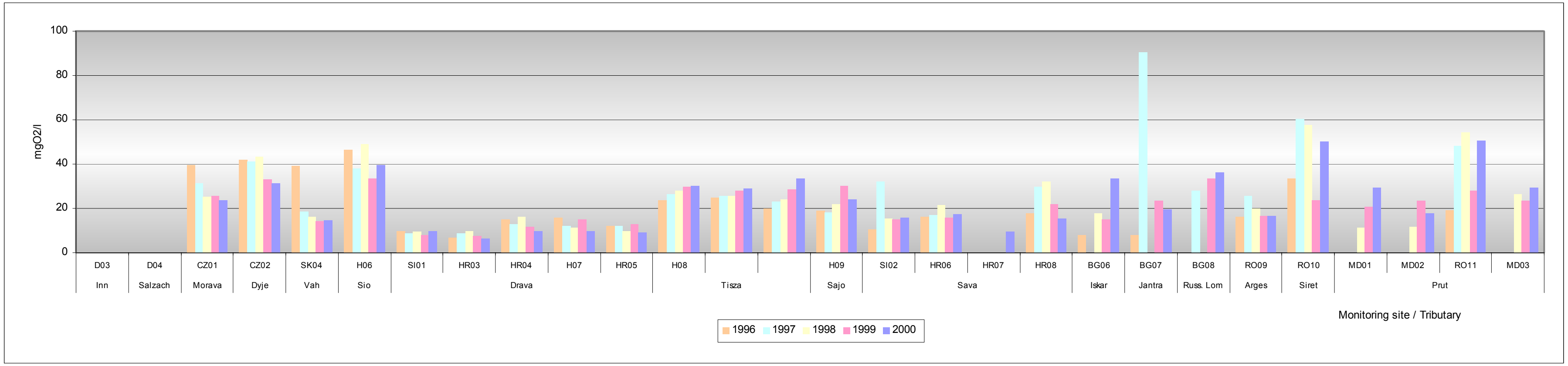

Fig. 8.1.4.28a: Spatial variation of COD-Cr – Tributaries

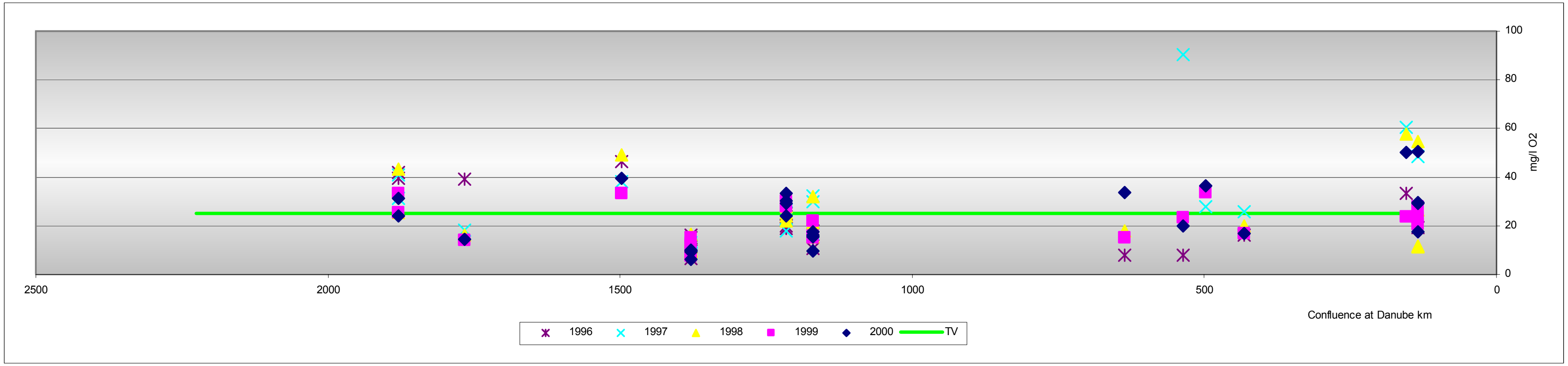

Fig. 8.1.4.28b: Spatial variation of COD-Cr – Tributaries

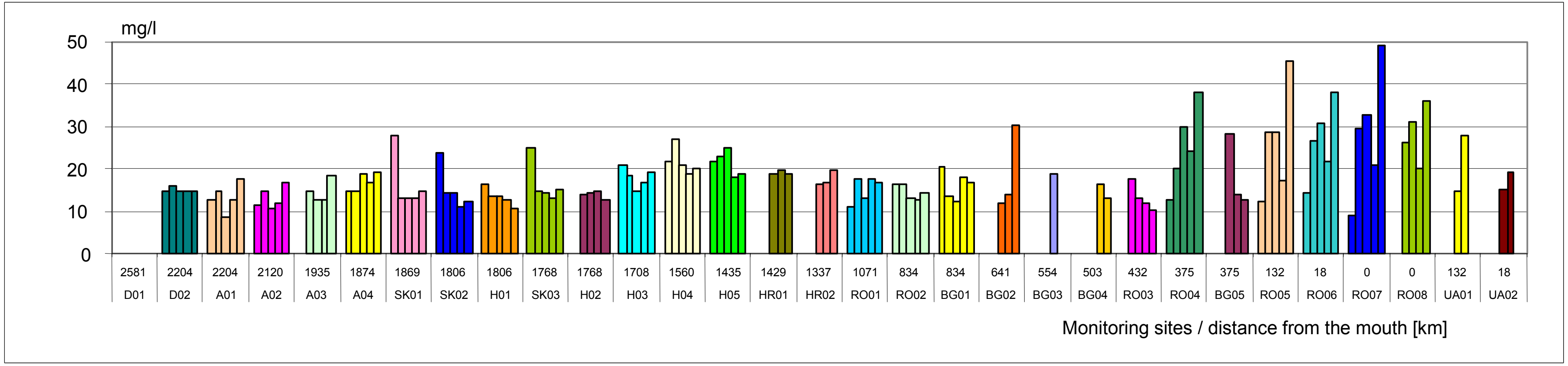

Fig. 8.1.4.29: Temporal trends of COD-Cr – Danube River

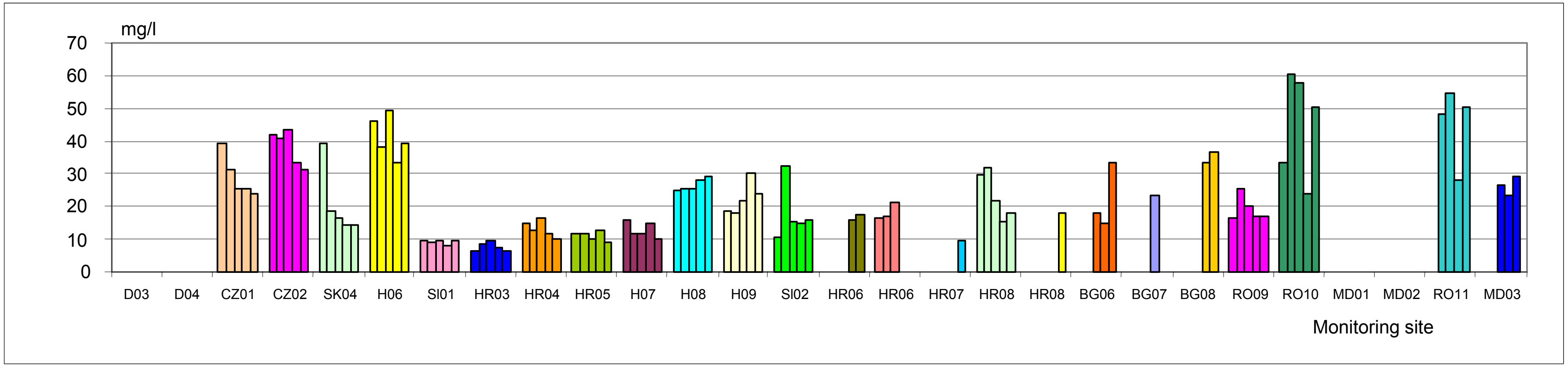

Fig. 8.1.4.30: Temporal trends of COD-Cr – Tributaries

It is well known that when a watercourse receives sewage effluent or effluent from animal farms, the levels of organic matter and ammonium rise, while the level of oxygen falls. In order to illustrate this relation in the Danube River and its tributaries, for each evaluated year a chart has been made in which both the BOD-5 values and ammonium content are represented versus the minimum dissolved oxygen values (**Fig. 8.1.4.31. – 8.1.4.35**). Significant relations between these determinands had been identified in monitoring sites listed in Table 8.1.4.2 below.

Table 8.1.4.2: Significant relations between the $N\text{-}NH_4$ and BOD_5 levels versus minimum dissolved oxygen.

Year	**River**	**Country code**	**$N\text{-}NH_4$ (mg/l)**	**BOD_5 (mg/l O_2)**	**DO Min. (mg/l O_2)**
1996	Dyje	CZ02	1.18	11.0	5.9
	Vah	SK04	1.00	6.5	5.2
	Sio	H06	1.30	9.5	7.2
	Arges	RO09	7.68	60.5	2.4
	Siret	RO10	1.50	6.3	0.2
1997	Morava	CZ01	1.16	7.2	6.2
	Djye	CZ02	1.05	6.5	6.2
	Sio	H06	1.14	9.5	6.4
	Jantra	BG07	2.95	-	6.6
	Arges	RO09	2.49	9.7	2.3
	Siret	RO10	3.05	7.1	5.4
1998	Dyje	CZ02	0.56	8.4	7.8
	Arges	RO09	2.86	7.0	3.0
1999	Morava	CZ01	0.88	9.1	8.2
	Dyje	CZ02	0.89	6.7	7.1
	Jantra	BG07	0.46	5.0	6.5
	Russenski Lom	BG08	0.19	8.8	5.6
	Arges	RO09	2.60	8.3	2.9
	Siret	RO10	0.54	5.3	5.5
2000	Sio	H06	0.49	7.6	6.2
	Russenski Lom	BG08	0.26	8.9	5.6
	Siret	RO10	0.93	7.0	6.8

Fig. 8.1.4.31 – 8.1.4.35: Correlation between ammonium content and biochemical oxygen demand versus minimum of dissolved oxygen

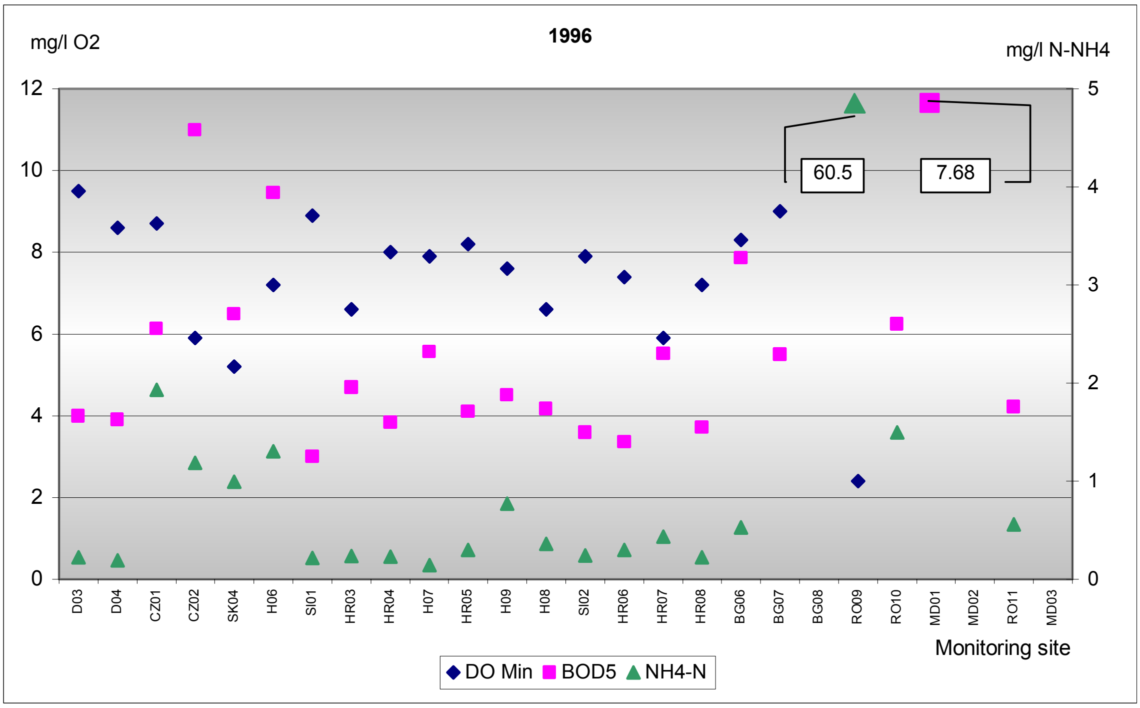

Fig. 8.1.4.31

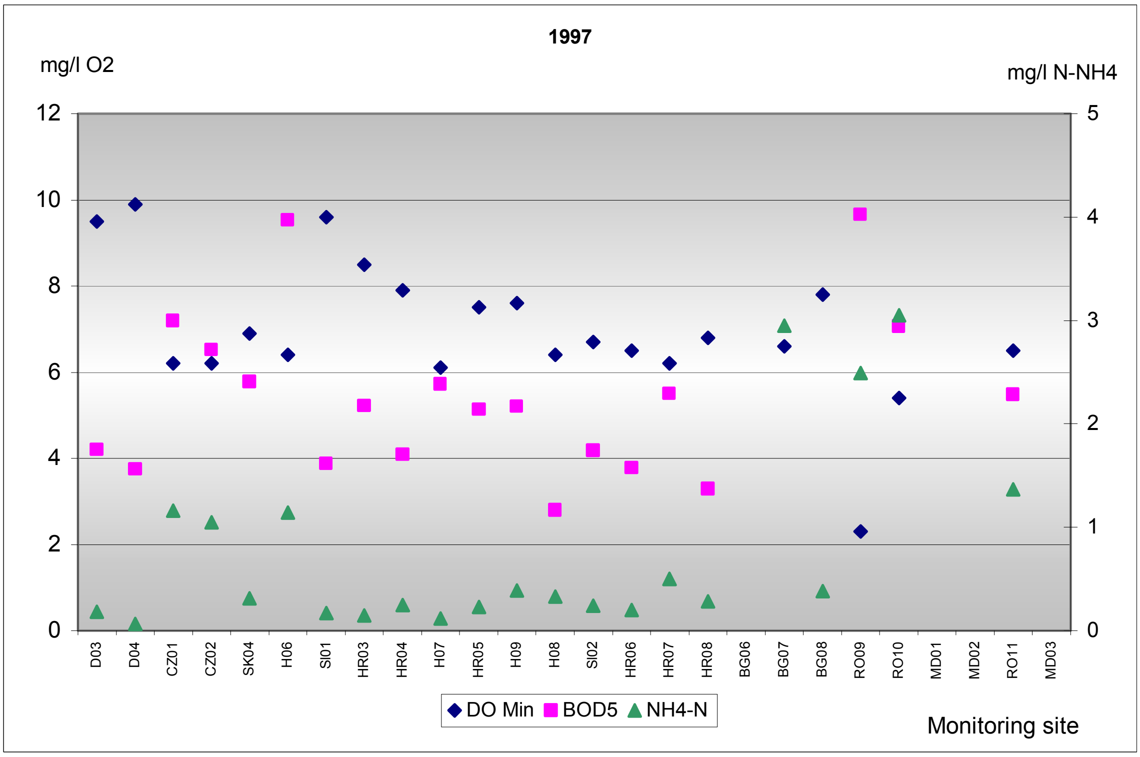

Fig. 8.1.4.32

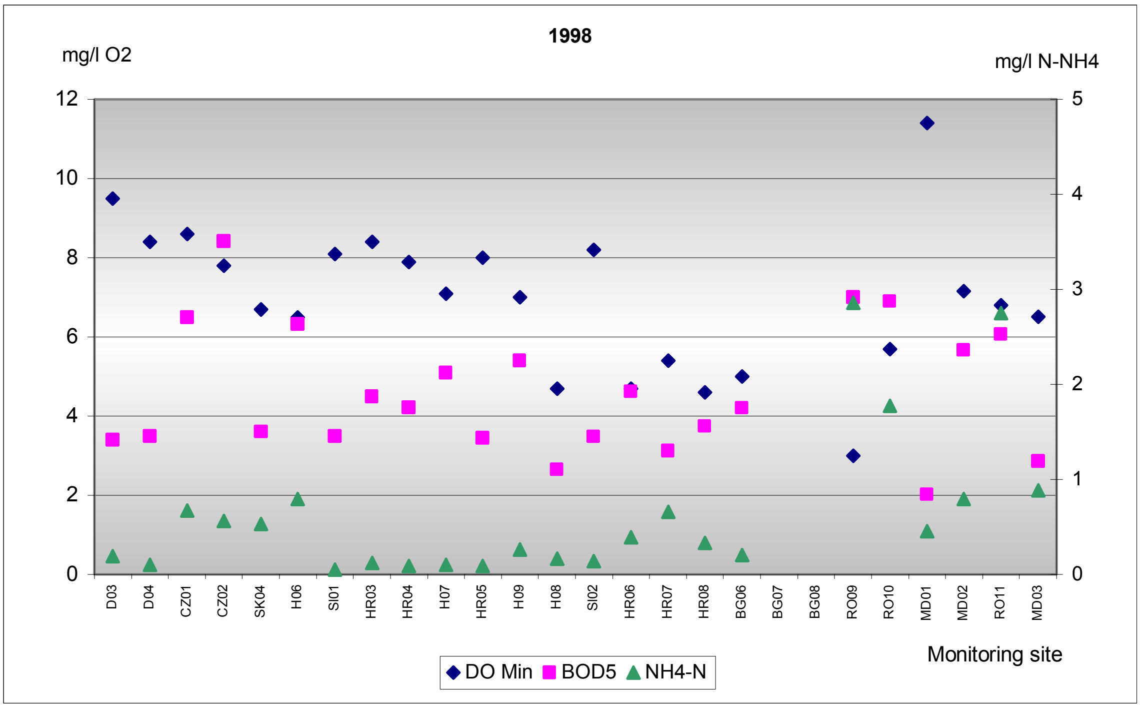

Fig. 8.1.4.33

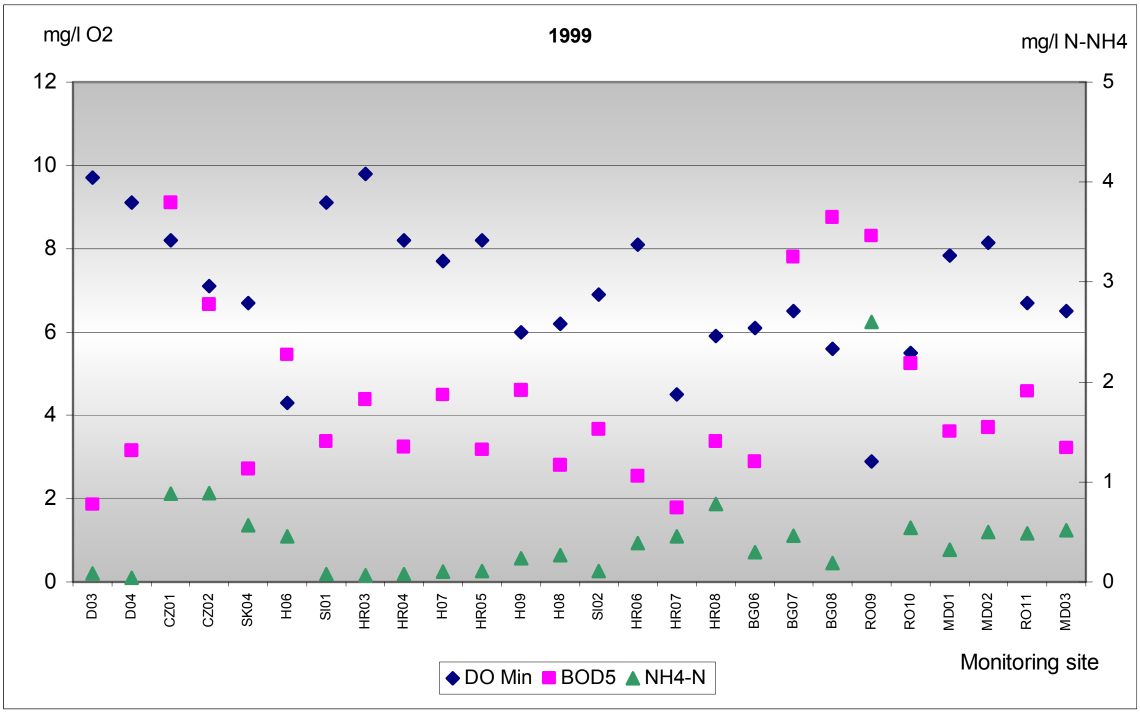

Fig. 8.1.4.34

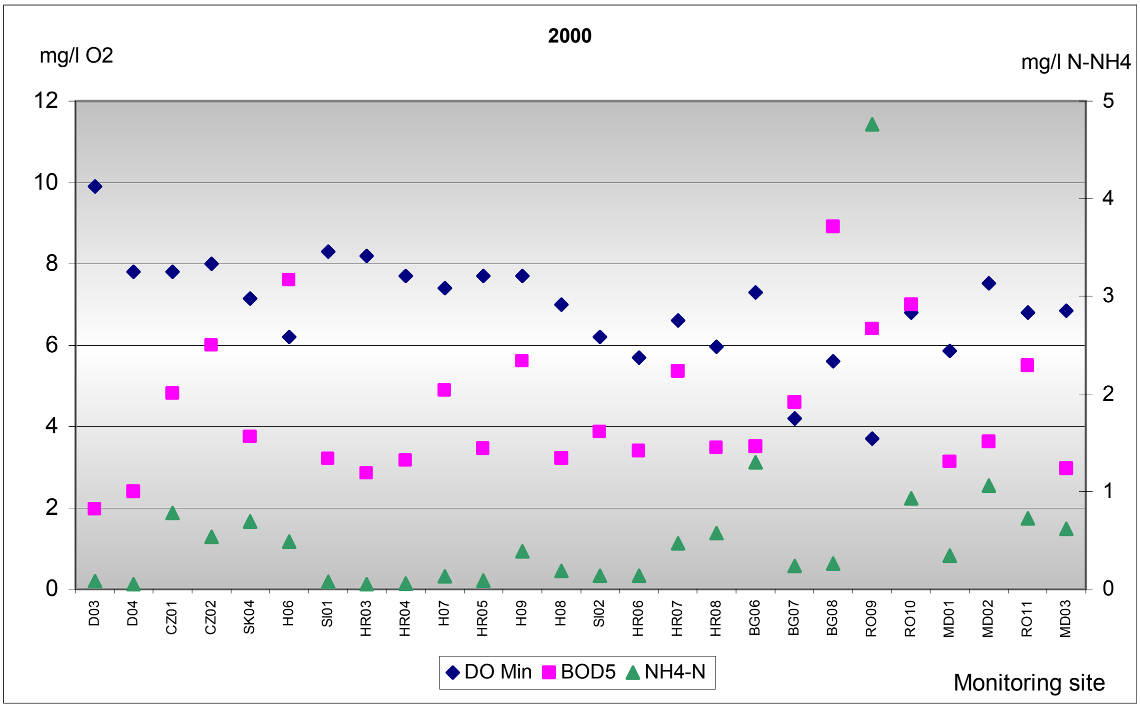
2000
mg/l O2
mg/l N-NH4
0
2
4
6
8
10
12
0
1
2
3
4
5
D03
D04
CZ01
CZ02
SK04
H06
SI01
HR03
HR04
H07
HR05
H09
H08
SI02
HR06
HR07
HR08
BG06
BG07
BG08
RO09
RO10
MD01
MD02
RO11
MD03
◆ DO Min
■ BOD5
▲ NH4-N
Monitoring site

Fig. 8.1.4.35

8.1.5. Organic Micropollutants

Among the main sources of organic micropollutants in surface waters industrial, urban activities and application of pesticides in agriculture can be mentioned.

Within the TNMN Programme, organic micropollutants that are regularly monitored are Lindan, p,p'-DDT, Atrazine, chloroform, carbon tetrachloride, trichloroethylene and tetrachloroethylene. Because of the low frequencies of measurements, trend analysis has not been possible to done for these determinands, so only some observations related to temporal patterns are mentioned.

When assessing organic micropollutants results of classification, percentage of monitoring sites satisfying limit values for different water quality classes is influenced very much by uneven number of measurements in particular years. As can be seen later, the number of monitoring sites without measurements has decreased significantly from 1996 to 2000, but still there is rather large group of monitoring sites without measurements of organic micropollutants.

Lindan (gamma isomer of hexachlorocyclohexane)

The distribution of monitoring sites according to the Classification System in the DRB for **Lindan** is shown in **Fig. 8.1.5.1**:

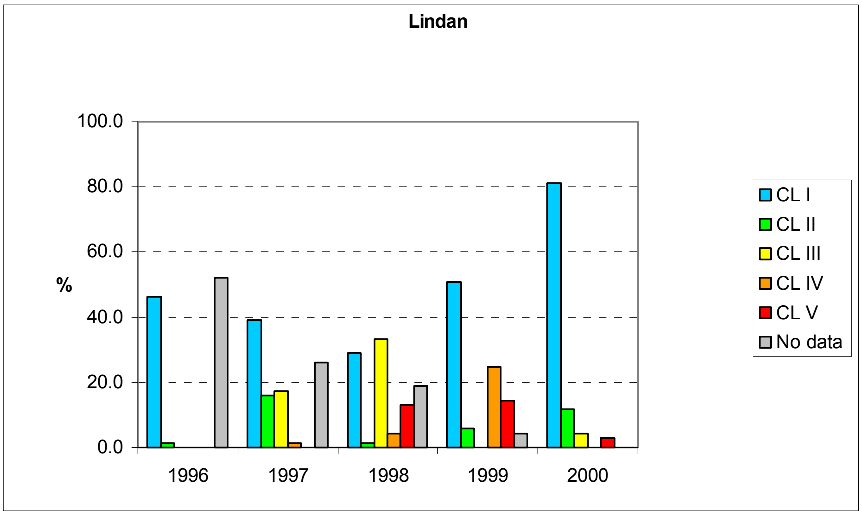

Fig. 8.1.5.1: Distribution of monitoring sites (%) according to the Quality Classification System in the DRB for **Lindan**

The assessment is made based on data reported from 69 monitoring sites (out of the assessment is 34 monitoring sites from Phase I List of Monitoring Sites, in which no measurements of Lindane had been done in 1996-2000):

- the number of monitoring sites corresponding to Class I decreases from 1996 to 1998 and then increases until 2000 up to 81.2 %;
- Class II is represented by a minimum value of 1.4 % in 1996 and 1998 and by a maximum of 15.9 % in 1997;
- no monitoring site corresponds to Class III in 1996 and 1999; in the other years Class III is represented by 4.3 % - 33.3% of sites;
- Class IV is absent in 1996 and 2000; during 1997 – 1999 perentage of sites in in this Class is in the range from 1,4 – 24,6 %;
- Class V is present during 1998 – 2000, with the minimum in 2000 (2.9 %) and the maximum in 1999 (14.5 %);

The pattern for Lindan concentrations in the Danube River is shown in **Fig. 8.1.5.2a** and **8.1.5.2b**.

In the upper Danube, Lindan is actually undetectable at the first two monitoring sites, Danube-Neu-Ulm (km 2581, D01) and Danube-Jochenstein (km 2204, D02), according to German results. For the rest four sites, Lindan is also undetectable during 1997–1999 even though there are differences among years, caused by the differences in reported limits of detection. According to Austrian data, from Danube-Jochenstein (km 2204, A01) to Danube-Wolfsthal (km1874, A04), Lindan seems to be detectable in 2000 only, at the level of 0.100 µg/l, the target value for Lindan.

In the middle section, all Lindan values are below 0.050 µg/l, the limit value for Quality Class I.

In the first part of the lower Danube, Lindan concentrations are much higher than 0.100 µg/l. From Danube-Bazias (km 1071, RO01) down to Danube-Pristol/Novo Selo (km 834, RO02), Lindan concentrations increase reaching c90 values up to 0.398 µg/l according to Romanian data. The higest values from this part are recorded mainly in 1999. It has to be mentioned that, similar to some other determinands, big differences exist between the reported data for the cross section from km 834 (RO02/BG01).

In the second part of the lower Danube Lindan c90 values are even above 0.20 µg/l, corresponding to Class IV. This is observed in all Romanian monitoring sites mainly in 1999. Again has to be mentioned that there are extremely high differences between Romanian and Bulgarian results in the same cross sections.

For the entire lower Danube, 46 Lindan c90 values exceeded the level set up as a target value.

The distribution of Lindan concentrations in selected tributaries is illustrated in **Fig. 8.1.5.3a** and **8.1.5.3b** and shows an inhomogeneous picture:

- those tributaries from the upper section, in which Lindan is detectable - the Morava-Lanzot (CZ01) and Dyje-Pohansko (CZ02), present Lindan concentrations below 0.05 µg/l;
- in the middle stretch, in Sio-Szekszard (H06), an extreme value is recorded in 2000 (5.75 µg/l); higher values that appear on Sajo-Sajopuspoki (H09) in 1996 and 1997 do not exceed the target limit;
- in the lower section, three tributaries - the Arges-Conf. Danube (RO09), Siret-Conf. Danube Sendreni (RO10) and Prut-Conf. Danube Giurgiulesti (RO11), show values above 0.100 µg/l, especially in 1999, with a maximum value of 0.321 µg/l on the Arges-Conf. Danube (RO09);
- majority of values characterising Lindan content, which were above the target limit, were observed on tributaries from the lower Danube.

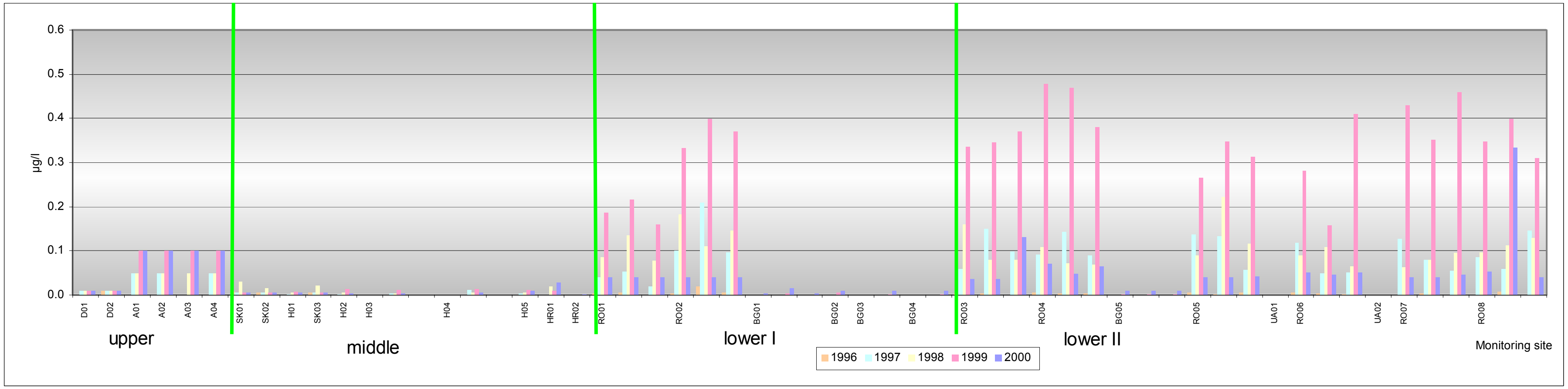

Fig. 8.1.5.2a: Spatial variation of Lindan – Danube River

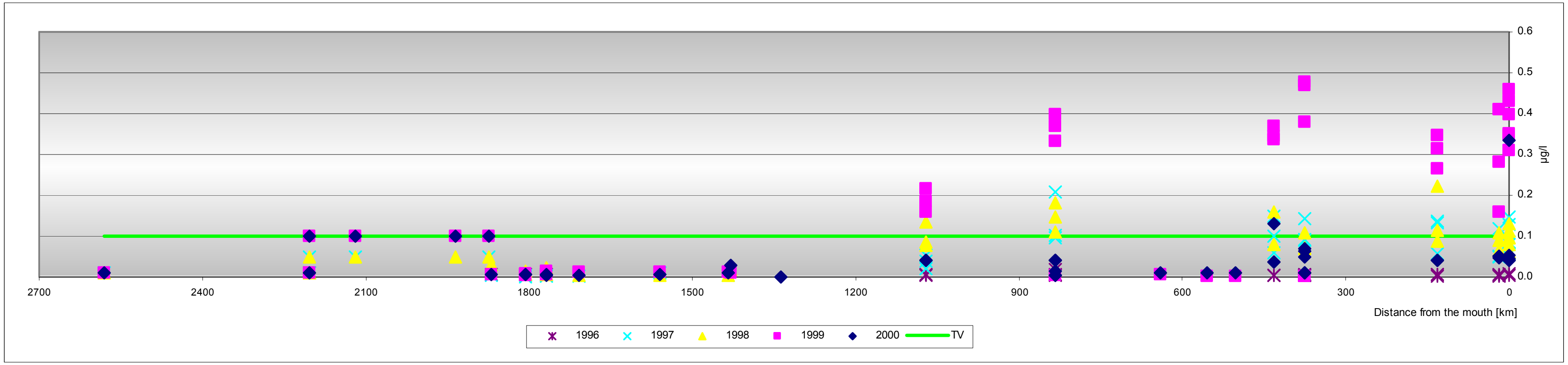

Fig. 8.1.5.2b: Spatial variation of Lindan – Danube River

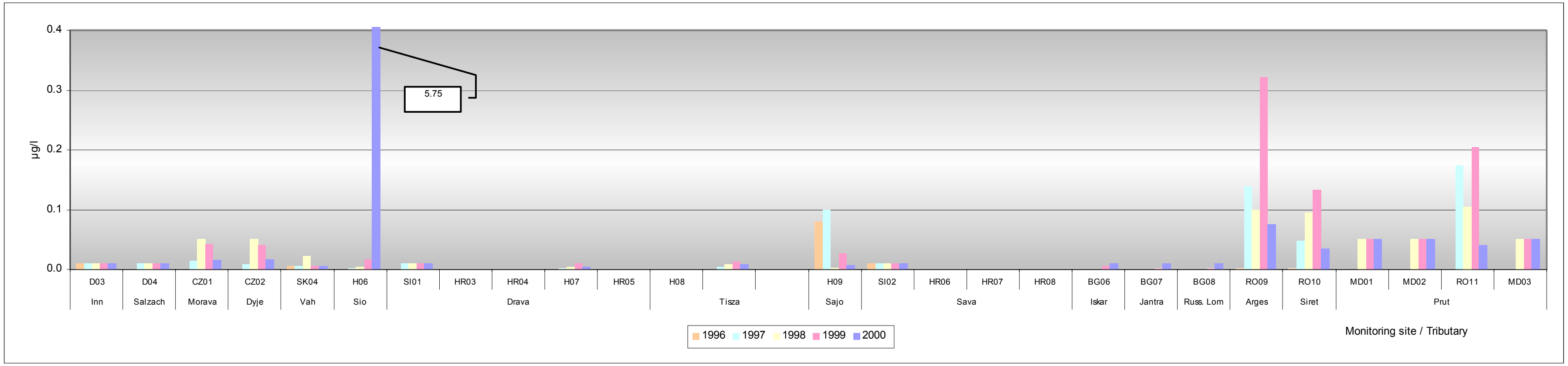

Fig. 8.1.5.3a: Spatial variation of Lindan – Tributaries

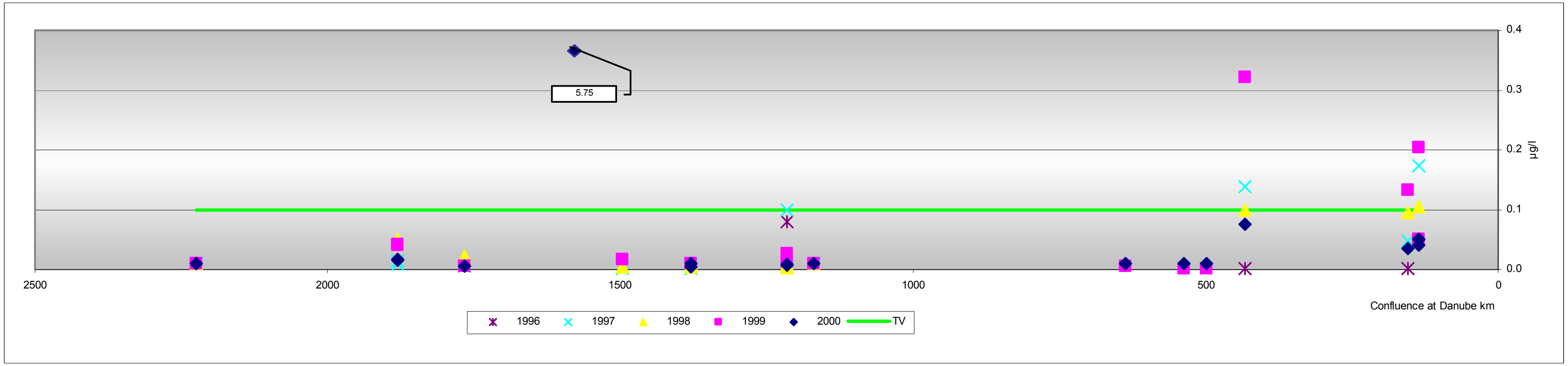

Fig. 8.1.5.3b: Spatial variation of Lindan – Tributaries

pp’-DDT (isomer of dichlorodiphenyltrichloroethane)

The distribution of monitoring sites according to the Classification System in the DRB for **pp’-DDT** is shown in **Fig. 8.1.5.4**:

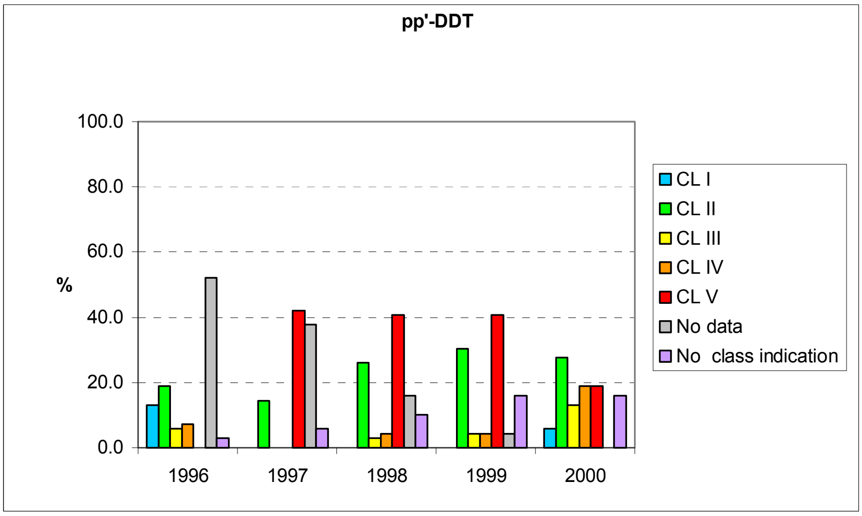

Fig. 8.1.5.4: Distribution of monitoring sites (%) according to the Quality Classification System in the DRB for **pp’-DDT**

The quality assessment is made based on data reported by 69 monitoring sites (out of the assessment is 34 monitoring sites from Phase I List of Monitoring Sites, in which no measurements had been done in 1996-2000):

- Class I is represented in 1996 and 2000 only, by 13.0 % and 5.8 % respectively;
- the percentage of monitoring sites within Class II is in the range from 14,5 – 30,4 %;
- Class III and Class IV have been represented by less than 10 % in the periond from 1996-1999, in 2000 13.0 % and 18.8 % of monitoring sites corresponded to Class III and Class IV, respectively;
- Class V is absent in 1996, but the number of sites within this class is approximately 40 % during 1997 – 1999 and less than 20 % in 2000;
- the additional category of “no class indication” (sites, in which limit of detection of p,p’-DDT measurement was higher than limit value for Class II, and therefore have not been classified) is represented in all five studied years.

The spatial variation of pp’-DDT concentrations for the Danube River is illustrated in **Fig**. **8.1.5.5a** and **8.1.5.5b**.

In the upper section of the river, the pp’-DDT concentrations level shows a similar profile with that of Lindan: is undetectable at first two monitoring sites, Danube-Neu-Ulm (km 2581, D01) and Danube-Jochenstein (km 2204, D02), according to German results. According to Austrian data, pp’-DDT is undetectable during 1997 – 1999; the only measurable concentrations appear in 2000, from Danube-Jochenstein (km 2204, A01) down to Danube-Wolfsthal (km 1874, A04), at the level of 0.05 µg/l.

The middle stretch is characterized by values below the limit of detection, according to Slovak results, excepting the value recorded at Danube-Komarno/Komarom (km 1768, SK03) – 0.080 µg/l in 1999. For the rest of the stretch, values below 0.050 µg/l are present.

In the first part of the lower Danube, pp’-DDT concentrations are much higher than in the middle stretch, They exceed 0.50 µg/l level in 1998 and 1999 from Danube-Bazias (km 1071, RO01) to

Danube-Pristol/Novo Selo (km 834, RO02), if the Romanian results are taken into account. According to Bulgarian data, values are below 0.10 µg/l.

The second part of lower Danube section is characterized by higher values than the first part - above 0.60 µg/l, recorded mainly in 1997 and 1999 from Danube-us. Arges (km 432, RO03) to Danube-Chiciu/Silistra (km 375, RO04). Much higher p,p'-DDT concentrations appear in three main arms of the Danube Delta –Chilia (RO06), Sulina (RO07) and Sf. Gheorghe (RO08). The maximum c90 value (1.498 µg/l) is observed at Danube- Sf. Gheorghe/Sf. Gheorghe arm (km 0, RO08) in 1999.

Fig. **8.1.5.6a** and **8.1.5.6b** show p,p'-DDT c90 values in selected tributaries. It can be seen that high p,p'-DDT concentrations are recorded only on Romanian tributaries - the Arges-Conf. Danube (RO09), Siret-Conf. Danube Sendreni (RO10) and Prut-Conf. Danube Giurgiulesti (RO11). The maximum value for tributaries (1.142µg/l) appears on the Siret-Conf. Danube Sendreni (RO10) in 1999.

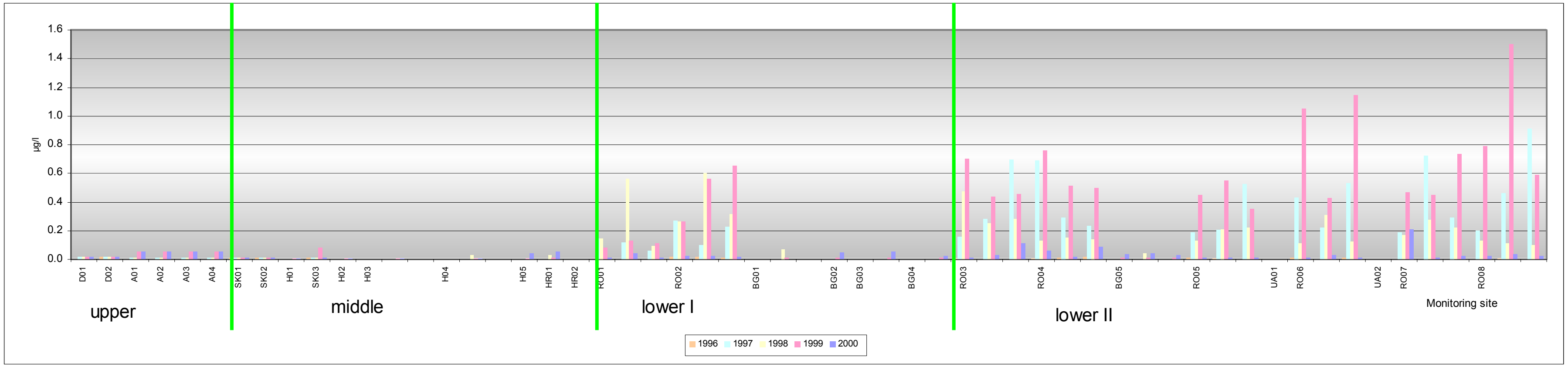

Fig. 8.1.5.5a: Spatial variation of pp'-DDT – Danube River

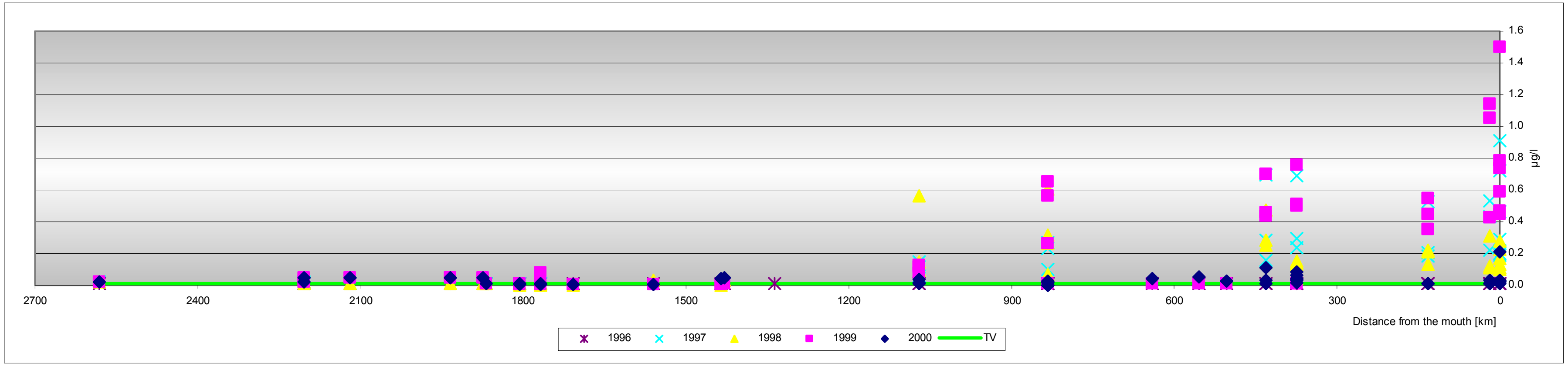

Fig. 8.1.5.5b: Spatial variation of pp'-DDT – Danube River

Note: In locations D01 (97-00), D02 (96-00), A01, A02, A03, A04 (99, 00) the values in the graph represent limits of detection that are higher than the target value.

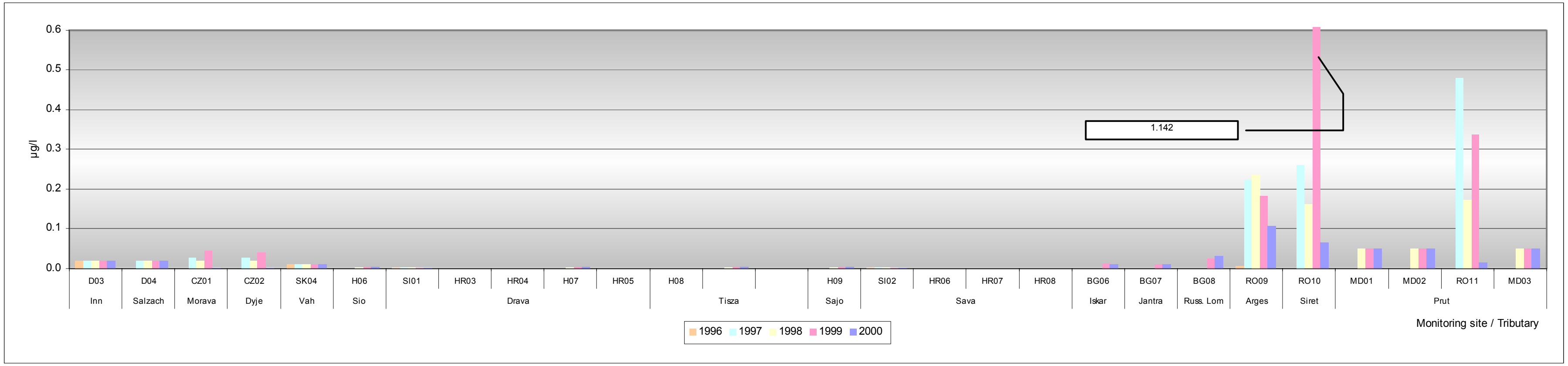

Fig. 8.1.5.6a: Spatial variation of pp'-DDT – Tributaries

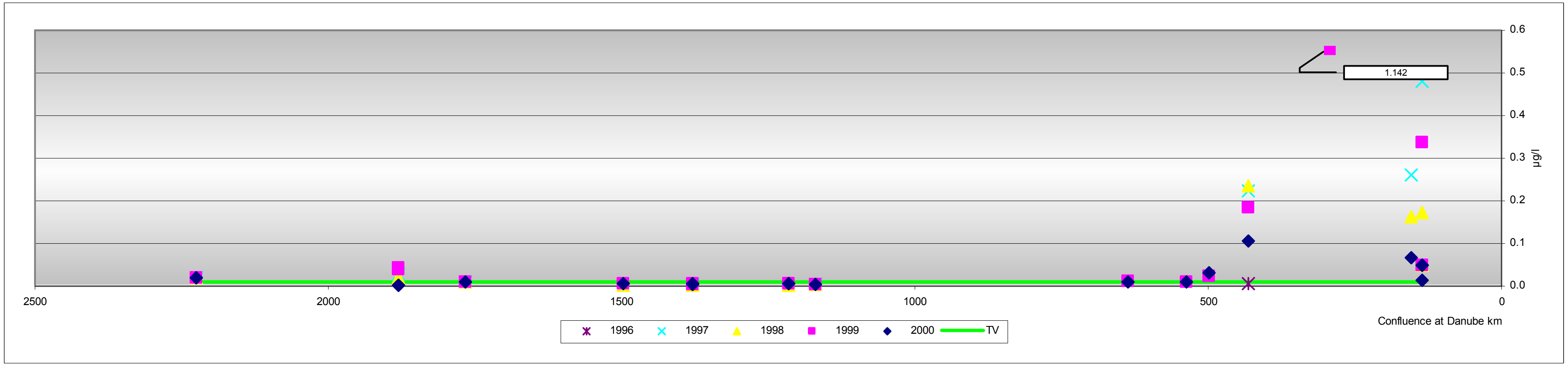

Fig. 8.1.5.6b: Spatial variation of pp'-DDT – Tributaries

Note: In locations D03 (96-00), D04 (97-00), MD01, MD02, MD03 (98-00) the values in the graph represent limits of detection that are higher than the target value

Atrazine

The distribution of monitoring sites according to the Classification System in the DRB for **Atrazine** is shown in **Fig. 8.1.5.7**:

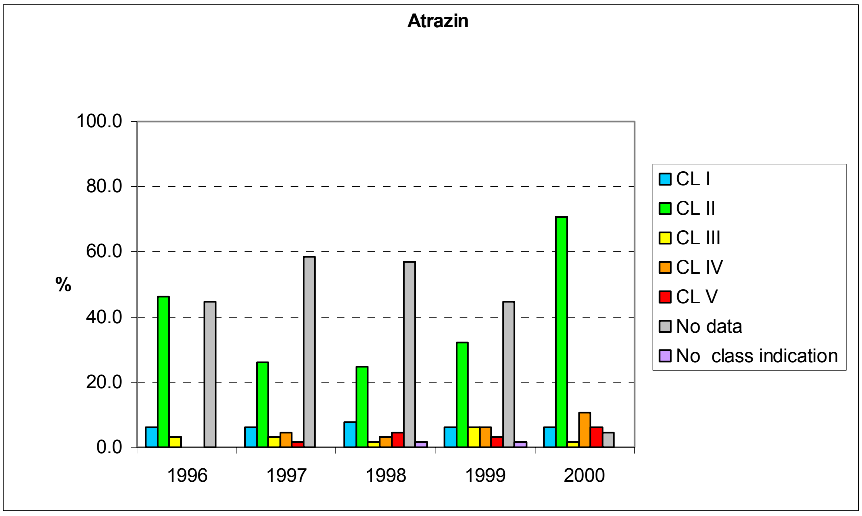

Fig. 8.1.5.7: Distribution of monitoring sites (%) according to the Quality Classification System in the DRB for **Atrazine**

The assessment is made based on data reported from 65 monitoring sites (therefore, out of the assessment is 38 monitoring sites from Phase I List of Monitoring Sites, in which no measurements had been done in 1996-2000):

- Class I is constantly represented by less than 8% of the considered monitoring sites;
- percentage of sites within Class II decreases from 1996 to 1998 (reaching minimum 24,6 %) and then increases till 2000 to the level of 70.8 %;
- the maximum percentage of sites within Class III is 6.2 % in 1999, in all other years percentage is below 4 %;
- Class IV is represented in years 1997 – 2000, with maximum 10.8 % in 2000;
- Class V is represented during 1997 – 2000, with the maximum value in 2000 (6.2%);
- only 1.5 % of considered sites have "no class indication" in 1998 and 1999 (sites, in which limit of detection was higher than limit value for Class II, and therefore have not been classified).

The Atrazine concentrations in the Danube River are illustrated in **Fig. 8.1.5.8a** and **8.1.5.8b**.

In accordance to German results, Atrazine is detectable in 1999 in Danube-Neu Ulm (km 2581, D01) and excepting 1997, in all studied years in Danube-Jochenstein (km 2204, D02). According to Austrian results, in the stretch from Danube-Jochenstein (km 2204, A01) to Danube-Wolfsthal (km 1874, A04) the only detectable values are recorded in 2000. In this stretch, no Atrazine concentration is above the target value (0.10 µg/l).

In the middle stretch from Danube-Bratislava (km 1869, SK01) to Danube-Szob (km 1708, H03) Atrazine concentrations are below 0.100 µg/l, excepting one value (0.164 µg/l) at Danube-Szob in 1997. From Danube-Dunafoldvar (km 1560, H04) to Danube-Hercegszanto (km 1435, H05), Atrazine concentrations are higher, with the maximum at Danube-Hercegszanto (km 1435, H05) in 1997 (0.50 µg/l). In the middle Danube 4 values are above the target limit.

In the first part of the lower Danube, Atrazine is below reported limit of detection (0.06 µg/l), from Danube-Bazias (km 1071, RO01) to Danube-Pristol/Novo Selo (km 834, RO02) in accordance to

Romanian results. On the basis of Bulgarian results, at Danube-Novo Selo/Pristol a very high c90 value (1.316 µg/l) respresents situation in 1998.

The second part of the lower Danube shows a similar pattern to the first one. In accordance to Romanian data, Atrazine is undetectable at the respective monitoring sites - from Danube-us. Arges (km 432, RO03) to Danube-Sf. Gheorghe arm/Sf. Gheorghe arm (km 0, RO08); if the Bulgarian data are taken into account, high Atrazine values - 0.618 µg/l and 2.134 µg/l - appear in 1998 and 2000, respectively, at Danube-Silistra/Chiciu (km 375, BG05). Big differences between the reported data at cross sections make the interpretation to be rather difficult.

For the entire lower Danube, among the Atrazine values 12 of them are above the target limit of this determinand.

Atrazine c90 values for selected tributaries are illustrated in **Fig. 8.1.5.9a** and **8.1.5.9b**. It can be seen that the profile is inhomogeneous, with Atrazine values corresponding to Quality Class V on the Morava-Lanzhot (CZ02) and Tisza-Tiszasziget (H08) - 0.930 µg/l in 1998 and 0.550 µg/l in 1999, respectively. Extremely high values appear on Sio-Szekszard (H06) and Sajo-Sajopuspoki (H09) - 4.550µg/l in 1999 and 5.250 µg/l in 1997. Concerning the measured Atrazine level in selected tributaries against the target value, 18 of them are above this limit.

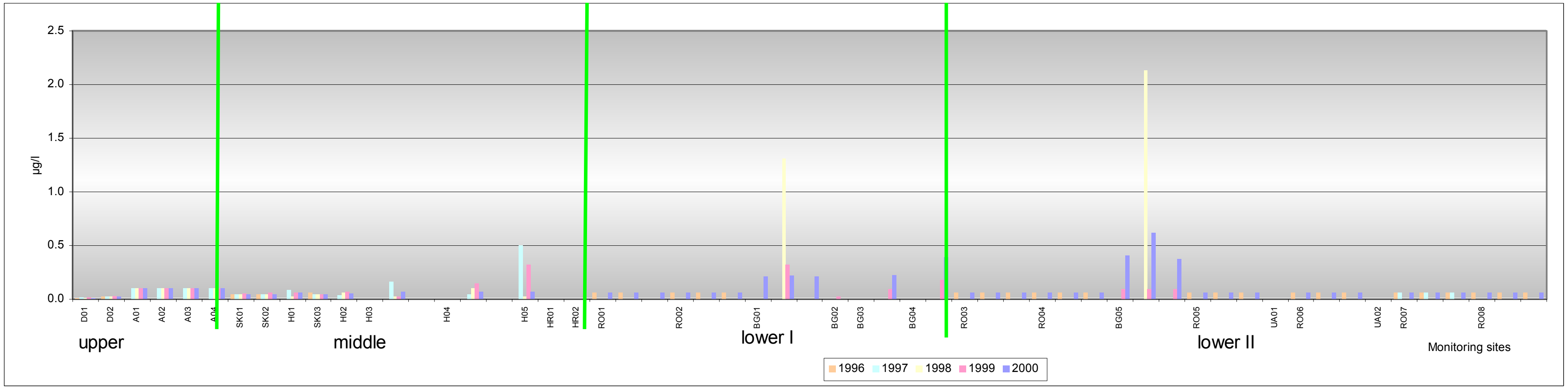

Fig. 8.1.5.8a: Spatial variation of Atrazin – Danube River

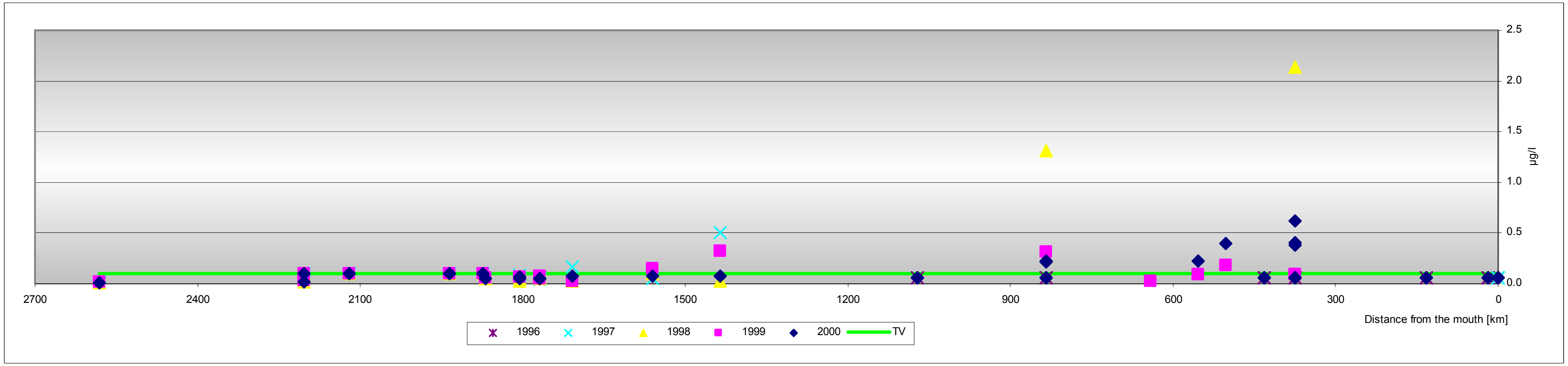

Fig. 8.1.5.8b: Spatial variation of Atrazin – Danube River

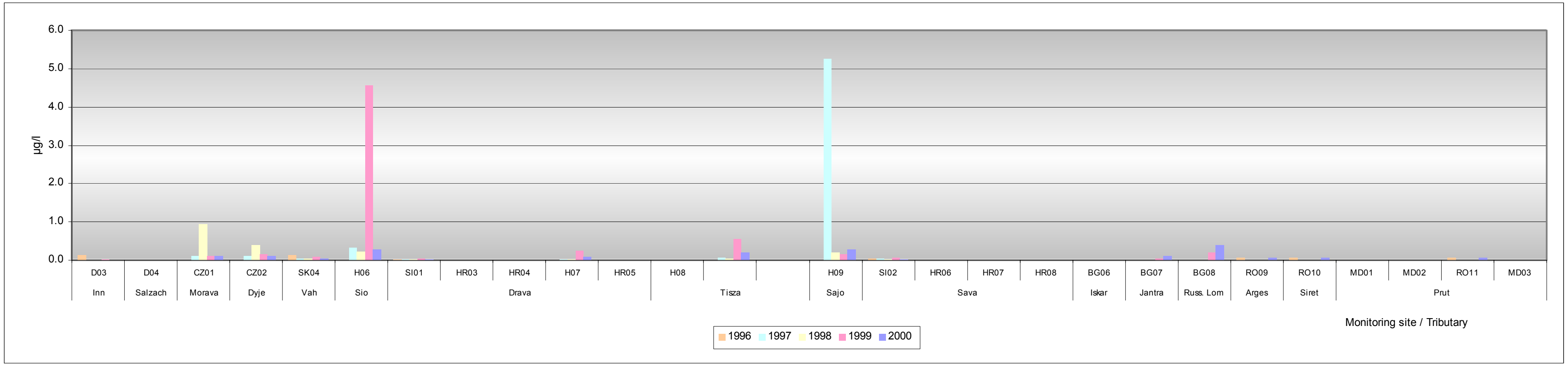

Fig. 8.1.5.9a: Spatial variation of Atrazin – Tributaries

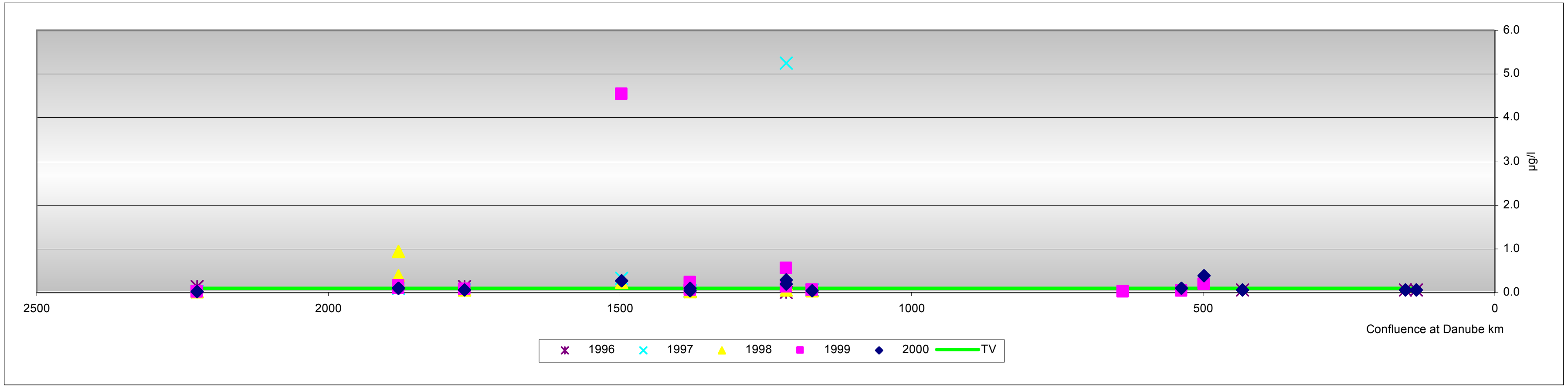

Fig. 8.1.5.9b: Spatial variation of Atrazin – Tributaries

Note: In location MD02 (98, 99) the values in the graph represent limits of detection that are higher than the target value.

Chloroform (trichloromethane)

The distribution of monitoring sites according to the Classification System in the DRB for **Chloroform** is shown in **Fig. 8.1.5.10**:

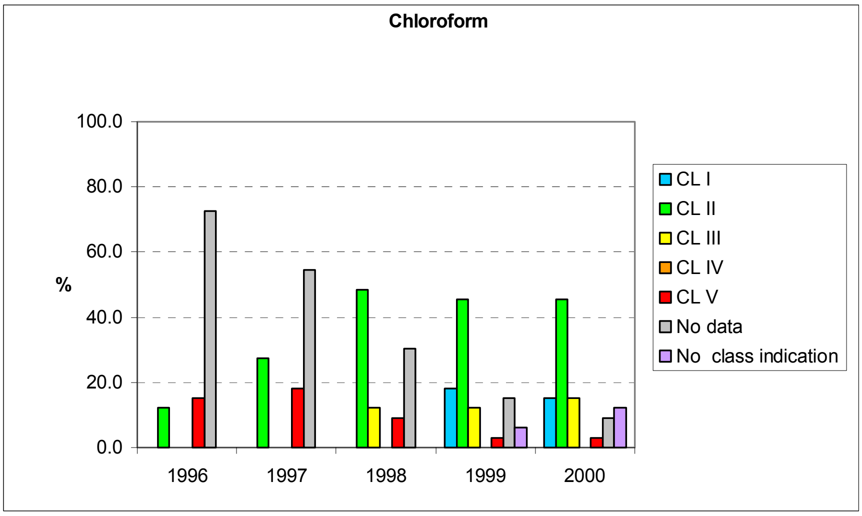

Fig. 8.1.5.10: Distribution of monitoring sites (%) according to the Quality Classification System in the DRB for **Chloroform**

Number of monitoring sites, in which chloroform was measured in 1996-2000, is very low - the assessment is made based on data reported from only 33 monitoring sites. Even from this low number of sites measurements were missing in more than 50 % in years 1996-97.
Completely without any measurements of chloroform during the whole period of years 1996-2000 were 70 monitoring sites.

The chloroform concentrations in the Danube River are shown in **Fig. 8.1.5.11a** and **8.1.5.11b**.

In the upper section, chloroform is undetectable during the entire studied time period. The differences in values exist because the reported limit of detection decreases from 1998 to 2000.

In the middle section, the concentration profile has very large limits of variation. A relevant example appears at Danube-Bratislava (km 1869, SK01), where chloroform is undetectable in 1999 but has a very high value in 1997 (189.1 µg/l). Downstream this monitoring site, from Danube-Medvedov/Medve (km 1806, SK02) to Danube-Komarno/Komarom (km 1768, SK03) according to Slovak data, chloroform shows concentrations values much higher than those reported by the Hungarian part at the respective cross sections. In the middle stretch, 18 concentrations are above the target limit (0.6 µg/l).

In the entire lower section, for only two monitoring sites data characterising chloroform content exist: Danube-Novo Selo/Pristol (km 834, BG01) in 2000 and Danube-Silistra/Chiciu (km 375, BG05) in 1999. All results show that chloroform is undetectable at the reported limit of detection of 0.02 µg/l.

The values of chloroform concentrations for selected tributaries are shown in **Fig. 8.1.5.12a** and **8.1.5.12b**. The measured concentrations are quite high, with 17 values above the target limit. The most elevated values are the following:

- the Morava-Lanzot (CZ02): 3.360 µg/l in 1997;
- the Vah-Komarno (SK04): 10.310 µg/l in 1996 and 81.800 µg/l in 1997;
- the Drava-Ormoz (SL01): 3.000 µg/l in 2000;
- the Sajo-Sajopuspoki (H09): 4.060 µg/l in 1996 and 2.900 µg/l in 1997;
- the Sava-Jesenice (SL02): 3.000 µg/l in 1999.

By comparing the results with those obtained by JDS it can be concluded that in the frame of JDS were not detected such high values as in the TNMN in case of several monitoring sites. High values of chloroform sporadically found in Danube River or its tributaries can indicate that sources of pollution were still not sufficiently under control (under assumption that analysis of chloroform was correct.) As can be seen later in the text, in Slovak section of Danube River and on Vah tributary also other substances from the group of volatile organic compounds are sporadically recorded in high concentrations.

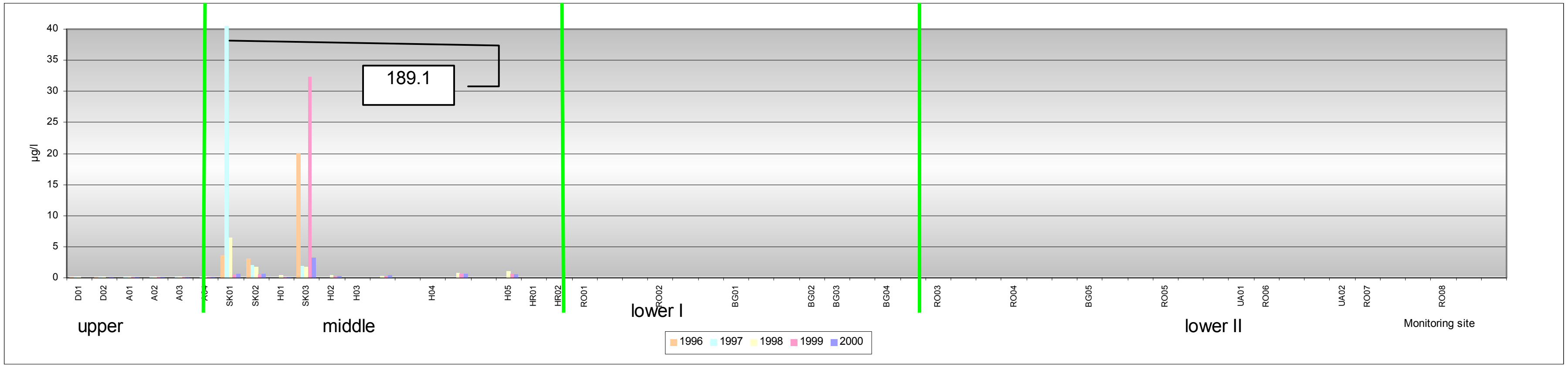

Fig. 8.1.5.11a: Spatial variation of Chloroform – Danube River

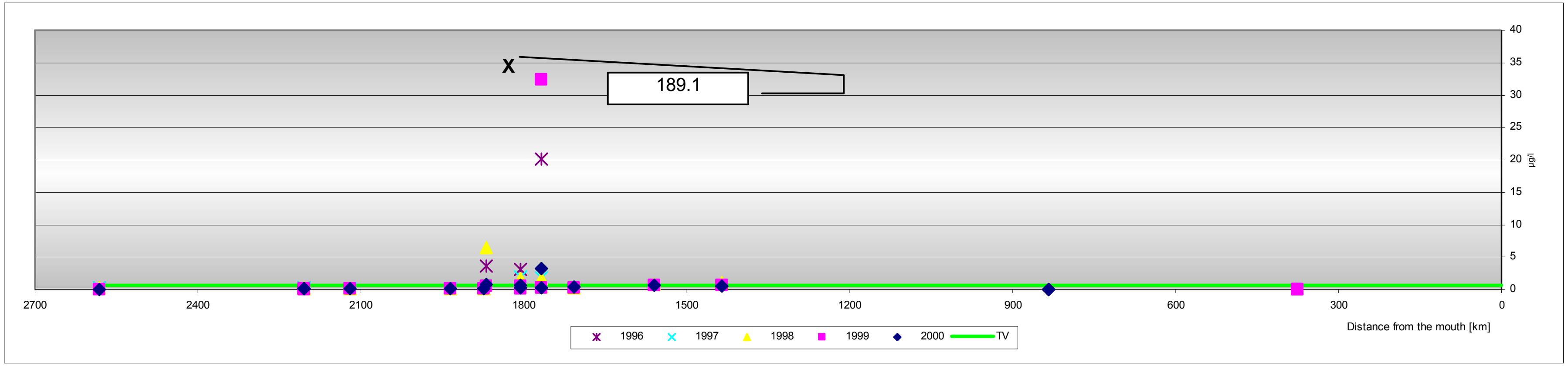

Fig. 8.1.5.11b: Spatial variation of Chloroform – Danube River

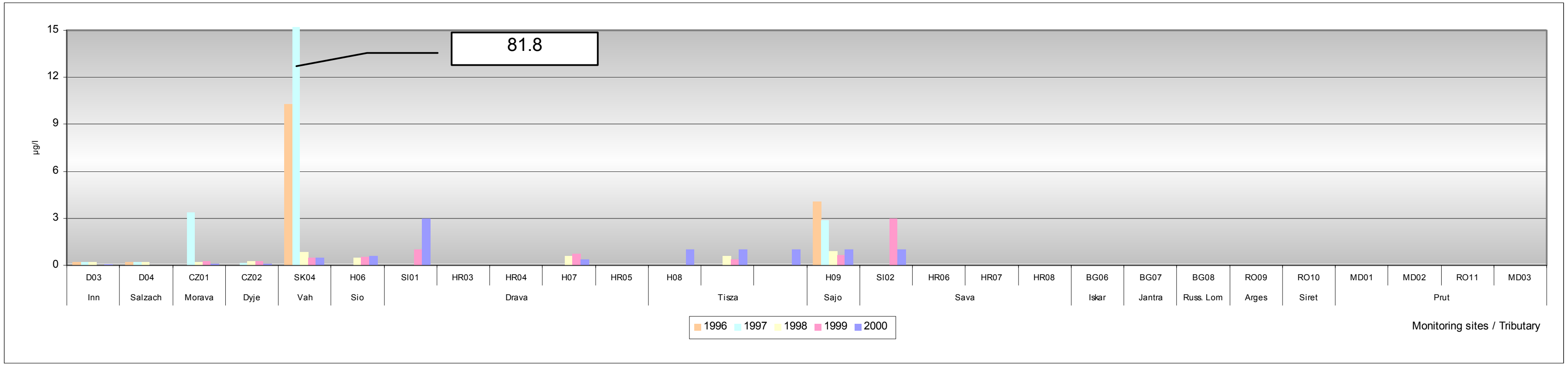

Fig. 8.1.5.12a: Spatial variation of Chloroform – Tributaries

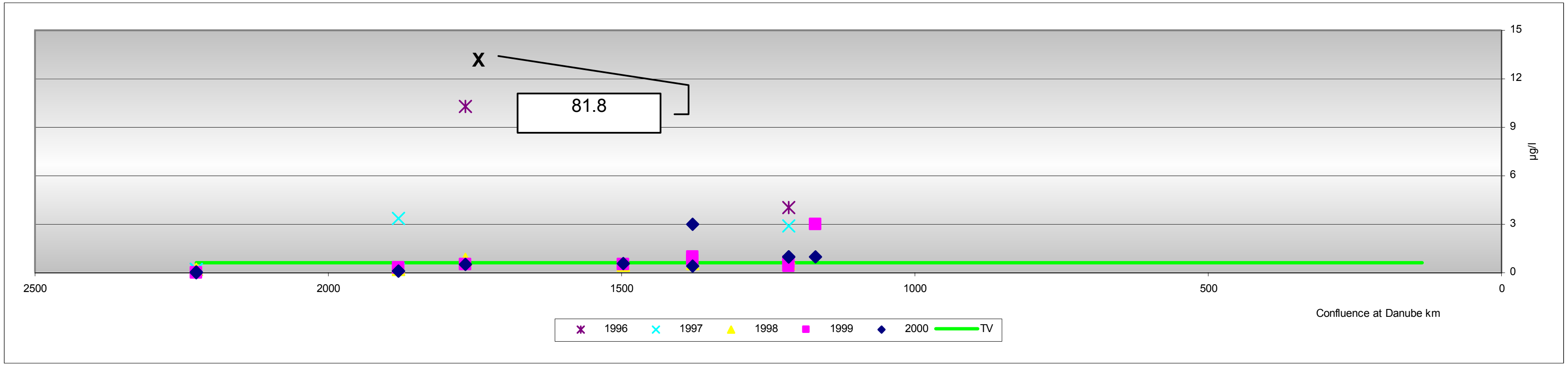

Fig. 8.1.5.12b: Spatial variation of Chloroform – Tributaries

Note: In locations SL01, SL 02 (99, 00) and H08 (00) the values in the graph represent limits of detection that are higher than the target value.

Carbon tetrachloride (tetrachloromethane)

The distribution of monitoring sites according to the Classification System in the DRB for **Carbon tetrachloride** is shown in **Fig. 8.1.5.13**:

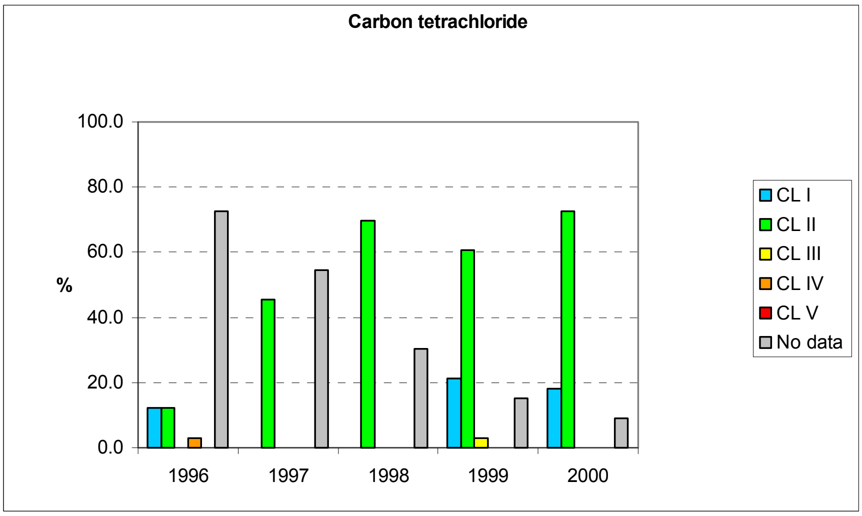

Fig. 8.1.5.13: Distribution of monitoring sites (%) according to the Quality Classification System in the DRB for **Carbon tetrachloride**

The situation in availability of data on tetrachloromethane is the same as in case of chloroform. The assessment is made based on data reported from only 33 monitoring sites, and absolutelly no measurements had been done in 1996-2000 in 70 monitoring sites.
Class II was prevailing in monitoring sites, but due to the lack of data it is not possible to provide a satisfactory picture on the occurance of the substance in water in the whole river basin.

The spatial profile for carbon tetrachloride in the Danube River is shown in **Fig. 8.1.5.14a** and **8.1.5.14b**.

Similar to chloroform, carbon tetrachloride shows undetectable values in the upper Danube, even if the levels look different (due to differences among limits of detection).

In the middle section of the Danube, tetrachloride is detectable in 1999 only according to Slovak data and mainly during 1998-2000 according to Hungarian data. The measurable concentrations for this stretch vary within the range 0.095 - 0.600 µg/l, with maximum at Danube-Dunafoldvar (km 1560, H04).

The entire lower section of the Danube as well as the corresponding tributaries has no reported data for this organic micropollutant, with two exceptions: Danube-Novo Selo/Pristol (km 834, BG01) in 2000 and Danube-Silistra/Chiciu (km 375, BG05) in 1999. All results show that carbon tetrachloride is undetectable at the reported limit of detection of 0.02 µg/l.

It has to be mentioned that no concentration measured in the Danube River is above the target limit (1.000 µg/l).

The measurable values for carbon tetrachloride in the selected tributaries are shown in Fig. 8.1.5.15a and 8.1.5.15b. The highest value observed in Sajo/Sajopuspoki (H09) – 2.460 µg/l in 1996. The concentrations values that appear at the level of 1.00 µg/l, in Drava-Ormoz (SL01), Sava-Jesenice (SL02) and Tisza-Tiszasziget (H08) are caused by the rather high limit of detection, equal to the target value for this determinand.

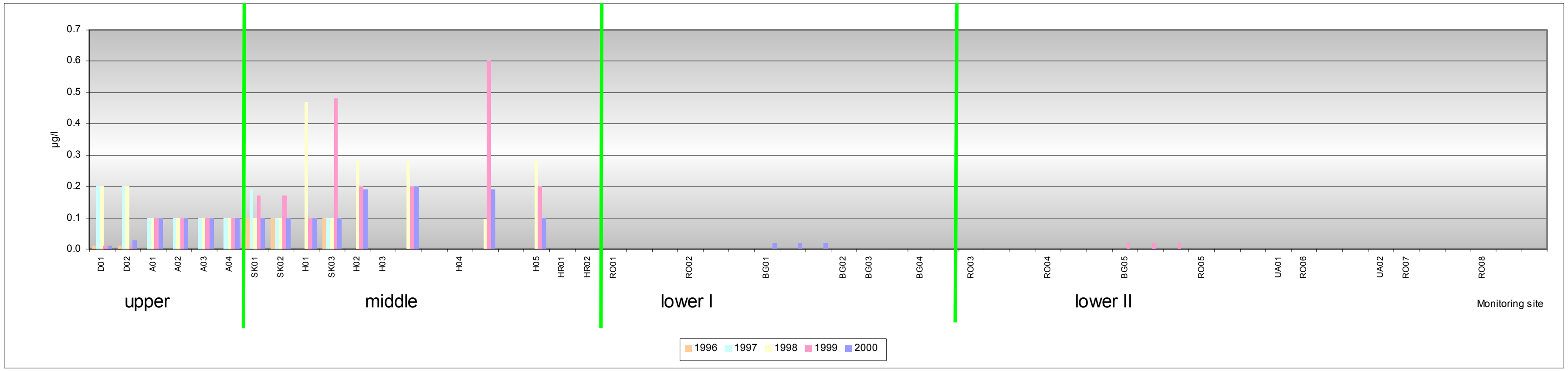

Fig. 8.1.5.14a: Spatial variation of Carbon tetrachloride – Danube River

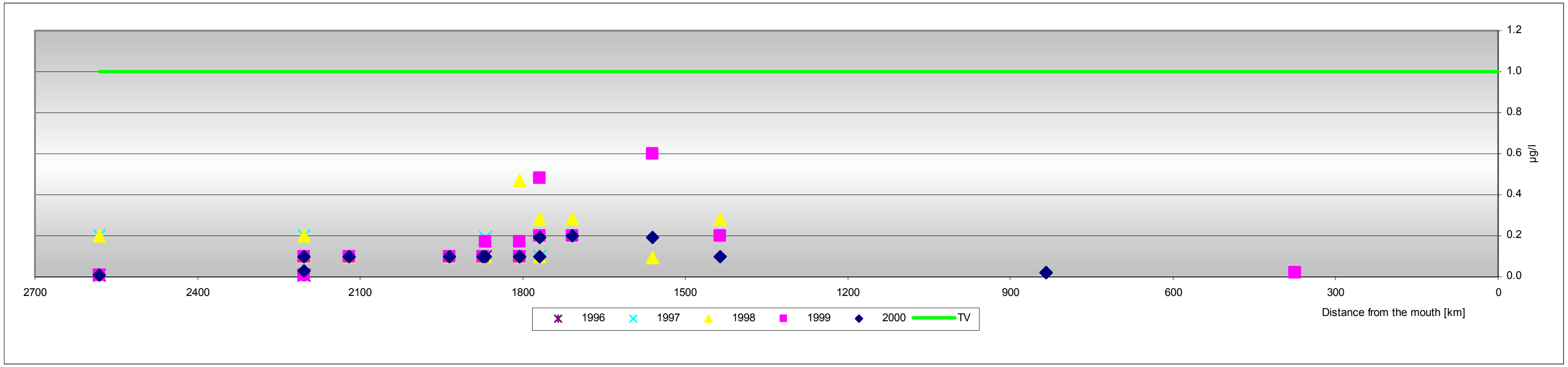

Fig. 8.1.5.14b: Spatial variation of Carbon tetrachloride – Danube River

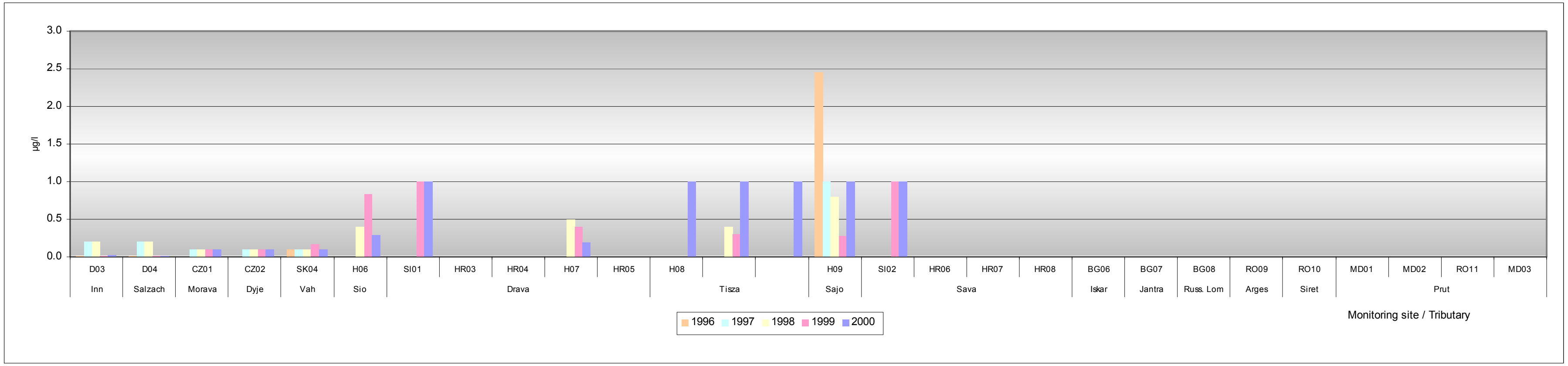

Fig. 8.1.5.15a: Spatial variation of Carbon tetrachloride – Tributaries

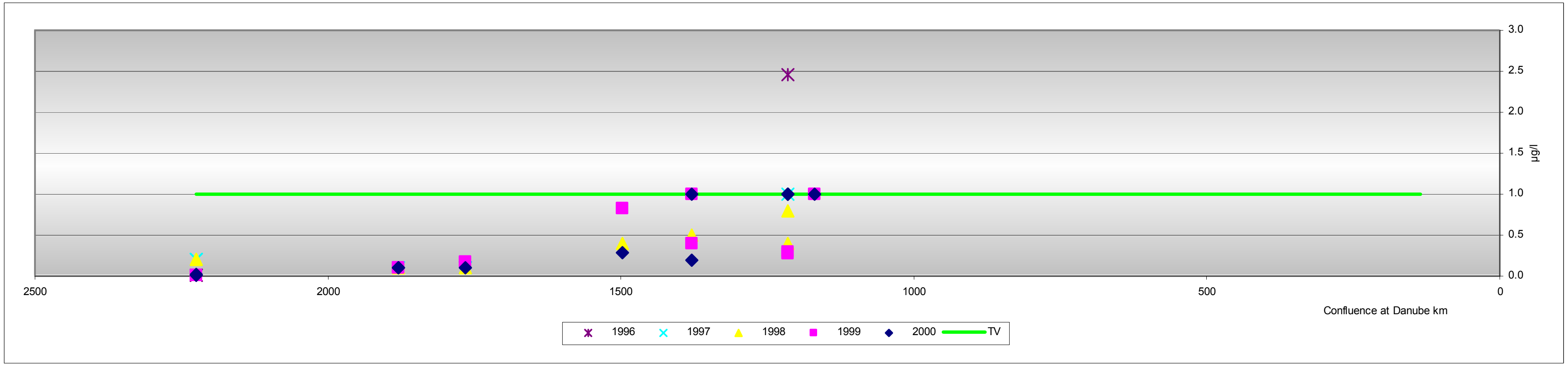

Fig. 8.1.5.15b: Spatial variation of Carbon tetrachloride – Tributaries

Trichloroethylene

The distribution of monitoring sites according to the Classification System in the DRB for **Trichloroethylene** is shown in **Fig. 8.1.5.16**:

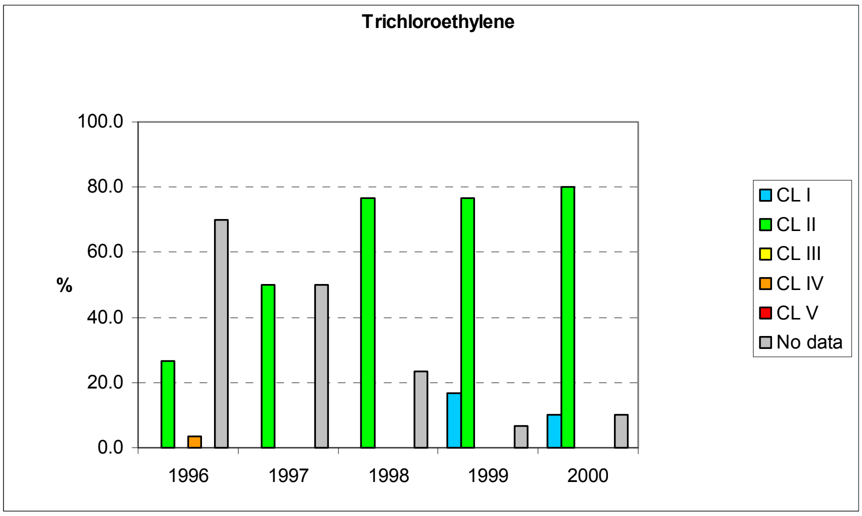

Fig. 8.1.5.16: Distribution of monitoring sites (%) according to the Quality Classification System in the DRB for **Trichloroethylene**

The assessment is made based on data reported from 30 monitoring sites, therefore without any measurement in 1996-2000 is 73 monitoring sites from Phase I List of Monitoring Sites. Number of sites with trichloroethylene is very low, but in the sites with measurements Class II is prevailing.

The spatial profile of trichloroethylene concentrations in the Danube River is illustrated in **Fig. 8.1.5.17a** and **8.1.5.17b**.

In the upper Danube, trichloroethylene is detectable in 1999 only at Danube-Neu Ulm (km 2581, D01) and Danube-Wolfsthal (km 1874, A04) and in 1999-2000 at Danube-Jochenstein (km 2204, D02), according to German data.

The middle stretch is characterized by undetectable levels of trichloroethylene, with three exceptions, all recorded in 1998, at Danube-Bratislava (km 1869, SK01), Danube-Dunafoldvar (km 1560, H04) and Danube-Herceszanto (km 1435, H05).

In the lower section, data for this determinand are reported from only one monitoring site - Danube-Silistra/Chiciu (km 375, BG05) in 1999, with undetectable values.

No concentration of trichloroethylene in the Danube River is above the target limit (1.00 µg/l).

Undetectable concentrations are observed also in almost all selected tributaries, relative to the reported limits of detection. The only measurable values appear on the Sajo-Sajopuspoki (H09); the maximum value - 2.42 µg/l in 1996 - is the only one above the target limit for trichloroethylene in tributaries – **Fig. 8.1.5.18a** and **8.1.5.18b.**

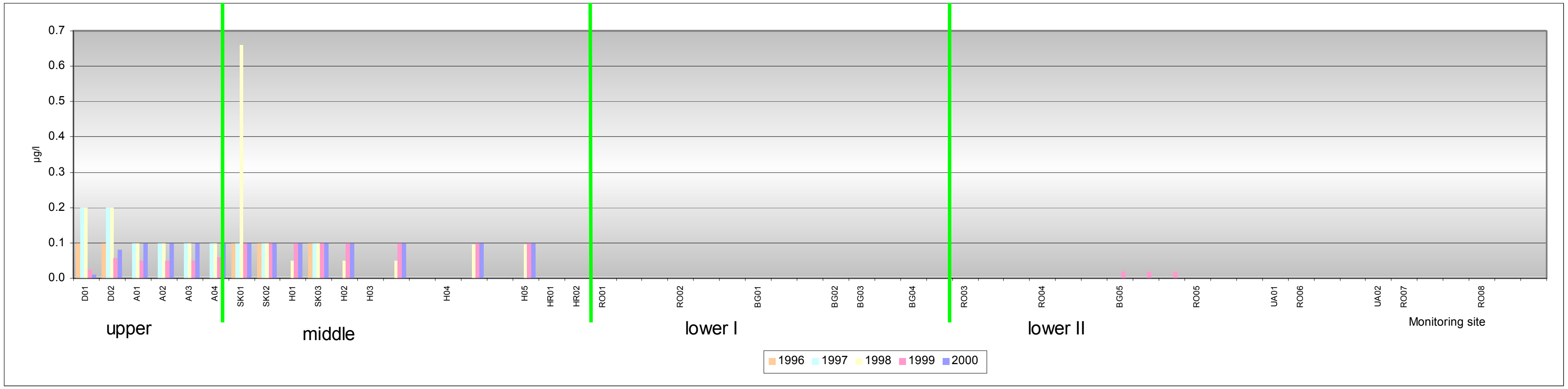

Fig. 8.1.5.17a: Spatial variation of Trichloroethylene – Danube River

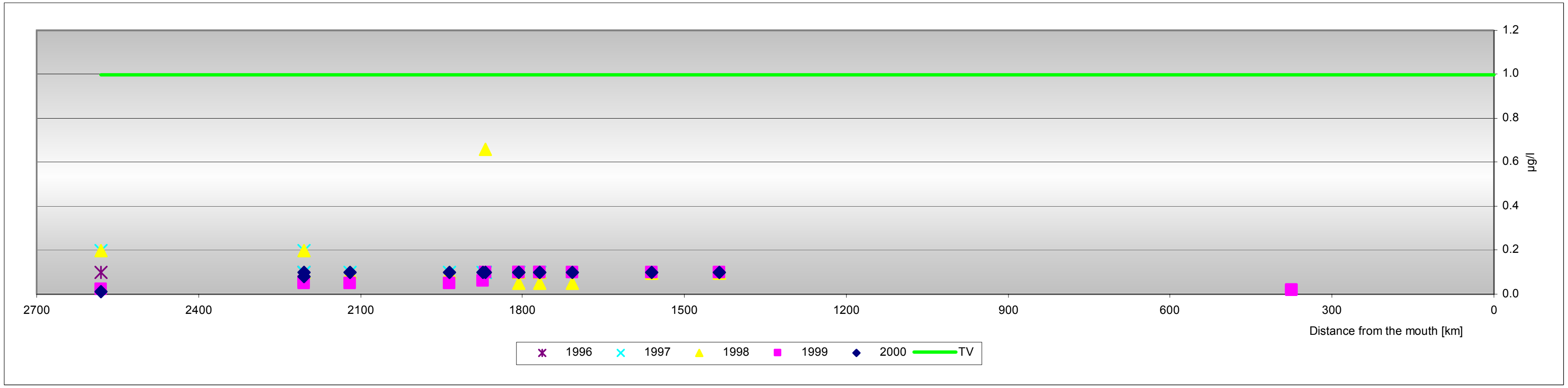

Fig. 8.1.5.17b: Spatial variation of Trichloroethylene – Danube River

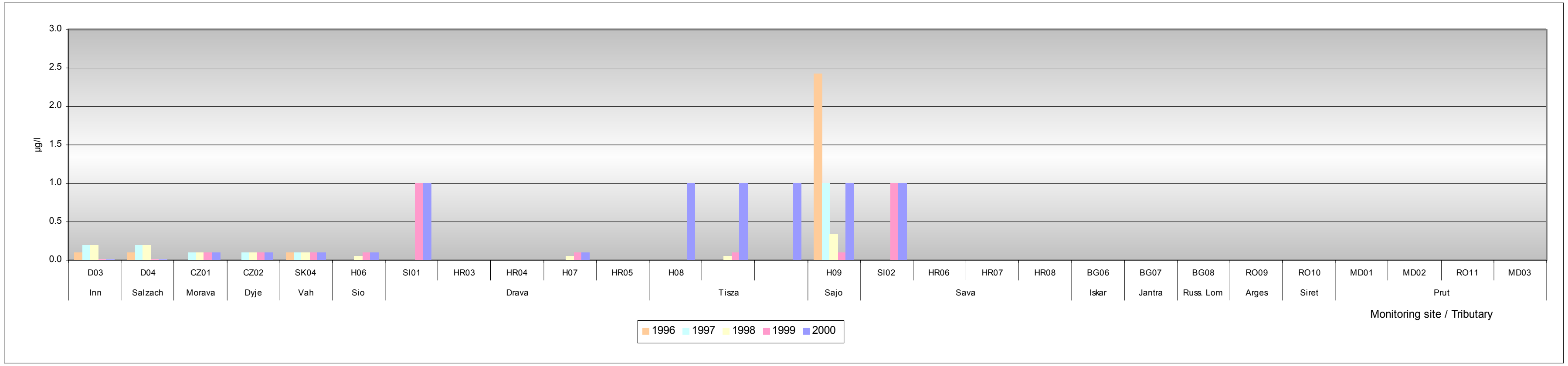

Fig. 8.1.5.18a: Spatial variation of Trichloroethylene – Tributaries

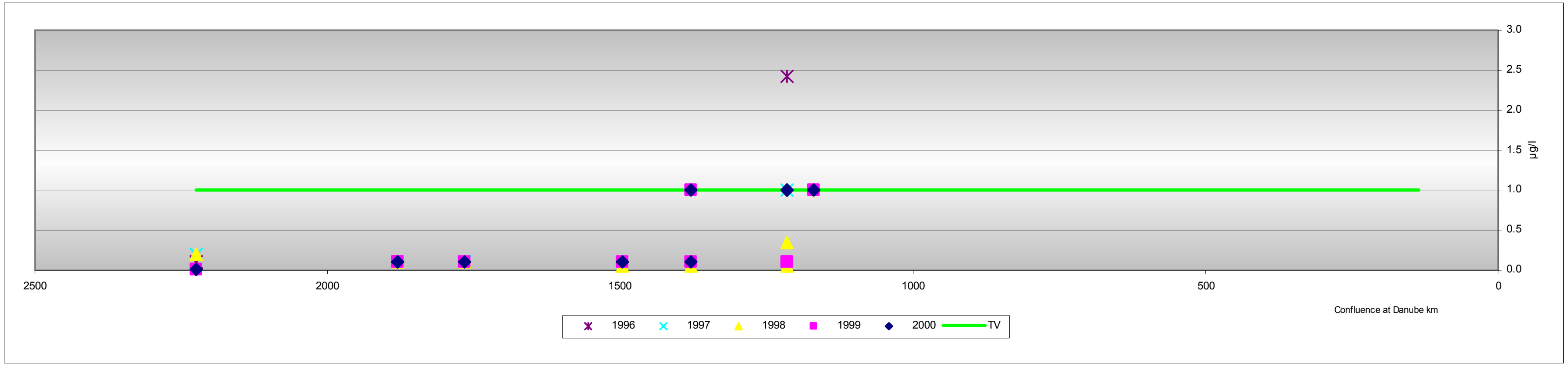

Fig. 8.1.5.18b: Spatial variation of Trichloroethylene – Tributaries

Tetrachloroethylene

The distribution of monitoring sites according to the Classification System in the Danube River basin for **Tetrachloroethylene** is shown in **Fig. 8.1.5.19**:

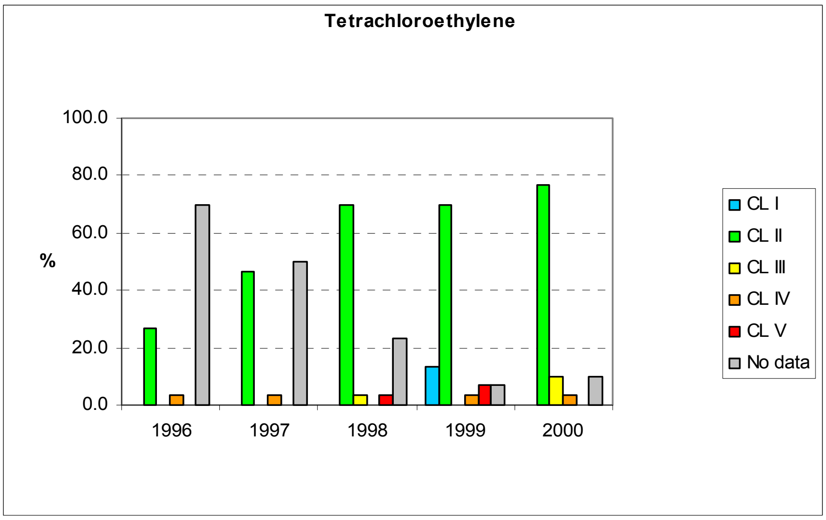

Fig. 8.1.5.19 : Distribution of monitoring sites (%) according to the Classification System in the Danube River basin for **Tetrachloroethylene**

The data on occurance of tetrachloroethylene were reported from 30 monitoring sites; out of the assessment is 73 monitoring sites, in which no measurements had been done in 1996-2000. Majority of sites with tetrachloroethylene measurement correspond to class II, but classes III – V are also represented.

The spatial profile of tetrachloroetylene concentrations in the Danube River is illustrated in **Fig. 8.1.5.19a** and **8.1.5.19b**. Unlike trichloroethylene, tetrachloroetylene is detectable at Danube-Neu Ulm (km 2581, D01) in 1998-2000 and at Danube-Jochenstein (km 2204, D02) in 1996 and 1999-2000 according to German data, but no value is above the target limit for this determinand (1.000 µg/l). If the Austrian data are taken into account, tetrachloroethylene is undetectable from Danube-Jochenstein (km 2204, A01) to Danube-Wolfsthal (km 1874, A04).

In the middle stretch, it can be noticed that values above 2.00 µg/l from Danube-Medvedov/Medve (km 1806, SK02) to Danube-Komarno/Komarom (km 1768, SK03), according to Slovak data. According to Hungarian data at the same cross sectioned, tetrachloroetylene is undetectable. Particularly at Danube-Bratislava (km 1869, SK01), an extreme high value was observed in 1999 – 16.5 µg/l. Also according to Slovak data, in the middle Danube 8 concentrations are above the target limit.

The profile of tetrachloroethylene concentrations measured in selected tributaries, illustrated in **Fig. 8.1.5.20a** and **8.1.5.20b**, presents the following features:

- tributaries from the upper Danube show undetectable levels of tetrachloroetylene, mainly during 1996 – 1998, even though the values are different within the five years (again, different limits of detection);
- in the middle Danube, on the Vah-Komarno (SK04) higher concentrations appears in 1999 and 2000 – 1.000 µg/l and 2.26 µg/l respectively, but only the second one is above the target limit;
- two concentrations above the target limit are also recorded on Sajo-Sajopuspoki (H09) – 2.420 µg/l in 1996 and 3.100 µg/l in 1997;
- it has to be mentioned that values that appear on the Drava-Ormoz (SL01), Tisza-Tiszasziget (H08) and Sava-Jesenice (SL02) tributaries have the same explanation as in the case of trichloroethylene - the reported values are the limits of detection, hence tetrachloroethylene was undetected at the respective monitoring sites.

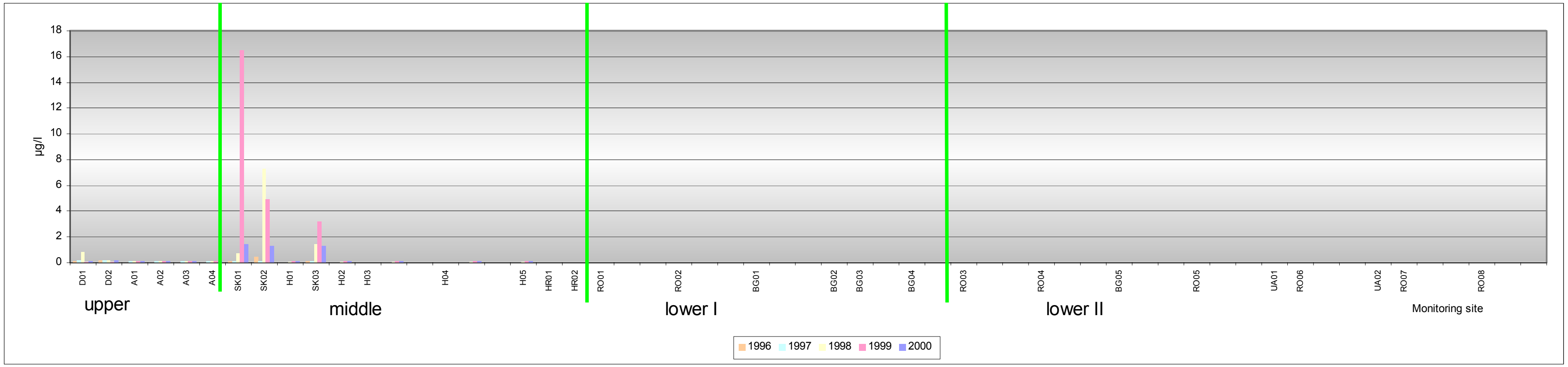

Fig. 8.1.5.19a: Spatial variation of Tetrachloroethylene – Danube River

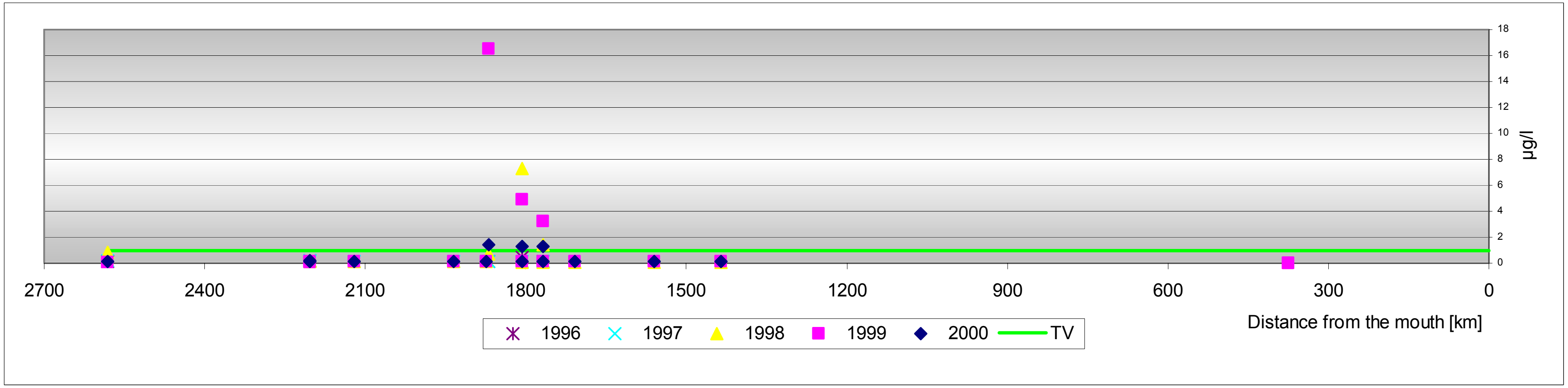

Fig. 8.1.5.19b: Spatial variation of Tetrachloroethylene – Danube River

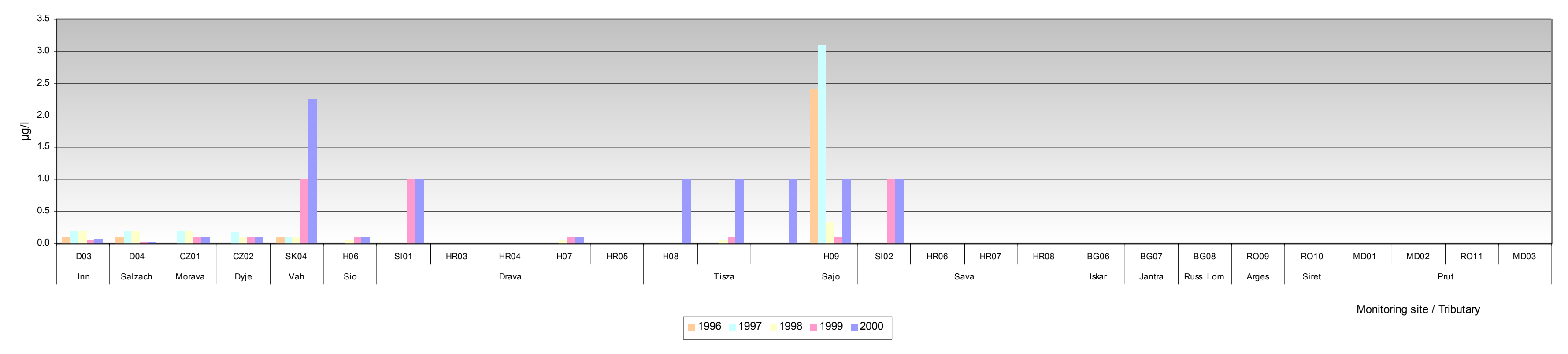

Fig. 8.1.5.20a: Spatial variation of Tetrachloroethylene – Tributaries

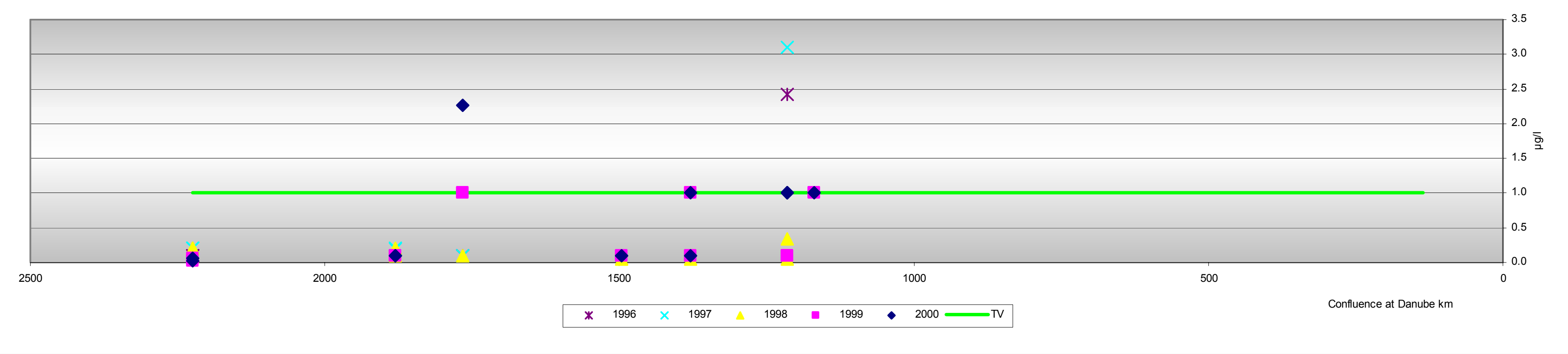

Fig. 8.1.5.20b: Spatial variation of Tetrachloroethylene – Tributaries

8.1.6. Results of Comaprison of TNMN data with Environmental Quality Standards of EU legislation

8.1.6.1. General comments regarding analytical data

It has to be noted that for some of the substances discussed in the following the data base shows considerable gaps, mainly in the lower stretch of the Danube River. If data are available the data set of one year sometimes consists of one or two measurements only. To avoid a further restriction of the overall picture such data have not been excluded from the evaluation.

In processing and representation of the data the following rules have been applied:

- Obviously erroneous data have been discarded
- All data sets of one year with at least one result greater than the LOD have been taken into consideration. The mean was calculated with the "LOD-method" in selected cases in addition with the "Zero-method"
- Data sets of one year where all data were below the LOD have not been included in the graph
- Mean values deviating from the reported LOD have been excluded when they obviously were produced by a LOD change within one year without any result greater than LOD (in the data base only one LOD per year and method can be stored, differing "less than" values within one year reflect a LOD change and result in a "mean of LODs" value which deviates from the stored LOD)

The mentioned limitations of the data base should be taken into account in the following assessment of the results. The focus should be better on the overall picture for a substance than on a single result.

8.1.6.2. Atrazine

For Atrazine a nearly complete data set is available. The LOD ranges between 0,01 and 0,06 µg/l, in a few cases up to 0,1 µg/l. Atrazine was included in the list of Priority Substances. With regard to the proposed EQS of 0,34 µg/l the Atrazine concentration at all sampling sites seems to be no problem even with the used worst case calculation of the mean (see **Figure 8.1.6.2.1**). In 1998 rather high values have been measured at two sampling sites which exceed the proposed EQS, but also at this sites the mean concentration went down below 0,34 µg/l in the consecutive years.

8.1.6.3. Cadmium (total)

The results for Cadmium (total) are characterised by high mean values in the range of 1 to 8 µg/l in lower part of Danube River (see **Figure 8.1.6.3.1**). The extreme values are caused by single data one order of magnitude higher than the rest of the data set. But even when this data are excluded the mean values lie very close to or even above the List 1 EQS of 1 µg/l for total Cadmium stipulated in CD 83/514/EEC (EEC 1983). Also an recalculation of the mean with the optimistic convention of setting values below LOD to zero does not change the situation because only few results are smaller than the method LODs (range: 0,01 - 1,0 µg/l). The results therefore indicate a severe Cadmium pollution for this Danube stretch although the concentration seems to decrease in 2000 in comparison particularly with 1997 and 1999. In the upper part of the river the mean concentrations are well below the EQS with exception of a few results in 1996/97.

8.1.6.4. Cadmium (dissolved)

For the derivation of EQS for metals FHI proposes to use the "added risk" approach, originally introduced in the Netherlands. The reasoning behind this approach is that the adaptation of the ecosystem in a certain region with a natural metal background concentration is part of the natural biodiversity of this ecosystem. With the assumption that in different adapted ecosystems the same amount of a metal added by human activities (maximum permissible addition - MPA) causes the same effect the EQSadd can be derived with the following equation:

EQSadd = Cbackground + MPA

where Cbackground is the natural metal background concentration of the region under concern. Cbackground estimates can be gained e.g. by evaluating monitoring data of pristine areas for the region. The MPA values are derived independently according to the procedure of Annex V, 1.2.6 of the WFD.

For Cadmium FHI proposes a MPA value of 0,08 µg/l for the dissolved fraction. Due to the fact that background concentrations may change along the Danube and may not be available for all regions, in a first approximative evaluation only the MPA was compared with TNMN results.
For Cadmium (dissolved) only few data and only for the upper part of Danube River are available in the data base. LOD ranges from 0,02 to 0,2 µg/l. With this very low EQS and the application of the LOD-method the results exceed the limit value in most cases (see Figure 8.1.6.4.1).

The situation might be improved by two measures:

- taking into account Cbackground once these vaules have been determined for the different river stretches
- using a more optimistic method for calculation of the mean

To show the influence of the second option an additional diagramm has been produced applying the "Zero-method" (see Figure 8.1.6.4.2).

8.1.6.5. p,p'-DDT

For p,p'-DDT in the upper part of the Danube practically all data are below LOD (LODs range between 0,005 and 0,05 µg/l). Downstream Hungary an increase in DDT concentration can be seen, resulting in mean values up to 0,4 µg/l. In this area the EQS of 0,01 µg/l for p,p'-DDT laid down in CD 86/280/EEC (EEC 1986) is exceeded in many cases (see **Figure 8.1.6.5.1**). Similar to Cadmium (total) change of the calculation method of the mean does not improve the situation because most of the data are above the method LODs.

8.1.6.6. Lead (dissolved)

As for the other metals data for the dissolved fraction of lead are very scarce and are only availbale for the upper stretch of the Danube (see figure **Figure 8.1.6.6.1**). The LOD ranges from 0,2 to 1 µg/l. Because of many less than values the influence of the calculation method is significant but even with the "LOD-method" most of the results are close to or below the MPA value of 1 µg/l proposed by the FHI (for explanation of MPA see Cadmium (dissolved)).

8.1.6.7. Lindane (gamma - Hexachlorocyclohexane)

Going down the Danube a sharp increase in Lindane concentration is noticable. The LOD of methods ranges from 0,001 to 0,1 µg/l. For Lindane one EQS is in force (0,05 µg/l laid down in CD 84/491/EEC (EEC 1984/2) for the sum of Hexachlorcyclohexane isomers). This value will be substituted by the FHI proposal of 0,02 µg/l in near future. While the EQS in force is only exceeded by the extreme values with new limit value the situation will get worse (see **Figure 8.1.6.7.1**). The influence of the calculation method is shown in **Figure 8.1.6.7.2**.

8.1.6.8. Mercury (total)

For Mercury CD 82/176/EEC (EEC 1982) states an EQS of 1 µg/l. The data base provides only results for the upper part of the Danube including Hungary and Croatia. For the lower part of the Danube no data for Mercury are available at all. LODs lie mainly within 0,1 to 0,2 µg/l. The existing results show only one exceedance of the EQS caused by an extreme concentration in 1999, which can be also observed downstreams throughout Hungary (see **Figure 8.1.6.8.1**). All other mean values are well below the List 1 EQS.

8.1.6.9. Mercury (dissolved)

Mercury is also included in the List of Priority Substances. FHI proposes an MPA of 0,036 µg/l for the dissolved metal fraction (for explanation of MPA see Cadmium (dissolved)). Again for the dissolved fraction are only very few data are available (see **Figure 8.1.6.9.1**) which in all cases exceed the limit value. The LODs (0,03 - 0,2 µg/l) lie very close or above the EQS which leads to high mean values when using the LOD-method. Switching to the Zero-method (see **Figure 8.1.6.9.2**) changes the picture dramatically. Mercury (dissolved) is one of the cases where the used convention for calculationg the mean influences the results of the compliance check to a very high degree.

8.1.6.10. Nickel (dissolved)

Nickel and its compounds is the fourth metal included in the Priority Substance list. Similar to other metals data are scarce for the dissolved fraction. Comparison with the proposed MPA of 0,6 µg/l (for explanation of MPA see Cadmium (dissolved)) shows exceedance of the EQS to a high extent for all results (see **Figure 8.1.6.10.1**). Also in this case the LODs (0,2 - 1,0 µg/l) are very close to the EQS. Therefore the influence of the calculation method was checked out (see **Figure 8.1.6.10.2**).

8.1.6.11. Chlorinated compounds (Tetrachlorethane, Tetrachlormethane, Trichlorethene, Trichloromethane)

For these four compounds the situation is very similar in many respects. For all substances EQS are laid down in CD 86/280/EEC (EEC 1986, Tetrachloroethane, Trichlorethane: 10 µg/l, Tetrachlormethane, Trichloromethane: 12 µg/l). Data for these compounds are only available in the upper stretch of the Danube. LODs range from 0,01 to 0,5 µg/l. For Tetrachlorethane, Tetrachlormethane and Trichlorethene the results are well below the respective EQS values (see **Figure 8.1.6.11.1 – 8.1.6.11.4**). Trichloromethane exceeds the EQS of 12 µg/l in one case and shows the highest concentration in general. Its also the only one of the four compounds which has been included in the list of Priority Substances. FHI prosposes an EQS of 3,85 µg/l which increases the number of exceeding concentrations to three in the five year period.

8.1.6.12. Recommendations for future changes in TNMN regarding the needs of the EU WFD

In future TNMN investigations it should be clearly distinguished between the terms limit of detection (LOD) and limit of quantification (LOQ) should be clearly defined, following the definitions used by the EU. A review of the ANAMETH-file having in mind this definitions should be carried out and both quantities included in future data sets.

The discussions on EU level concerning the statistical quantity used for compliance checking and the calculation of this quantity in the case of less than values should be carefully followed and the results integrated in the TNMN to keep up comparability of the data and compliance with EU legislation, which is of utmost importance for at least the half of the riparian states.

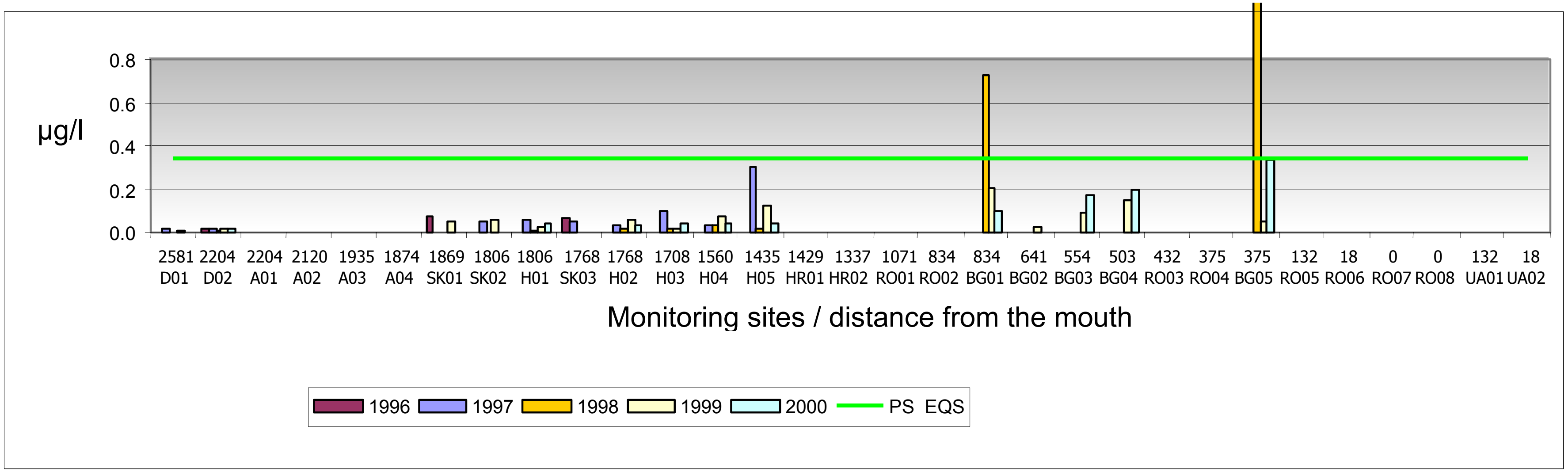

Figure 8.1.6.2.1: Atrazine

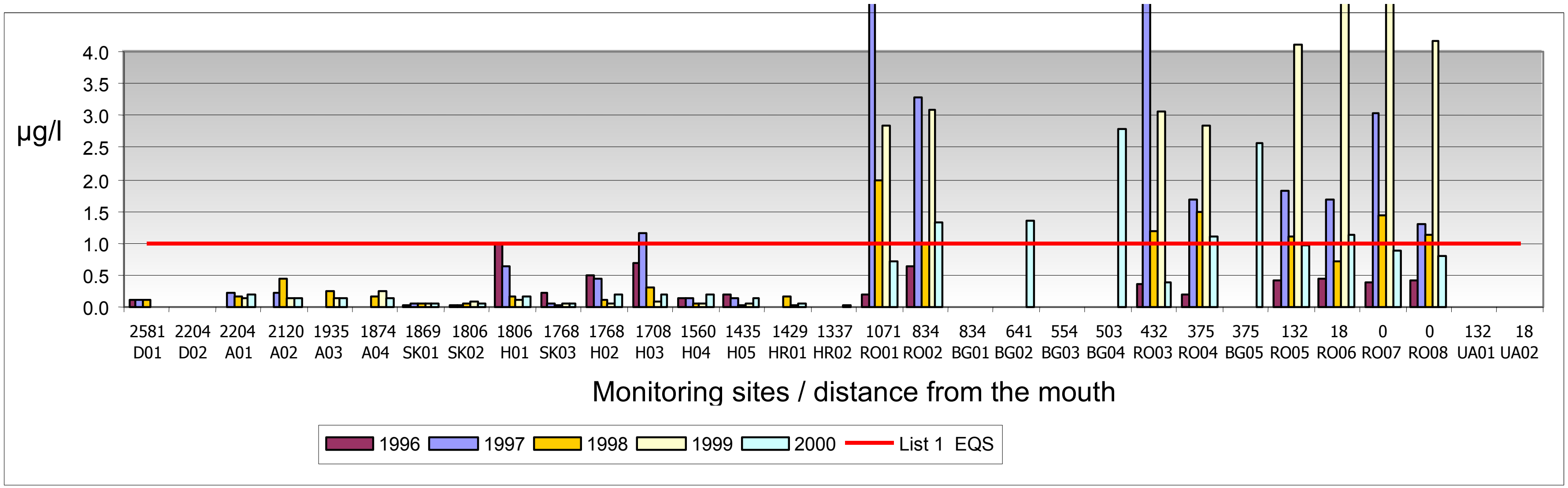

Figure 8.1.6.3.1: Cadmium (total)

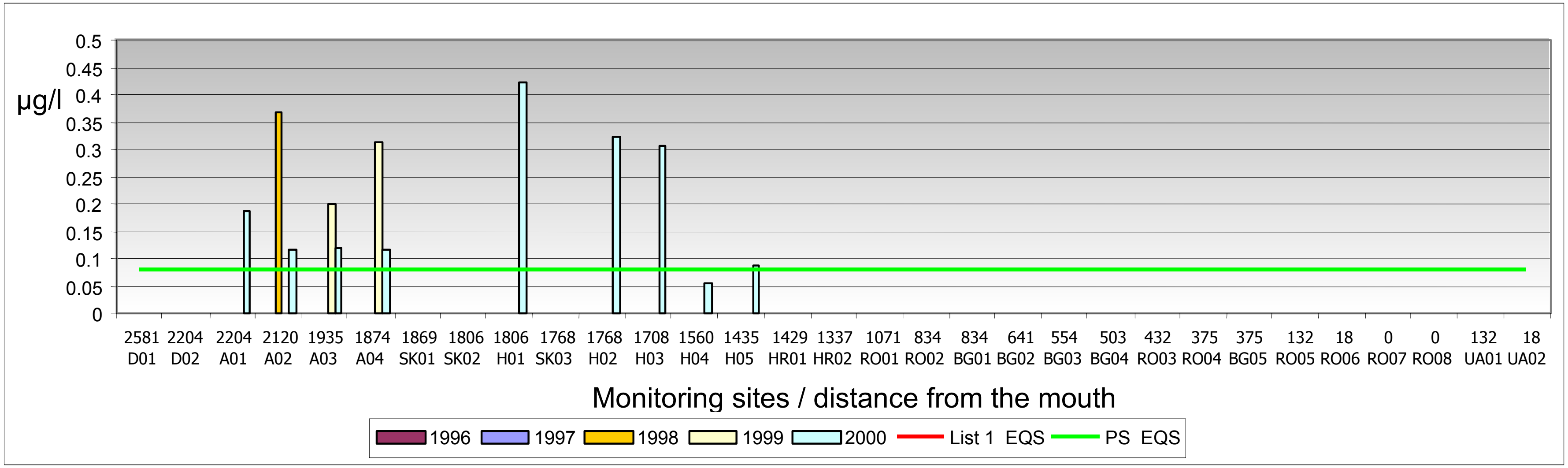

Figure 8.1.6.4.1: Cadmium (dissolved) - LOD method

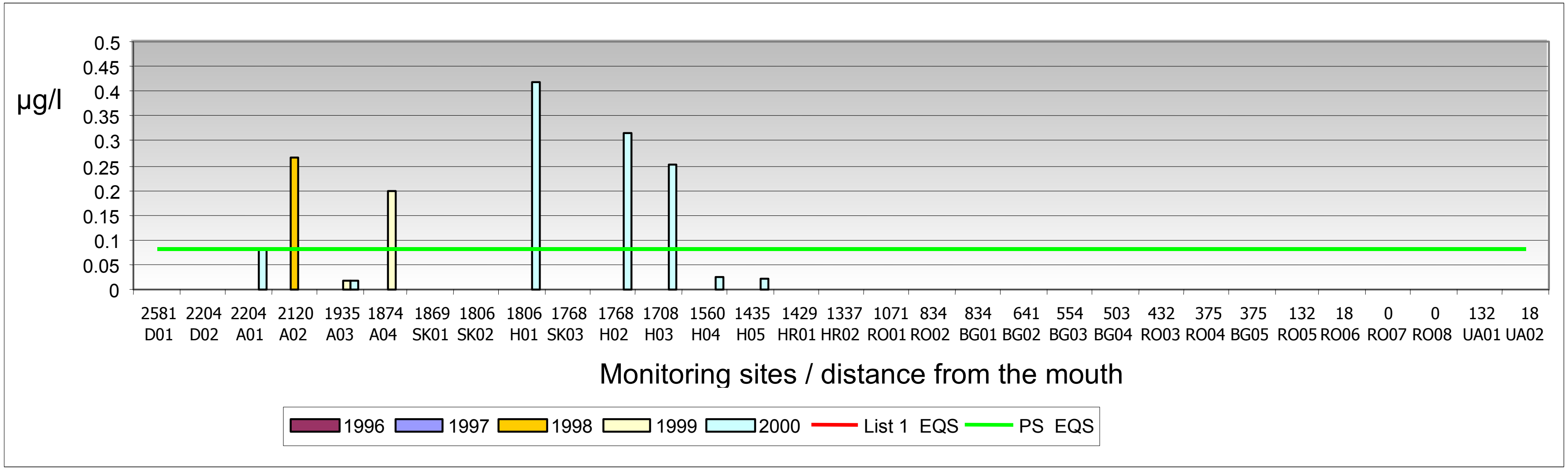

Figure 8.1.6.4.2: Cadmium (dissolved) - Zero-method

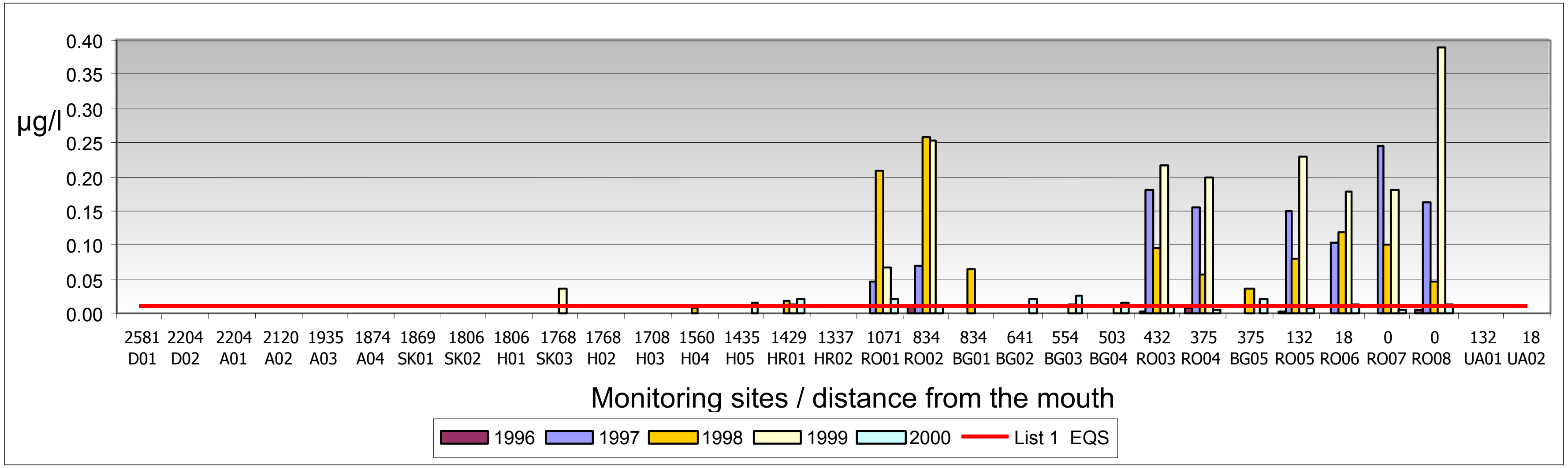

Figure 8.1.6.5.1: p,p-DDT

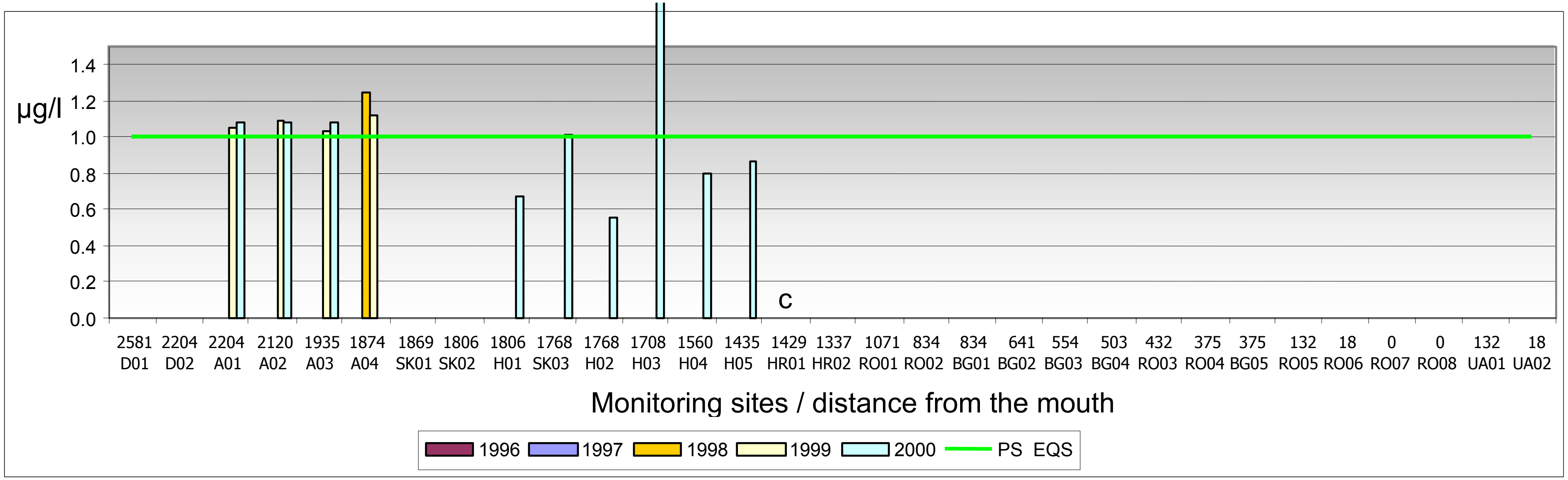

Figure 8.1.6.6.1: Lead

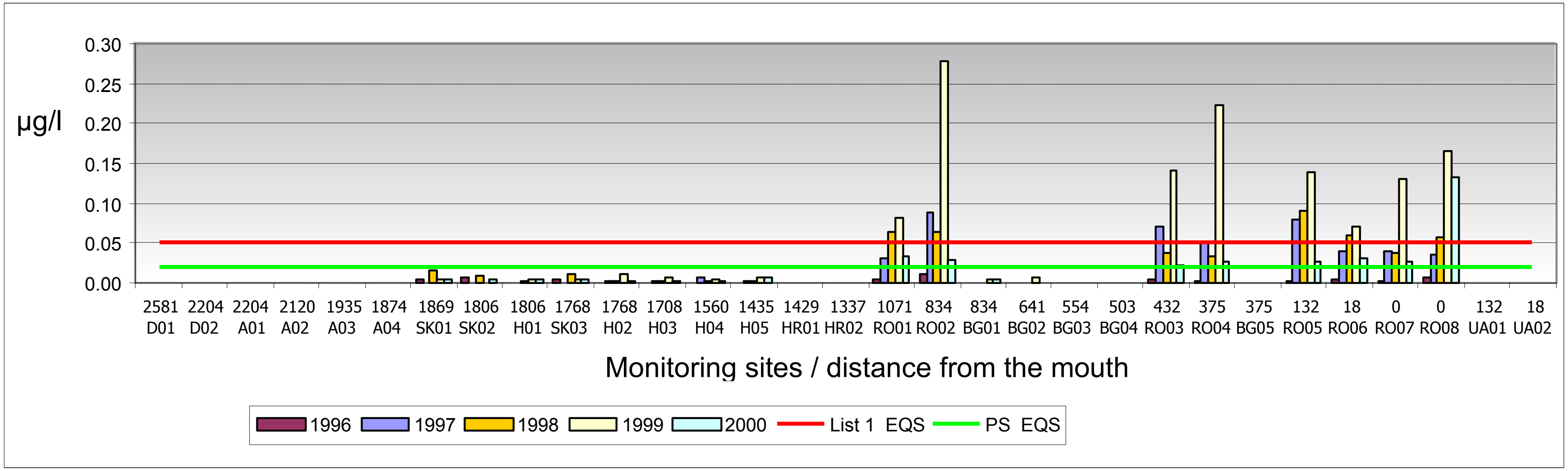

Figure 8.1.6.7.1: Lindane

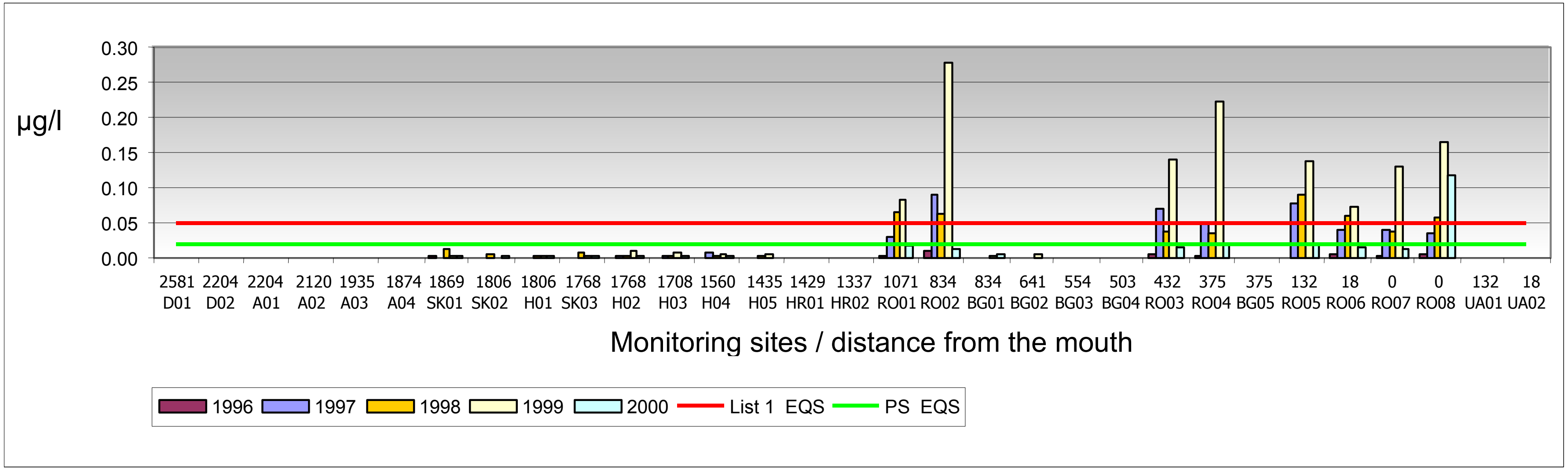

Figure 8.1.6.7.2: Lindane - Zero-method

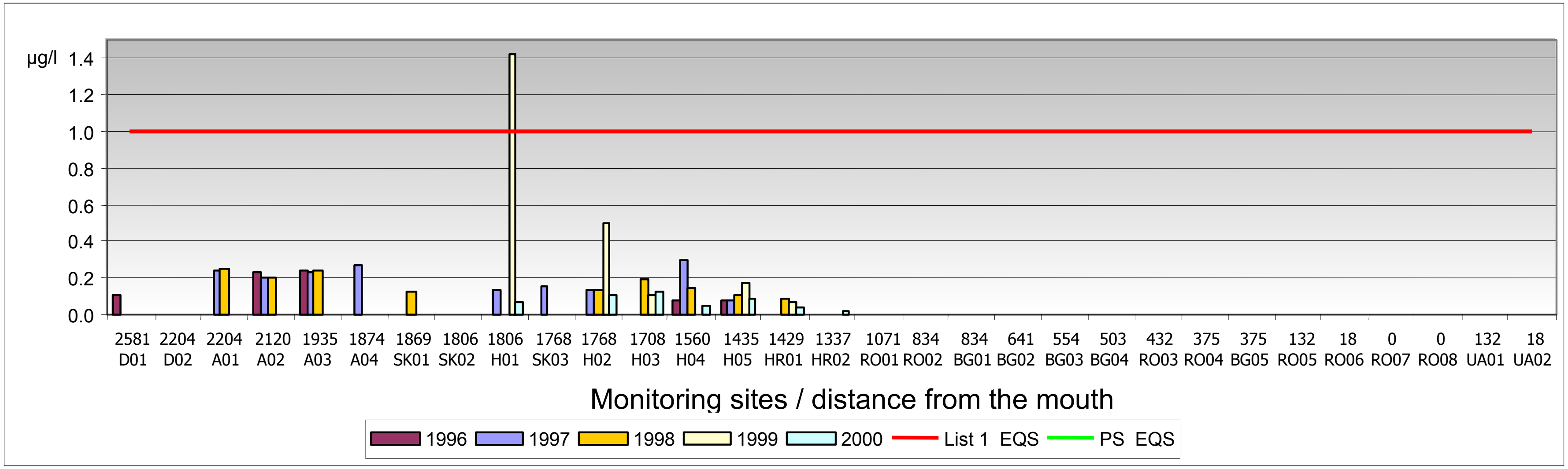

Figure 8.1.6.8.1: Mercury (total)

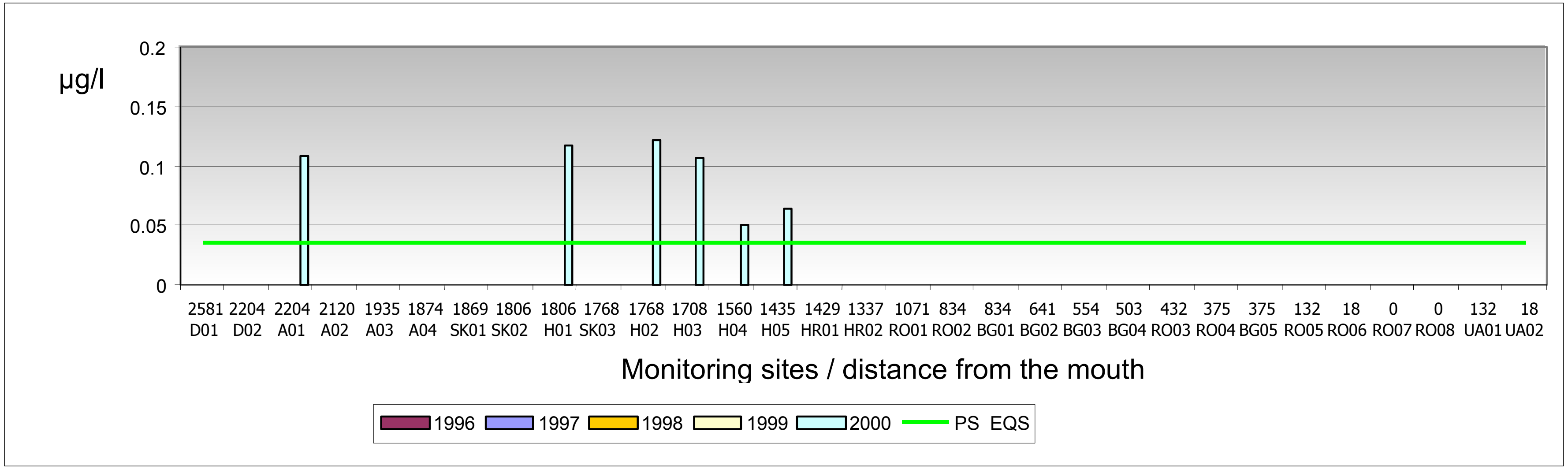

Figure 8.1.6.9.2: Mercury (dissolved) - Zero method

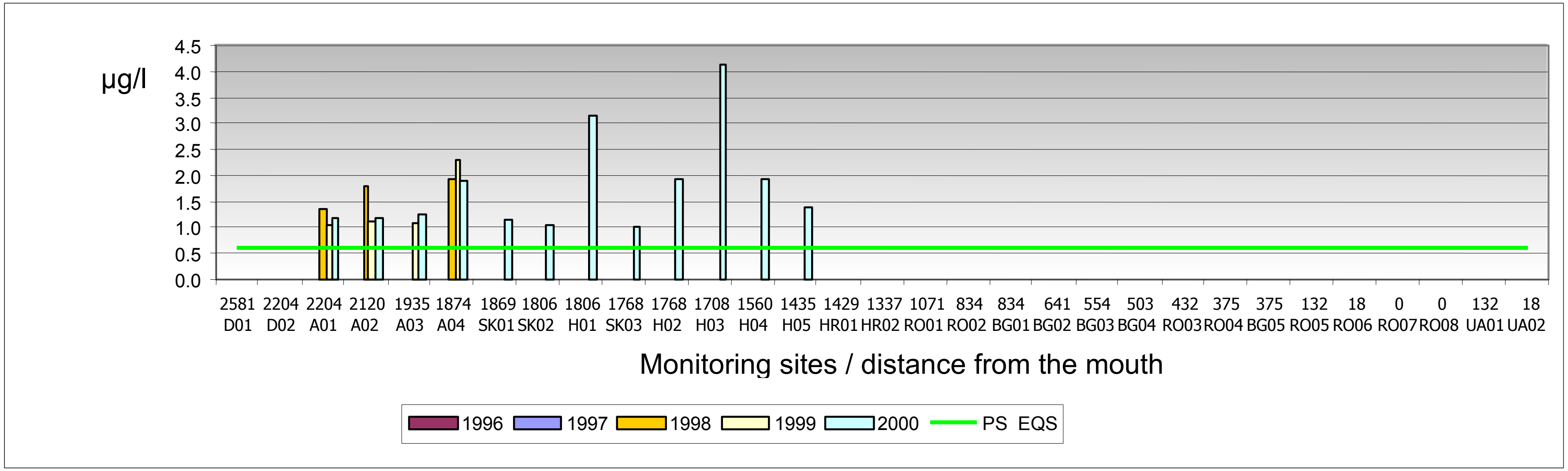

Figure 8.1.6.10.1: Nickel (dissolved)

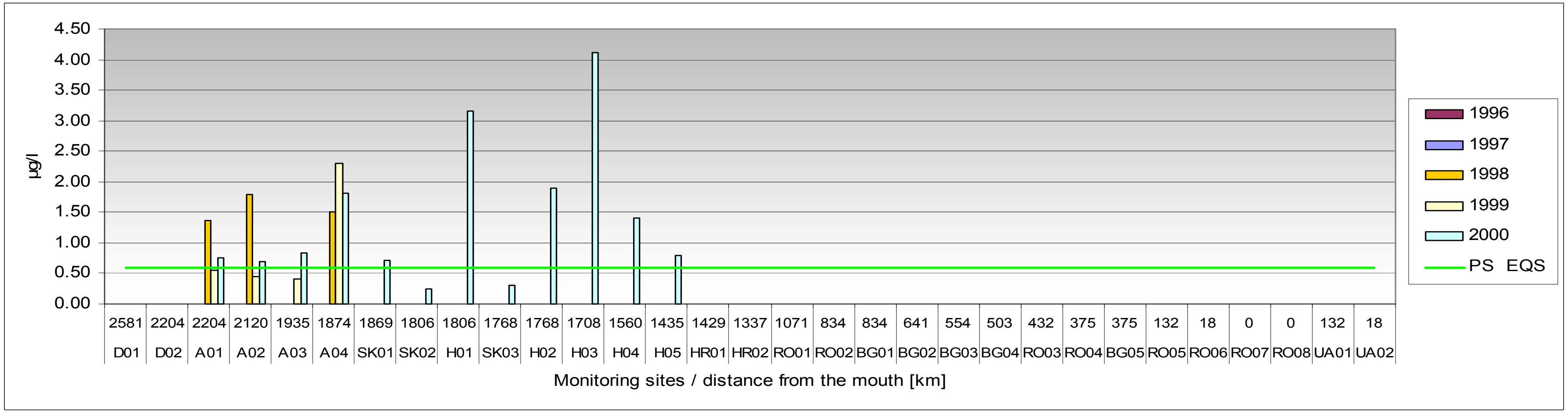

Figure 8.1.6.10.1: Nickel (dissolved) -Zero method

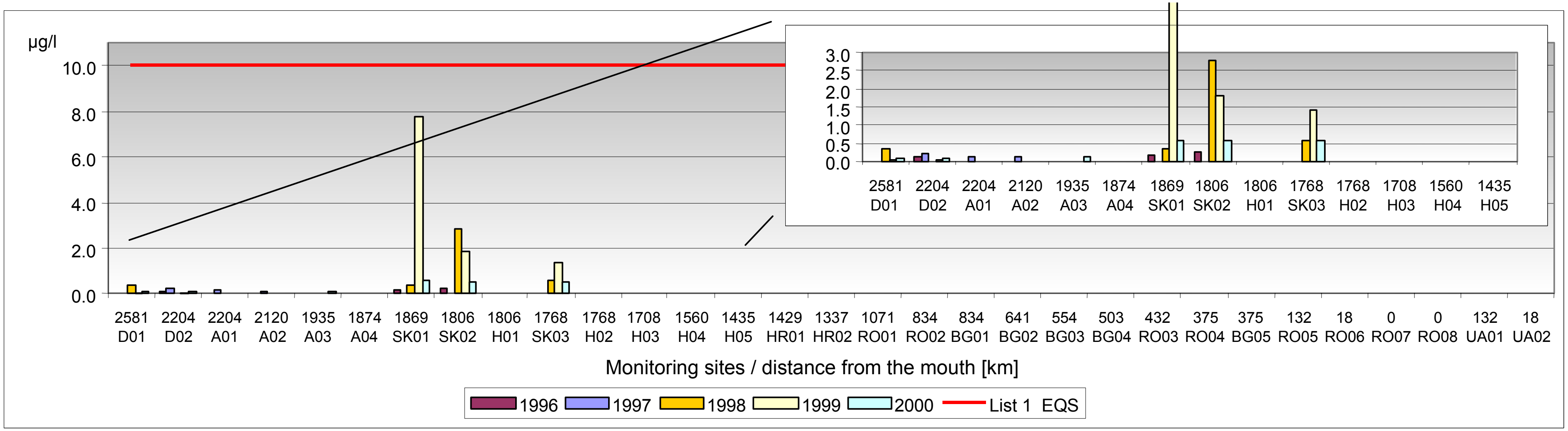

Figure 8.1.6.11.1: Tetrachloroehtene

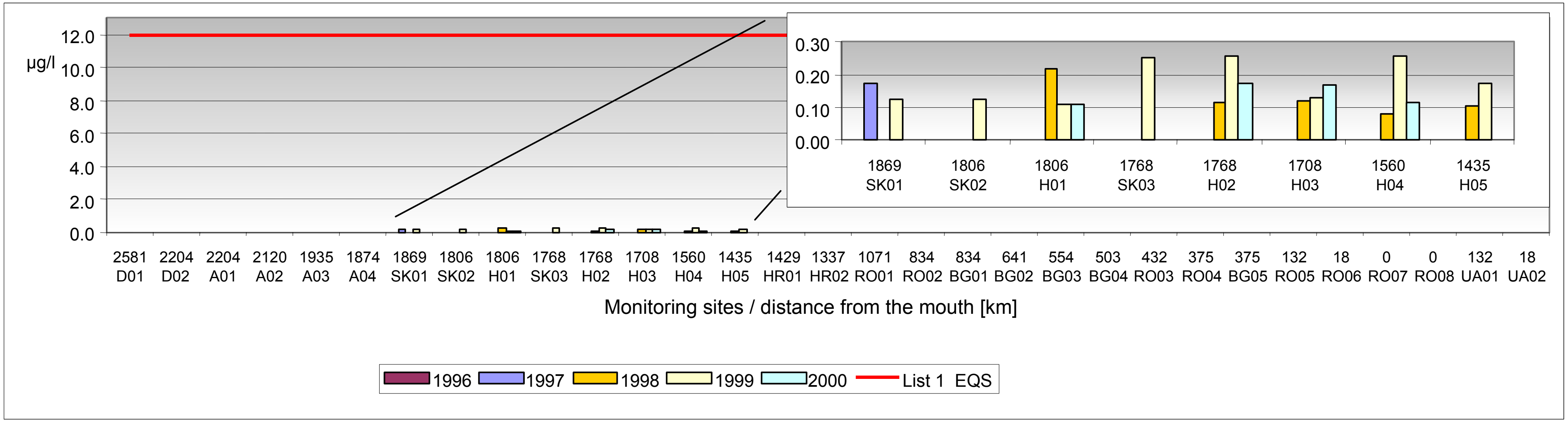

Figure 8.1.6.11.2: Tetrachloromethane

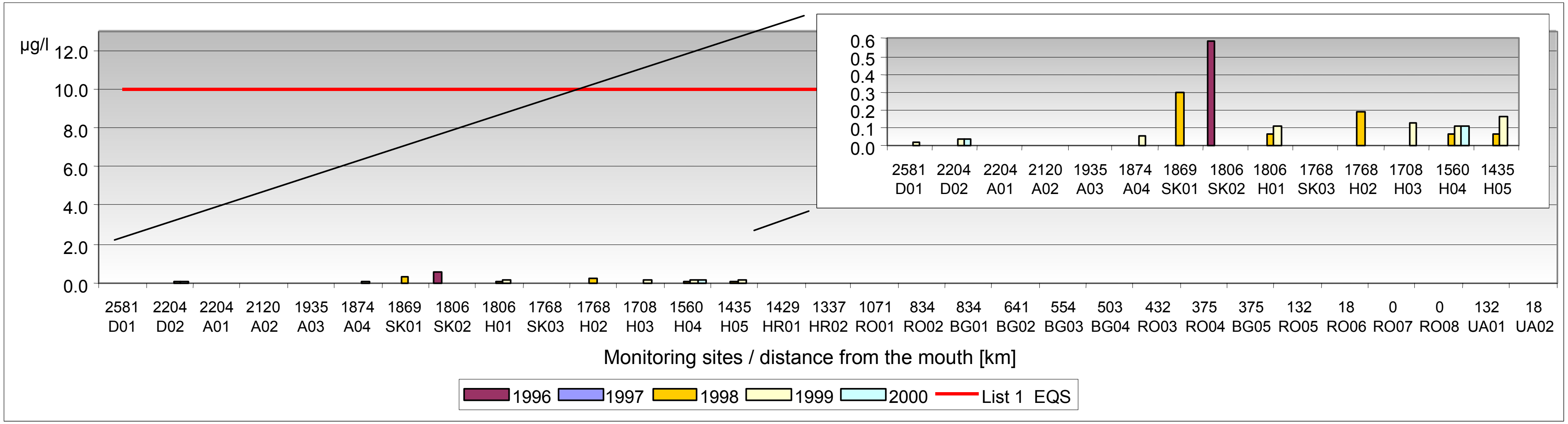

Figure 8.1.6.11.3: Trichloroethene

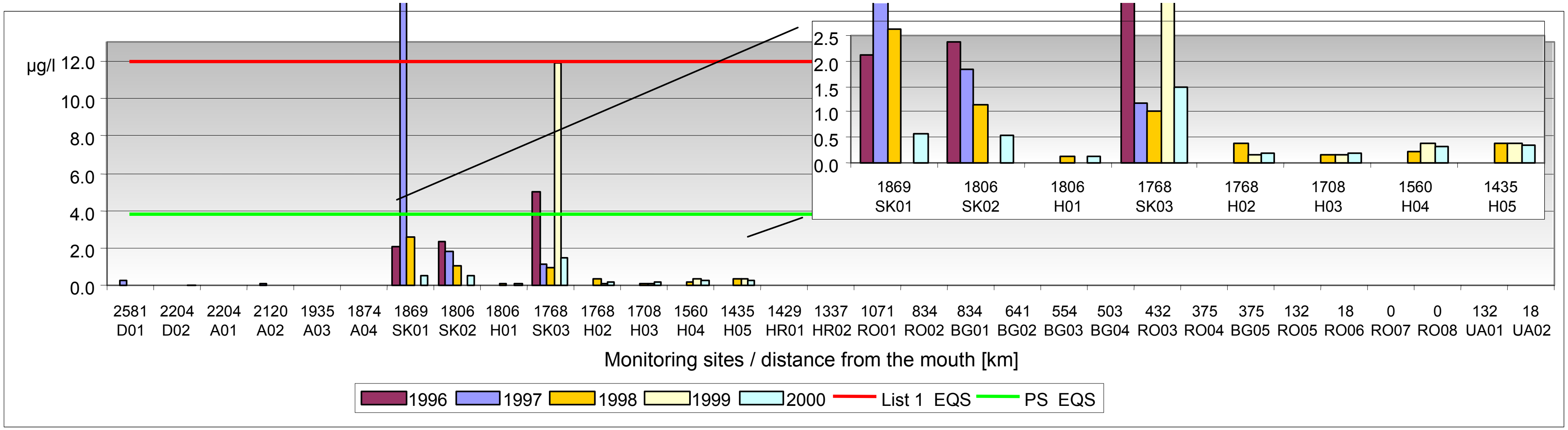

Figure 8.1.6.11.4: Trichloromethane

8.2. Evaluation of Biological Determinands

8.2.1. Phytoplankton biomass – concentration of the chlorophyll-*a*

First of all it should be stated that results of the measurements within TNMN database during period 1996 – 2000 are very heterogenious (Tab.8.2.1.1). Almost all data from the 1996 are missing (only upper two sites data are present). Upper part of the Danube and upper tributaries are covered by data (1997-2000) completely (up to 1439 r.km of the Danube). Part of the Danube from 1337 r.km was monitored very sporadicaly, only a few data from Bulgaria are present.

Interpretation of the results can be only based on data which are at disposal from the TNMN database. Therefore the only upper part of the Danube and selected tributaries can be evaluated (r.km 2581 – 1435).

The Danube stretch between Neu-Ulm and Wolfsthall belongs to the class I - II, the characteristic values ranged from 2,0 to 43,4 µg/l. Last station of the Austrian part of the Danube (Wolfsthal) belongs to class III (50,8 µg/l) in the year 1998. Other investigated years (1999 – 2000) show class I.

Left side tributary Morava brings to the Danube waters with higher concentrations of chlorophyll-a, probably due to the higher algae growth in the reservoirs (e.g. Nové Mlýny).

Chlorophyll-a in the Danube section between Bratislava and Szob increased in 1998, in following years situation improved (class II and I). Leftside tributary Váh contained more algae in the plankton (class III - II). In the lower parts of this section (1560 – 1435 r.km) phytoplankton biomass increased (class III), characteristic values ranged between 56 and 88 µg/l. Based on the results it can be stated, that Sio is the most eutrophicated tributary in this part of the Danube (class III - IV). Better situation is in Drava and Sajó (class I), while Tisza in Tiszasziget shows increase of the eutrophication during the period 1997-2000.

Lower part of the Danube is represented only by some sporadic results from the Bulgarians section. Characteristic values were between 6,8 and 54,4 µg/l, which results to the class I - III.

Tab.8.2.1.1: Characteristic values of the concentration of the chlorophyll-a of the TNMN stations during period 1996-2000.

D - Danube site (rkm) T, T/T Tributaries (site)	**Chlorophyll-a (µg/l)**				
	1996	**1997**	**1998**	**1999**	**2000**
D D01-Neu-Ulm (2581)	5,2	2,0	28,8	8,4	8,9
T/T D04-Salzach (Laufen)					
T D03-Inn (Kirchdorf)					
D D02-Jochenstein (2204)	27,8	3,6	30,0	21,4	21,5
D A01-Jochenstein (2204)	18,0	20,2	28,6	13,1	14,1
D A02-Abwinden-Asten (2120)			35,8	15,6	13,8
D A03-Wien-Nussdorf (1935)			42,8	19,7	12,3
D A04-Wolfsthal (1874)	18,0	43,4	50,8	18,7	11,7
CZ02-Dyije (Břeclav) T/T		6,5	37,4	58,8	63,3
CZ01-Morava (Lanžhot) T		3,8	38,3	98,9	53,5
D SK01-Bratislava (1869)		7,1	45,9	27,9	21,3
D SK02-Medveďov/Medve (1806)		8,2	54,6	33,8	18,4
D H01-Medveďov/Medve (1806)		37,4	55,7	32,0	24,3
D SK03-Komárno/Komárom (1768)		10,0	55,5	39,7	24,6
D H02-Komárno/Komárom (1768)		49,7	83,1	52,7	26,8
SK04-Váh (Komárno) T		10,7	75,5	27,7	33,6
D H03-Szob (1708)		59,3	44,6	29,9	27,7
D H04-Dunafoldvar (1560)		72,5	88,0	58,4	56,0
T Sio (Szekszard-Palanka)		136,3	68,1	74,3	236,0
D H05-Hercegszanto (1435)		71,9	87,0	49,0	76,0
T H07-Drava (Dravaszabolcs)		19,0	15,5	14,4	12,3
D HR01-Batina (1429)					
D HR02-Borovo (1337)					

D - Danube site (rkm) **T, T/T Tributaries (site)**	**Chlorophyll-a (µg/l)** **1996**	**1997**	**1998**	**1999**	**2000**
T HR03-Drava (Varazdin)					
H09-Sajo (Sajopuspeki) T/T		16,7	9,7	5,0	11,1
H08-Tisza (Tiszasziget) T		14,9	29,5	48,7	84,0
T SL01-Drava (Ormoz)					
T HR04-Drava (Botovo)					
T HR05-Drava (D.Miholjac)					
T SL02-Sava (Jesenice)					
T HR06-Sava (Jasenice)					
T HR07-Sava (us.Una Jasenovac)					
T BIH01-Sava (Jasenovac)					
T/T BIH02-Una (Kozarska Dubica)					
T/T BIH03-Vrbas (Razboj)					
T/T BIH04-Bosna (Modrica)					
T HR08-Sava (ds.Zupanja)					
D RO01-Bazias (1071)					
D RO02-Pristol/Novo Selo Harbour (834)					
D BG01-Novo Selo/Pristol (834)			6,5	20,5	23,8
D BG02-us.Iskar-Bajkal (641)					
T BG06-Iskar (Orechovitza)					
D BG03-ds.Svishtov (554)					54,4
T BG07-Jantra (Karantzi)					46,0
D BG04 - us.Ruse (503)					15,4
T BG08-Russenski Lom (Basarbovo)					16,6
D RO03-us.Arges (432)					
RO09-Arges T					
D RO04-Chiciu/Silistra (375)					
D BG05-Silistra/Chiciu (375)			17,7		13,8
RO10-Siret T					
MD01-Prut (Lipcani) T					
MD02-Prut (Leuseni) T					
MD03-Prut (Giurgiulesti) T					
RO11-Prut (Giurgiulesti) T					
D RO05-Reni-Chilia/Kilia arm					
D UA01-Reni-Chilia/Kilia arm					
D RO06-Vilkova-Chilia arm/Kilia arm					
D UA02-Vilkova-Chilia arm/Kilia arm					
D RO07-Sulina-Sulina arm					
D RO08-Sf.Gheorghe arm-Gheorghe arm					

CLASSIFICATION SCALE	I.	II.	III.	IV.	V.
µg/l	≤25	≤50	≤100	≤250	>250

Conclusion

1. Spatial coverage of Danube River basin by data on chlorophyll-a in TNMN is not complete. Only the upper part of the Danube and the main tributaries were monitored during period 1997-2000 in a way as it was proposed within TNMN. Only a few data were obtained from Bulgarian section.
2. Statistical values correspond to class I - III according to the above mentioned classification scale.
3. Only the Sio river (left side tributary) was in class IV during 1997 and 2000.
4. Results from the lower part of the Danube were in the class I – III as well.

Recommendation

1. It is stated that the Danube is eutrophicated river. More attention should be focused to the monitoring of determinands characterizing eutrophication mainly in the lower part of the river. This will enable to obtain coherent database along the River Danube and its main tributaries.
2. The measurements of the chlorophyll-a content should by monitored at least 10-12 times per year to obtain sufficient database for evaluation trends and changes.

8.2.2. Saprobic index of macrozoobenthos

Interpretation of the results can be only based on data which are at disposal from the TNMN database. Therefore only some parts of the Danube River and selected tributaries can be evaluated.

It should be said that database of the results of the measurements within TNMN is very heterogenious during period 1997 – 2000 (Tab. 8.2.2.1). Data from 1996 were missing. As it was mentioned in case of chlorophyll-a, data from the Danube River and its tributaries for mentioned period were very rare. Upper part of the Danube up to Borovo was investigated from the point of macroinvertebtares only. As for the tributaries, some of them were monitored up to Romanian stretch of the Danube.

Based on the results can be stated that the Danube and tributaries of the monitored TNMN station belong to the class II – II-III. Maximum values of Saprobic Indices ranged from 1,77 to the 2,7. This means β – α mesosaprobity. Only the Sava river (downstream Zupanja and Jasenice) belong to the worse classes in the first two years (III – III-IV) which means strong or very high pollution (up to polysaprobity). However within next two years the situation improoved (II-III; β– α mesosaprobity).

The differences show slight positive trend of pollution reduction within the investigated years. Generaly, based on this results can be said that Danube and its some tributaries were moderatelly or criticaly polluted.

Table 8.2.2.1: Saprobic Indices of macrozoobenthos of TNMN stations in the years 1997-2000.

D - Danube site (rkm)	**Saprobic index of macrozoobenthos**			
T, T/T Tributaries (site)	**1997**	**1998**	**1999**	**2000**
D D01-Neu-Ulm (2581)				
T/T D04-Salzach (Laufen)		2,12	2,03	2,25
T D03-Inn (Kirchdorf)		1,86	1,77	1,85
D D02-Jochenstein (2204)		2,26	2,27	2,19
D A01-Jochenstein (2204)	2,11	2,09	2,00	2,19
D A02-Abwinden-Asten (2120)	2,08		2,00	2,00
D A03-Wien-Nussdorf (1935)	1,93	2,19	2,00	2,20
D A04-Wolfsthal (1874)	2,14	2,15	2,10	2,20
CZ02-Dyje (Břeclav) T/T	2,40	2,20	2,13	2,16
CZ01-Morava (Lanžhot) T	2,71	2,30	2,23	2,15
D SK01-Bratislava (1869)	2,08	2,04	2,54	1,98
D SK02-Medveďov/Medve (1806)	2,12	2,09	2,18	1,99
D H01-Medveďov/Medve (1806)		2,20	2,18	2,00
D SK03-Komárno/Komárom (1768)	2,11	2,12	2,27	2,11
D H02-Komárno/Komárom (1768)		2,25	2,27	2,10
SK04-Váh (Komárno) T	2,70	2,45	2,42	2,26
D H03-Szob (1708)		2,11	2,24	2,26
D H04-Dunafoldvar (1560)				
H06-Sio (Szekszard-Palank) T				2,38
D H05-Hercegszanto (1435)				
T H07-Drava (Dravaszabolcs)				
D HR01-Batina (1429)				
D HR02-Borovo (1337)				2,24
T HR03-Drava (Varazdin)				
H09-Sajo (Sajopuspeki) T/T				
H08-Tisza (Tiszasziget) T				

D - Danube site (rkm)	**Saprobic index of macrozoobenthos**			
T, T/T Tributaries (site)	**1997**	**1998**	**1999**	**2000**
T SL01-Drava (Ormoz)		2,34	2,35	2,52
T HR04-Drava (Botovo)				
T HR05-Drava (D.Miholjac)				
T SL02-Sava (Jesenice)		2,57	2,32	2,36
T HR06-Sava (Jasenice)	2,60	2,80	2,50	2,24
T HR07-Sava (us.Una Jasenovac)	2,70	2,40	2,50	2,03
T BIH01-Sava (Jasenovac)				
T/T BIH02-Una (Kozarska Dubica)				
T/T BIH03-Vrbas (Razboj)				
T/T BIH04-Bosna (Modrica)				
T HR08-Sava (ds.Zupanja)	3,70	2,90	2,60	2,34
D RO01-Bazias (1071)				
D RO02-Pristol/Novo Selo Harbour (834)				
D BG01-Novo Selo/Pristol (834)				
D BG02-us.Iskar-Bajkal (641)				
T BG06-Iskar (Orechovitza)				
D BG03-ds.Svishtov (554)				
T BG07-Jantra (Karantzi)				
D BG04 - us.Ruse (503)				
T BG08-Russenski Lom (Basarbovo)				
D RO03-us.Arges (432)				
RO09-Arges T				
D RO04-Chiciu/Silistra (375)				
D BG05-Silistra/Chiciu (375)				
RO10-Siret T				
MD01-Prut (Lipcani) T				
MD02-Prut (Leuseni) T				
MD03-Prut (Giurgiulesti) T				
RO11-Prut (Giurgiulesti) T				
D RO05-Reni-Chilia/Kilia arm				
D UA01-Reni-Chilia/Kilia arm				
D RO06-Vilkova-Chilia arm/Kilia arm				
D UA02-Vilkova-Chilia arm/Kilia arm				
D RO07-Sulina-Sulina arm				
D RO08-Sf.Gheorghe arm-Gheorghe arm				

CLASSIFICATION SCALE	I.	I.-II.	II.	II.-III.	III.	III.-IV.	IV.
	unpolluted	low polluted	moderately polluted	criticaly polluted	strongly polluted	very high polluted	extensively polluted
	≤1,25	≤1,75	≤2,25	≤2,75	≤3,25	≤3,75	>3,75

Conclusion

1. The TNMN data of the Saprobic Index of macrozoobenthos are not complete, only the upper part of the Danube (up to 1337 r.km) and some tributaries were monitored during period 1997-2000.
2. It is evident that some countries included saprobic index of bioseston into the database instead of saprobic index of macrozoobenthos. Such results were excluded from the evaluation.
3. In the Danube and some tributaries the statistical characteristics correspond to the class II – II-III in accordance with used seven-class classification scale.
4. Only the Sava River (stations downstream Zupanja and Jasenice) belongs to the worse classes in the first two years (III – III-IV), however within next two years the situation improved (II-III).
5. Based on the results can be said that the Danube and its some tributaries were moderately or criticaly polluted, the slight positive trend appeared within the years.
6. Saprobic Indices in the Danube and its some tributaries were in the range of β – α mesosaprobity.

Recommendation

1. In the future more characteristics of the macrozoobenthos is needed (e.g. number of taxa, diversity or other indices, list of species) for the evaluation development and changes of the invertebrates in the Danube.
2. The investigation of the macrozoobenthos should be monitored at least 2-3 times per year and on the whole stretch of the Danube to obtain sufficient database for evaluation trends and changes.
3. Connecting to the Water Framework Directive (2000/60/EC) more communities should be monitored (e.g. phytobenthos).

8.2.3. Microbiological determinands

Based on the obtained results (see Tab.8.2.3.1) it can be stated that some data from upper part of the Danube, some data from lower part of the Danube and data from tributaries of the middle and lower part of the Danube (Dava, Una, Vrbas, Bosna, Iskar, Jantra, Arges, Prut) are missing.

In the period 1996-2000 the faecal pollution represented by the **Total Coliforms** range predominantly within class II-IV in the Danube and its tributaries. The worse situation was in Tisza (class V) in the year 1998. Class I was obtained at some Danubian stations on the Romanian-Bulgarian stretch of the river in the year 1996 only. In the next years there classes II-IV were observed. This evoke idea to check the method used for investigation of the Total Coliforms in the laboratory.

Beside Tisza (Tiszasiget), there are other tributaries bringing faecal pollution to the Danube (Váh, Siret). However, data of the tributary (Rusenski Lom and Arges), that were classified during Joint Danube Survey as the worst ones, are almost missing.

Water quality of the Danube is influenced not only by the mentioned tributaies, but predominantly by direct antropogenic impacts caused by the raw or treated sewages and diffuse impact from the agriculture.

Looking to the TNMN border stations it is shown that the measurements between countries were not harmonized. In some cases (Medve/Medveďov, Komárno/Komárom, Novo Selo/Bristol, Chiciu/Silistra, Sava) the differences are within two or three classes at the same stations in particular year.

Below Čunovo (Gabčíkovo) Reservoir and Iron gate Reservoir the number of the Total Coliforms decreased that in some years it resulted to the II (I) class. The reason is that due to the sedimentation processes bacteria that are attached to solids particles are stored in the sediments of the reservoir.

Sedimentation can be also reason for the relatively possitive situation in the Danube Delta (I-II class).

Data of the Total Coliforms from the Danube shows that pollution ranged almost between moderate and critical, in some cases strong pollution appeared. There is no trend in faecal pollution in the longitudinal profile of the Danube river. Similarly, there are no significant changes comparing individual years.

Based on the data of **Faecal Coliforms** faecal pollution of the Danube belong to the class I - IV during period 1996-2000. The Danube in Komárom (1998) was in the class V only. The extensive pollution was observed in Váh (2000), Tisza (1998) and Siret (1998).

In 1996 the low pollution is shown in the lower part of the Danube even though data from this stretch are very rare. First class was also in Bazias (1997, 1999) and Pristol/Novo Selo (1999).

Decrease of the number of Faecal coliforms due to the sedimentation can be seen in Medveďov/Medve but not downstream of Iron Gates.

In the 1999 the Danube from Jochenstein (r.km 2204) to Hercegszanto (r.km 1435) was critically polluted except Wolfsthal (r.km 1874) where was class IV.

Faecal pollution of the Danube Delta characterized by the Faecal Coliforms was slightly higher (I.-III.class) than indicated by the Total Coliforms (class I-II).

Similarly as Total Coliforms, results on Faecal Coliform bacteria did not pointed out any significant change or trend in the longitudinal profile of the
The methods of analyses were probably not fully harmonized between countries at TNMN border stations as it was in case of Total Coloforms. In Medve/Medveďov and Komárno/Komárom the differences were in two classes. Big differences within numbers of Faecal Coliform bacteria were in Siret in the individual years (64 – 920 000 CFU per 100 ml).

Tab. 8.2.3.1.: Statistical values of microbiological analyses of Total Coliforms and Faecal Coliforms in TNMN stations in the period 1996-2000.

Total coliforms (CFU per 100ml)					**D - Danube site (rkm)**	**Faecal coliforms (CFU per 100ml)**				
1996	**1997**	**1998**	**1999**	**2000**	**T, T/T Tributaries (site)**	**1996**	**1997**	**1998**	**1999**	**2000**
					D D01-Neu-Ulm (2581)					
					T/T D04-Salzach (Laufen)					
					T D03-Inn (Kirchdorf)					
19200	1920	16900	10760	22380	D D02-Jochenstein (2204)	1280	332	1325	1460	2230
12600	1460	11760	14900	18720	D A01-Jochenstein (2204)	1460	116	1430	1290	2840
					D A02-Abwinden-Asten (2120)					
4530	1750	17300	10900	10820	D A03-Wien-Nussdorf (1935)	721	316	1258	1820	2520
31000	11000	204000	127000	56600	D A04-Wolfsthal (1874)	12000	3070	14000	22000	6360
1056	8260	8200	10860	7160	CZ02-Dyje (Pohansko) T/T	552	2100	3560	3200	3280
578	1260	5500	4600	10800	CZ01-Morava (Lanžhot) T	220	430	2200	1390	3100
27600	4400	10630	13600	19000	D SK01-Bratislava (1869)	9600	1520	4210	5000	3680
7220	920	3420	3020	3950	D SK02-Medveďov/Medve (1806)	2200	300	880	1100	500
		160000	5400	4200	D H01-Medveďov/Medve (1806)			17000	2400	1300
260000	24200	38100	21700	118000	D SK03-Komárno/Komárom (1768)	44800	4360	7520	6170	7900
		540000	46400	92000	D H02-Komárno/Komárom (1768)			220000	3500	16000
214000	63000	135800	205000	390000	SK04-Váh (Komárno) T	72600	18900	34400	53500	158300
		172000	13226	13510	D H03-Szob (1708)			36667	5100	5367
		295000	24700	23800	D H04-Dunafoldvar (1560)			70000	6000	11667
		50000	31000	20000	H06-Sio (Szekszard-Palank) T					
		662000	18000	28500	D H05-Hercegszanto (1435)			80000	1500	8000
		170000	25500	24700	T H07-Drava (Dravaszabolcs)			22000	1300	2730
		35500	22610	8890	D HR01-Batina (1429)					
		2290	7600	2230	D HR02-Borovo (1337)					350
13900	7500	23900	11000	11000	T HR03-Drava (Varazdin)					
		488000	50000	30000	H09-Sajo (Sajopuspeki) T/T			40000	6000	5600
		1921000	251083	255167	H08-Tisza (Tiszasziget) T			145634	18974	23527
14000	27600		8630	15170	T SL01-Drava (Ormoz)				4450	4050
5470	7910	17700	12200	6520	T HR04-Drava (Botovo)					
20980	49800	36010	9810	3060	T HR05-Drava (D.Miholjac)					
22000	27800		29000	52200	T SL02-Sava (Jesenice)				7000	3520
43800	9300	39630	43800	35000	T HR06-Sava (Jasenice)					1800
24000	24000	24000	24000	24000	T HR07-Sava (us.Una Jasenovac)					4960
					T BIH01-Sava (Jasenovac)					
					T/T BIH02-Una (Kozarska Dubica)					
					T/T BIH03-Vrbas (Razboj)					
					T/T BIH04-Bosna (Modrica)					
23100	45700	42600	15000	19500	T HR08-Sava (ds.Zupanja)					2350
1178	8270	10634	5700	7667	D RO01-Bazias (1071)		96	677	47	922
303	4300	6667	777	7467	D RO02-Pristol/Novo Selo Harbour (834)	16	1334	250	45	1357
		490334	146500	2504	D BG01-Novo Selo/Pristol (834)					
					D BG02-us.Iskar-Bajkal (641)					
					T BG06-Iskar (Orechovitza)					
					D BG03-ds.Svishtov (554)					
					T BG07-Jantra (Karantzi)					

Total coliforms (CFU per 100ml)					D - Danube site (rkm) T, T/T Tributaries (site)	Faecal coliforms (CFU per 100ml)				
1996	1997	1998	1999	2000		1996	1997	1998	1999	2000
				140000	D BG04 - us.Ruse (503)					
				40000	T BG08-Russenski Lom (Basarbovo)					
	4845	2452	2567	16000	D RO03-us.Arges (432)		310	190	758	6830
					RO09-Arges T					
204	13733	92133	19067		D RO04-Chiciu/Silistra (375)	10	8067	24100	1280	
		163334		32667	D BG05-Silistra/Chiciu (375)					
350	16000	24000	920000		RO10-Siret T	64	810	920000	1300	
					MD01-Prut (Lipcani) T					
	35000	16000	16000	16000	MD02-Prut (Leuseni) T		16000	3600	2100	430
					MD03-Prut (Giurgiulesti) T					
	9200	16000	9200		RO11-Prut (Giurgiulesti) T		2200	16000	220	
193	7367	2867	7640		D RO05-Reni-Chilia/Kilia arm	16	3167	1527	1630	
					D UA01-Reni-Chilia/Kilia arm					
63	6934	2434	3864		D RO06-Vilkova-Chilia arm/Kilia arm	11	2500	1664	4467	
					D UA02-Vilkova-Chilia arm/Kilia arm					
110	7467	2300	6757		D RO07-Sulina-Sulina arm	7	2400	1860	490	
	9834	1811	3474		D RO08-Sf.Gheorghe arm-Gheorghe arm		507	1727	2700	

I.	II.	III.	IV.	V.	CLASSIFICATION SCALE	I.	II.	III.	IV.	V.
≤500	≤10000	≤100000	≤1000000	>1000000	(CFU/100 ml)	≤100	≤1000	≤10000	≤100 000	>100000

Conclusion

1. Data on presence of bacteria (Total Coliforms and Faecal Coliforms) in TNMN databases are not complete for the river basin.
2. Data from the upper part of the Danube (up to Borovo) and the main tributaries monitored during period 1998-2000 are more homogenous than lower part of the Danube.
3. Characteristic values of the Total Coliforms result to the class I - IV in the Danube and the tributaries except for Tisza in the year 1998 (class V).
4. Statistical values of the Faecal coliforms show similar situation to the Total Coliform bacteria. The data ranged from class I to IV in the Danube and the tributaries except for Tisza (1998), Váh (2000) and Danube in Komárno (1998) where the extensive pollution was observed.

Recomendation

The results from the Danube and its tributaries were evaluated according to the about mentioned classification scheme. The EU Bathing Water Quality Directive (76/160/EEC) is now in the period of the revision.

It is recomended to wait for the new version of the mentioned EU Directive and re-valuate data from five years period (1996-2000).

For the TNMN the additional determinands should be included into the programme.

9. Conclusions and recommendations

The objective of this report was to assess water quality in Danube River basin, including classification and identification of spatial and temporal changes. The basis for assessment are data on physico-chemical and biological determinands collected in the frame of TNMN in five-years period 1996 – 2000.

The basis for assessment of spatial and temporal changes were 90 %-iles of yearly data sets, which is able to express also unfavourable situations that occurred in particular year in the monitoring site. The 90 %-iles create also the basis for classification of water quality, but in case of frequency of measurements lower than eleven the maximum value was used for comparison with limit values for different water quality classes.

Results of classification are given in Annex I, assessment of water quality on the basis of physico-chemical determinands is in chapter 8.1 and assessment based on biological determinands in chapter 8.2.

To supplement interpretation of heavy metals and micropollutants content in water of Danube River basin, comparison of TNMN data had been done with Environmental Quality Standards (EQS) of EU legislation. Existing EQS for List I substances together with proposed EQS for Priority Substances had been used for the comparison. For this purpose, not 90 %-iles, but mean values calculated with „LOD-method“ and in selected cases also with „Zero-method“ were used.

General characteristics

Suspended solids content increases slightly from upper to lower Danube section; as concerning its tributaries, some of them show significantly higher concentrations of suspended solids than the Danube River itself – Tisza, Russenski Lom, Arges, Siret and Prut.

Values of pH show a slight alkaline medium; values exceeding 8.50 are present mainly in the middle Danube, where, correlated with dissolved oxygen concentrations, show the influence of primary productivity and organic matter load. This pH distribution along the Danube River is in accordance also with results obtained from Joint Danube Survey.

Conductivity values do not present significant variations along the main course of the river. However, after an intermediate decrease after confluence with Sava River, a slight increase is observed in the lower Danube. From tributaries, Sio and Prut present relatively higher salts content.
Excluding only few values (at Danube-Batina, rkm 1429), alkalinity shows a constant spatial pattern in the upper and in the middle Danube; slightly increasing values appear in the second part of the lower Danube. As concerning the tributaries, higher alkalinity values are present on Sio and Russenski Lom.

Nutrients

From the different fractions analyzed within the TNMN Programme, ammonium-N, nitrite-N, nitrate-N, ortho-phosphate-P and total phosphorous were chosen for assessment of nutrient content in waters. Information on organic and total nitrogen are sparce and can not provide a good picture on situation in the river basin.

Ammonium-N and nitrite-N present an increasing profile from upper to lower Danube, which is much more significant in case of ammonium-N. From existing data along the Danube itself, 53.3 % of ammonium-N and 37.2 % nitrite-N values are above the target limit for these determinands. For tributaries, rather high values appear on the Morava, Dyje, Vah and Sio in the upper and middle Danube and on Jantra, Arges, Siret and Prut in the lower Danube section. A special concern should be paid to the ammonium-N content recorded on the Arges tributary, where all five values of C90 characterising situation in different years in period from 1996-2000, are above the limit for Class V; these extremely high values, correlated with BOD_5 values, show the impact of untreated or insufficiently treated waste waters from municipalities.

Unlike the ammonium-N and nitrites-N, the spatial distribution of nitrate-N concentrations show a decrease from upper and middle to lower Danube. From data for the Danube itself, 27.1% are above the target value, whereas 33.1% are above this limit in monitored tributaries. Tributaries with the highest content of nitrates-N are Morava, Dyje, Sio in the upper/middle part, and Iskar, Russenski Lom, Arges and Prut in the lower part of river basin.

Orthophosphate-P shows a similar spatial pattern with total phosphorous, both characterized by a slight increasing profile from upper to lower Danube; concerning the exceeding of the target value, 17.6% of orthophosphate-P and 11.3% of total P values are above this limit along the Danube River, while 45.2% of orthophosphate-P and 57.3% of total P values are above this limit in tributaries.

Heavy metals

Within the framework of TNMN in the Danube River Basin eleven heavy metals are regularly analyzed in water both as total and dissolved forms (for dissolved forms data are available only from 1998 to 2000, and even not for the whole river basin). Excepting the conservative element aluminium, ten of them were chosen to be discussed in the quality assessment of the Danube River water and its tributaries; out of these, eight heavy metals are of a particular importance due to the fact that they are considered as priority substances for the Danube River Basin - four of them are listed in the list of Priority Substances included in Annex X of the Water Framework Directive (cadmium, lead, mercury and nickel) and the other four belong between priority substances specific to the Danube River Basin (arsenic, copper, chromium and zinc).

Except manganese, where a maximum spatial profile is present in the middle Danube, for most of the discussed heavy metals the general pattern is increasing from upper and middle to the lower Danube. Further, the heavy metals content in some tributaries – mainly those located in the lower Danube - is higher than the content in the Danube River itself.

According to the classification for the Danube River Basin and regarding the exceeding of the target values, the assessed data for the total heavy metals forms led to the following conclusions:

- the contamination of the Danube River water is rather high in case of lead and copper, with 57.3% of values for lead and 56.7% values for copper above the target limit; in tributaries, these percentages are 52.8% for lead and 21.6% for copper.
- the contamination pattern of the Danube itself for cadmium and mercury can be characterized with 47.4% of values exceeding cadmium target level and 36.6% of values exceeding mercury target level; however, it has to be mentioned the lack of data for mercury in the lower Danube cannot provide a comprehensive picture in this respect. In tributaries, the situation is better for cadmium, with 32.4% above the quality target but worse for mercury with 63.2% above this limit.
- as regarding the contamination of the Danube river and its tributaries by arsenic, chromium, nickel and zinc, it can be roughly said these watercourses are unpolluted from this point of view; the percentages of exceeding the target values in the Danube and in selected tributaries are the following: arsenic – 8.7% in Danube River and 16.1% in tributaries, chromium – 1.3% in Danube River and 0% in tributaries, nickel – 0% in Danube River and 2.1% in tributaries and zinc – 10.5% in Danube River and 12.9% in tributaries. However, the lack of data for these heavy metals in the lower Danube section has to be mentioned again.

Because the analysis of heavy metals in water column only cannot provide a very good picture of this kind of pollution, the assessment of the heavy metals content in both sediment and suspended solids may be a better approach in this respect.

Oxygen regime

In order to assess the water quality of the Danube River and its tributaries from the point of view of oxygen regime, four determinands were used - dissolved oxygen in terms of concentration, biochemical oxygen demand (BOD) and chemical oxygen demand by $KMnO_4$ and $K_2Cr_2O_7$ (COD_{Mn} and COD_{Cr}).

Dissolved oxygen concentrations generally show positive results, with only 7.4% of values below the quality target in the Danube River and 8.6% in selected tributaries. Oxygen concentration decreases from upper to lower part of the Danube River, lowest values reaching in the section from Danube-Bazias to Danube-Novo Selo/Pristol. From tributaries, low oxygen content was also identified in those located in the lower part of the river basin.

BOD values indicate that 13.3% of values are above the target value in the Danube River (mainly in the middle and in the lower sections) and 35.9% in tributaries. Organic pollution expressed by BOD increases along the Danube, reaching its maximum in the secion from Danube-Dunafoldvar (rkm 1560, H04) to Danube-Pristol/Novo Selo (rkm 834, RO02). Tributaries most polluted by degradable organic matter are Morava, Dyje and Sio in the upper/middle part and Russenski Lom and Arges in the lower part.

For COD_{Cr}, from all values 22.4% for the Danube itself and 39.7% for tributaries are above the quality target; the picture is more positive in case of COD_{Mn} - no value above this limit for the Danube River and 18.2% for tributaries. Measurements of COD_{Cr} and COD_{Mn} show the highest values in the lower part of the Danube River.

In order to obtain a more complete pattern of oxygen regime, beside the 10 percentiles for dissolved oxygen, both the minimum and maximum values were used in assessment, the results being in good correlation with previous data (*Joint Danube Survey - 2001*). Also, the results confirm the critical problems that occur in the tributaries which regularly serve as recipient of untreated or not adequately treated waste water from industry and municipalities (the Arges tributary).

Organic micropollutants

Within the TNMN Programme, organic micropollutants that are regularly monitored are Lindan, pp'-DDT, Atrazine, chloroform, carbon tetrachloride, trichloroethylene and tetrachloroethylene. During the five studied years, the content of these organic compounds presents very large limits of variation due to the fact that there are big differences among the reported limits of detection.

The organochlorine compounds (Lindan and pp'-DDT) show almost the same spatial profile, with an increasing pattern from upper and middle to lower Danube; concerning the exceeding of the target value for Lindan, 23.8% from all values are above this limit in the Danube River water and 9.1% in tributaries. These percentages are higher in case of pp'-DDT: 70.5% for the Danube itself and 54.2% for tributaries.

The polar pesticide Atrazine is undetectable at most of the monitoring sites along the Danube River, but 12.5% of the data are above the target limit (as far as the data are available). In tributaries, 30% of values are above the quality target; the maximum values of Atrazine were found in rivers Sio and the Sajo.

For the volatile organic compounds, data are available for upper and middle Danube only. Chloroform and tetrachloroethylene present values above the target limits as it follows: 29.0% in the Danube and

39.5% in tributaries for chloroform and 13.6% in the Danube and 7% in tributaries for tetrachloroethylene. The situation is better in the case of tetrachloromethane and trichloroethylene - in the Danube River water, no value is above the target limit for these compounds, while in tributaries the same percentage of all data (2.3%) is above this value for both those determinands.

Biological determinands

In the group of biological determinands generally there were problems with unsufficient spatial coverage of Danube River Basin, needed for meaningful interpretation of these data. From existing results can be concluded that chlorophyll-a corresponds to class I – III, only Sio River to class IV in 1997 and 2000.

Regarding saprobic index of macrozoobenthos, by using Austrian standard ÖNORM M6232 the values in Danube River basin and some tributaries correspond to classes II – II-III. Only Sava River was characterized by worse quality class (III – III-IV), however, within the years the situation had been improved. Based on the results it can be concluded that Danube River and tributaries were moderately or critically polluted.

Water quality from microbiological point of view corresponded to classes I – IV in the Danube River. Tributaries Vah, Tisza, Siret can be characterized as extensively polluted, however, data from many important tributaries are missing. Sedimentation has positive effects to number of total coliforms below Gabčíkovo Reservoir, Iron Gates and in Danube Delta as well.

An important part of the report is the evaluation of the water quality changes in time period from 1996 to 2000, main question being whether the water quality is improving or deteriorating. Water quality changes in time depend on both natural characteristics like occurance of flood events, events of low flows, periods of sunny warm weather and antropogenic activities like discharges of waste waters, agricultural practises, accidental events. Taking into account great heterogeneity of the countries in Danube River basin, their water management practices, and in majority of them their transforming economics, both trends can be expected and should be detected.

Regarding indicators of **organic pollution** BOD, COD_{Mn} and COD_{Cr}, there is not their common trend observed. The year-to-year fluctuation rises from COD_{Mn} to BOD and to $COD_{Cr.}$
Decreasing tendency of BOD from 1997/98 to 2000 was observed in section from Danube-Neu Ulm (km 2581) to Danube-Abwindedn-Asten (km 2120), at the cross section Danube-Medvedov/Medve (km 1806) and Danube Komarno/Komarom (km 1768); further from Danube-Borovo (km 1337) to Danube-Bazias (km 1071), in Danube-Reni/Chilia arm/Kilia arm (km 132) and Danube –Vilkov/Kilia arm/Chilia arm (km 18). In evaluated period 1996-2000, BOD values in 2000 belonged to the lowest in majority of monitoring sites located in Danube River. From tributaries, a decreasing trend of BOD can be observed in Inn, Salzach, Dyje, Vah, Drava and Arges, whilst the sites at Tisza River and its tributary Sajo show a reverse behaviour.

Comparing the 90%-iles of different years of determinands characterizing content of **nitrogen** in waters, it appears that in general nitrate-N shows the less changes whereas ammonium –N and nitrite-N fluctuate to a great extent.

For nitrate-N concentrations the ratio of changes from year to year is apart from some exceptions low for the Danube itself, but higher for tributaries. At River Arges (RO09) and Prut (RO11, MD03) it amounts one to three. Despite the implications of seasonal affects this fluctuation seems to be very high. For ammonium-N annual variations exceed 100 % at quite a number of monitoring sites and even amount 300 %. This picture can be a result of natural variations but might be also an indicator for accidentally detected impacts, e.g. when a specific yearly data set contains samples that were taken just after an incident like flood event, effluence of manure or breakdown of a water treatment plant.

In the Danube River, ammonium-N shows a decreasing tendency from 1996 to 2000 in the upper part and in the middle section in Slovakian monitoring sites. In majority of tributaries located in the upper and middle Danube, generally ammonium-N seems to decrease, excepting Croatian sites located on Sava River.

Looking at nitrate-N, its content decreases in Morava and Dyje. A clear decreasing trend from 1996 to 1999 is visible on the Sio. An opposite temporal variation appears on the Sajo and Arges.

Phosphorus content was measured as a total P and ortho-phosphate P. From upper/middle part, decreasing tendency is seen in the section from Danube-Bratislava (km 1869) down to Danube-Szob (km 1708), an exception appears at Danube-Medvedov/Medve (km 1806). Further downstream, variance between the years increases and specific problem arises with comparability of data in cross sections measured by two neighbouring countries. From tributaries, decreasing tendency was observed in Drava-Varazdin (HR03), but the rest of monitoring sites located on this tributary present a relative stable state. No temporal changes were observed in Tisza River, even the variation is low there.

Concerning total P, the variance between years is much higher than that of ortho-phosphates. Generally, total P temporal distribution in monitoring sites located on Danube River is rather scattered, or tendency of development is opposite if data for the same cross section, but provided by two countries, are taken into account (Danube-Novo Selo/Pristol). From tributaries the decrease of total P is visible in Arges and Siret, especially taken into account high values reached in 1996 that did not occur in the next period.

The **heavy metals** content is strongly dependent on quantity and nature of suspended solids, which is the reason of natural variations and trends that might hide the effect of anthropogenic contaminations. High values of heavy metals often reflect situations with high loads of suspended solids and flood events and statistical parameter used also in this report (90%-ile) – could be influenced by these processes. For this five-years evaluation, data on total concentration of heavy metals in water samples had been used, because data related to dissolved fraction are not available in sufficient extent. Anyway, some restrictions related to the trend analysis of heavy metals has to be mentioned again – sparse data sets and detection limits, that had changed rapidly over the years. Besides it seems that there are differences in analytical methods or extraction methods because in many cases data from monitoring sites, which are shared by two countries, do not fit together.

As a result of above mentioned factors, rather big yearly variations were observed - up to three times at most of the monitoring sites. Further, can be concluded, that there was practically no coincidence between the developments of the different heavy metals along the Danube. In spite of these uncertainties, it seems that development of heavy metals content in some tributaries is positive – decrease is indicated in Drava river (cadmium, chromium, copper, lead, nickel and zinc), in Arges (cadmium, chromium, copper, lead), Prut (cadmium, chromium, lead), in Siret (chromium, copper, lead).

From **biological determinands**, slight positive trend appeared within the evaluated years in case of saprobic index of macrozoobenthos, but no significant trend in microbiological determinands has been observed.

From comparison of TNMN data with EQS of EU legislation it can be concluded that:

- atrazine concentrations at sampling sites seem to be no problem in comparison with proposed EQS, even if the mean was calculated by using the worst case calculation
- mean values of total cadmium in lower part of Danube lie very close or even above the List I EQS stipulated by Directive 83/514/EEC. In the upper part of the river mean concentrations are below the EQS with exceptions of few results in 1996/97.
- for p,p-DDT in the upper part of the Danube practically all data are below LOD; downstream Hungary the EQS laid down by Directive 86/280/EEC is exceeded in many cases. Change of calculation method did not improve this situation.

- in case of lindane two EQS could be used – existing EQS laid down by Direcitve 84/491/EEC and proposed new EQS. Whilst the existing EQS is exceeded only by extreme values, with new limit the situation will be worse.
- for total mercury very limited data are available, and these existing results show only one exceedance of the EQS. For Tetrachloroethane, Tetrachloromethane and Trichloroethylene the results are below existing EQS. Trichloromethane exceeds the EQS in one case. This is the only one of the four compounds which has been included in the list of Priority Substances. New proposed EQS causes an increase the number of exceeding values to three in the five-year period.

Recommendations

Assessment of water quality is very much dependent on availability and comparability of data provided from countries in the river basin, if the purpose is to provide reliable information to decision makers and public. This report used data from the first five years of joint monitoring programme of Danubian countries in the River basin that have not yet fulfil all requirements on frequency and data quality and comparability, although the situation is improving in the years. The gaps were discovered during the process of data interpretation, mainly regarding data comparability – it was revealed in several cases that data from the same cross sections provided by two countries would result in different final information, for example in trend assessment. Great problems were identified in case of availability of data on biological determinands, data on heavy metals and organic micropollutants. Even frequencies of measurements were such low in case of some determinands that prevent reliable interpretation.

The main recommendations related to TNMN are the following:

- Enhance TNMN in terms of keeping agreed set of physico-chemical and biological determinands and their frequencies by countries participating in TNMN. Specifically relevant in this respect is the group of organic micropollutants, biological determinands and some heavy metals. In addition, “newly” recommended determinands like dissolved phosphorus and heavy metals in dissolved phase should be improved in this way.

- Exert an effort to further improvement of quality of data and to harmonize the methods to an extent that will ensure data comparability between the countries. In addition, after finding out of not satisfactory results repeatedly from proficiency testing organised for laboratories involved in TNMN, the laboratories should analyse the reasons of this, propose and implement the measures for improvement, which would be reported and discussed in the MLIM-EG.

- Laboratories involved in the TNMN should try to keep limits of detection agreed for selected determinands for TNMN. It should be ensured that limits of detection of determinands are at least on sufficiently low level enabling comparing the results of analysis with target values set for the determinands.
- In near future it should be clearly distinguished between the terms limit of detection (LOD) and limit of quantification (LOQ) taking into account definitions used by the EU. TNMN database should be adjusted in this sense, including both characteristics.

- More attention should be paid in the future to determinands characterising eutrophication, mainly in the lower part of the river basin. If the Danube River is generally considered as eutrophicated river, on the basis of international monitoring it should be allowed to evaluate this process, together with identification of the most critical areas.

- Much more attention should be paid to the microbiological analyses. As in the present time would be rather difficult to ensure proficiency testing for microbiological determinands in Danube River basin, it is recommended to focus mainly to methodological problems and to enhance at least cooperation of neighbouring countries in DRB in this field.

- In connection to the WFD, more biological communities should be monitored in the Danube River basin, e.g. phytobenthos. In addition, discussion on inclusion of additional indices should start.

- It is recommended to report the dissolved oxygen in terms of both concentration and saturation, the latter being more relevant in this respect.

- Only very small fraction of specific organic micropollutants has been able to assess on the basis of TNMN data. Taking into account new needs in the field of monitoring of priority substances Tand other substances discharged in significant quantities in waters in Danube River Basin, inclusion of new specific substances relevant for Danube River basin is necessary. This process is recommended to do by utilisation of information from both JDS and from national surveys performed.

Abbreviations

c90	90 percentile
c10	10 percentile
DRB	Danube River Basin
DRPC	Danube River Protection Convention
EAF	Expert Advisory Forum Priority Substances
EC	European Commission
EQS	Environmental Quality Standard
FHI	Fraunhofer-Institute
JAP	Joint Action Plan for the Danube River Basin
LOD	Limit of Detection
MAC	Maximum allowable concentration
PS	Priority Substances
SOP	Standard Operational Procedure
TNMN	TransNational Monitoring Network
WFD	Water Framework Direcive

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Annex 1

Classification tables