Improved Management of Contaminated Aquifers by Integration of Source Tracking, Monitoring Tools and Decision Strategies

Action A.2.3 Data from national monitoring

Agencija RS za okolje
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SUMMARY

Data from national monitoring from 2005 to 2010 were evaluated for compliance on individual sampling site. Chemical status of groundwater sub-body Ljubljansko polje and Ljubljansko barje was assessed for each year in the period from 2005 to 2010. Statistically significant and sustained long-term trends 1995 – 2010 were determined for all parameters on individual sampling sites. Special attention was paid to pollution in different groundwater layers at automatic measuring stations Hrastje and Mercator.

KEYWORDS

groundwater, monitoring, pollution, sampling site, automatic measuring station, compliance, chemical status, long-term trends

1. NATIONAL GROUNDWATER MONITORING

Environmental Agency of the Republic of Slovenia has been carrying out national groundwater quality monitoring since 1987. Monitoring started first on alluvial aquifers with most intense land use on their surface. Groundwater of Ljubljansko polje has been monitored since the beginning for several reasons. Aquifer of Ljubljansko polje having special characteristics regarding groundwater quantity as well as quality has been used for drinking water supply of capital Ljubljana since 1890. There is very high risk of groundwater pollution because of urban, industrial and agricultural area on the surface of the aquifer.

1.1 National groundwater monitoring network

In the period from 2005 to 2010 state monitoring network on Ljubljansko polje and Ljubljansko barje had 17 – 22 sampling sites.

Structure of national monitoring network is shown in Table 1.

Table 1: Sampling site objects of the national monitoring network on Ljubljansko polje and Ljubljansko barje in the period 2005 – 2010

Year	Total no. of SS	DW wells	Industry wells	Boreholes	AMS boreholes
2005	17	6	4	3	4
2006	20	7	4	3	6
2007	22	7	3	6	6
2008	22	7	3	6	6
2009	17	7	3	5	2
2010	17	7	3	5	2

SS – sampling site; DW – drinking water; AMS – automatic measuring station

Position of individual sampling sites is shown in Appendix A (Map 1 and Map 2).

1.2. Sampling frequency

In table 2 yearly sampling frequency on individual sampling site in the period 2005 – 2010 is given.

Table 2. Sampling frequency on individual sampling site in the period 2005 - 2010

Sampling site (SS)	SS Code	X	Y	2005	2006	2007	2008	2009	2010
PODGORICA 1991	P50360	105918	469152	2	2	2	2	2	2
DOLSKO	P50380	105355	474811	NA	NA	4	2	2	2
JARŠKI PROD (III) JA-3	P50420	105004	465716	2	4	4	2	2	2
BROD (Br-11) LV-0477	P54101	107203	458470	2	2	2	2	2	2
ROJE LV-0377	P54220	106965	461306	2	2	2	2	2	2
ŠENTVID (IIa) 0581	P54280	106457	460325	2	4	4	2	2	2

Sampling site (SS)	SS Code	X	Y	2005	2006	2007	2008	2009	2010
DEKORATIVNA	P54340	104950	459810	2	3	NA	NA	NA	NA
AMS MERCATOR, V-1	P54350	104845	459827	NA	4	4	2	2	2
AMS MERCATOR, V-2	P54351	104843	459831	NA	2	2	1	0	0
KLEČE (VIII a) 0543	P54380	104753	461314	2	4	4	2	2	2
STOŽICE LV-0277	P54460	104761	462973	2	2	2	2	2	2
NAVJE-LIMNIGRAF	P54580	101914	462581	NA	NA	4	2	2	2
AMS HRASTJE, V-1	P54700	103453	465865	2	4	4	2	2	2
AMS HRASTJE, V-2	P54702	103449	465862	2	2	2	1	0	0
AMS HRASTJE, V-3	P54704	103445	465866	2	2	1	1	0	0
AMS HRASTJE, V-4	P54706	103449	465869	2	2	1	1	0	0
HRASTJE (I a) 0344	P54720	102944	466549	2	4	4	2	2	2
ELOK-ZALOG	P54860	101646	466263	2	2	2	2	2	2
KOTEKS-ZALOG 0371	P54900	102792	470260	2	2	2	2	2	2
IŠKI VRŠAJ, V-7	P58062	90852	461112	NA	NA	4	NA	NA	NA
IŠKI VRŠAJ, V-8		90852	461112	NA	NA	NA	2	2	2
IŠKI VRŠAJ 1Agl	P58060	90883	461229	2	3	NA	NA	NA	NA
IŠKI VRŠAJ 4Agl	P58063	90787	460915	NA	1	NA	NA	NA	NA
BOROVNIŠKI VRŠAJ VB-480	P58120	88650	450301	2	4	4	2	2	2
OP-1	P58150	93330	460680	NA	NA	4	2	2	2
DBP-10	P58170	96791	459641	NA	NA	4	2	NA	NA

NA – not active

1.3 Parameters analyzed

The groundwater monitoring programme is yearly prepared according to long-term occurrence of individual parameter in groundwater. Groundwater samples in the period 2005 – 2010 were analysed for 50 up to 190 chemical and physical parameters. Minimal selection of parameters is basic parameters, metals and metalloids. In most samples triazines and related pesticides as well as chlorinated volatile aliphatic organic compounds were determined. Less frequently pesticides of other chemical groups, mineral oils as well as benzene and its methylated derivatives were analyzed.

Table 3: Parameters analysed in groundwater samples

Parameter Groups	Parameters
Parameters measured at sampling	T_{water}, pH, Conductivity (20 °C) , Oxygen, Redox potential
Basic parameters	Turbidity, Color, COD by $KMnO_4$ (COD_{Mn}), Total organic carbon (TOC), Ammonium, Nitrite, Nitrate, Sulphate, Chloride, Phosphate, Sodium, Potassium
Group pollution parameters	Mineral oils, Adsorbed organic halogens (AOX), Polychlorinated biphenyls

Parameter Groups	Parameters
	(PCB)
Metals and metalloids	Mn, Fe, Al, Sb, As, Ba, Be, B, Cu, Zn, Cd, Co, Sn, Cr (VI-val.and total), Mo, Ni, Se, Ag, Sr, Pb, Ti, V, Hg
OCP	Aldrin, DDT (p,p), DDT (o,p), DDE (p,p), DDD (p,p), DDD (o,p), Dieldrin, Endosulphane (alfa), Endosulphane (beta), Endosulphane sulphate, Endrin, alpha-HCH, beta-HCH, gama-HCH, delta-HCH, Heptachlor, Heptachlor-epoxyd
Triazines and related pesticides with metabolites (GC/MS, pH = 7)	Acetochlor, Alachlor, Atrazine, Azoxystrobin, Bromoxynyl, Bromopropylate, Cyanazine, Desethyl-atrazine, Desisopropyl-atrazine, Diazinon, Dichlobenil, Dichlofluoanid, Dichlorvos, 2,6-Dichlorobenzamid, Dimethenamid, Dimethoate, Fenitrothion, Fenthion, Folpet, Hexazinone, Ioxynil, Captan, Chlorbenzilate, Chlorfenvinphos, Chlorpyrifos-methyl, Chlorpyrifos -ethyl, Malathion, Metalaxyl, Mevinphos, Metazachlor, Metolachlor, Napropamide, Omethoate, Parathion-methyl, Parathion-ethyl, Pendimethalin, Pirimicarb, Prometryn, Propiconazol, Procymidone, Propazine, Secbumeton, Simazine, Terbuthylazine, Terbutryn, Tetradifon, Triadimefon, Trifluralin, Vinclozolin
Phenyl-urea and related pesticides (HPLC at pH=7)	Bromacil, Diuron, Isoproturon, Chlorobromuron, Chlorotoluron, Linuron, Metamitron, Metobromuron, Metribuzin, Monolinuron, Monuron
Phenoxyacetic and related pesticides, bentazon (GC/MS, pH=2)	Bentazon, Dicamba, 2,4-D, 2,4-DB, 2,4-DP, MCPA, MCPB, MCPP, Silvex, 2,4,5-T
Metholachlor metabolites	OXA, ESA
	Glyphosate
	Methyl-*terc*-buthyl-ether (MTBE)
Volatile halogenated aliphatic hydrocarbons (LHCH)	Trichloromethane, Tribromomehtane, Bromdichloromethane, Dibromochloromethane, Trichloronitromethane, Tetrachloromethane, Dichloromethane, 1,1-dichloroethane, 1,2- dichloroethane, 1,1-dichloroethene, 1,2- dichloroethene, Tetrachloroethene, 1,1,2-trichloroethene, 1,1,1- trichloroethene, 1,1,2- trichloroethane, 1,1,2,2-tetrachloroethane, Trichlorofluoromethane, Difluorodichloromethane, Heksachlorobutadiene
Aromatic compounds	Benzene, Toluene, Xylene, Mesithylene, 1,2,3-trichlorobenzene, 1,2,4-trichlorobenzene, 1,3,5- trichlorobenzene

According to their physical and chemical properties as well as intensity of their application in 2010 following additional pesticides were analysed: Chlorothalonil, Pirimiphos-methyl, Flufenacet, Benalaxyl, Diflufenican, Fluquinconazole, Fenpropidin, Clomazone, Trifloxyistrobin, Triasulfuron, Amidosulfuron, Nicosulfuron, Foramsulfuron, Prosulfuron, Mesotrione, Dimethomorph, Thiametoxame, Thiacloprid.

2. DATA FROM NATIONAL MONITORING

Sampling and analysis has been carried out since 1995 by two laboratories accredited for water analysis, laboratories of Public Health Institute in Ljubljana and Maribor. Yearly audit of sampling as well as analytical procedures has been carried out by ARSO since 2007.

All results were checked, out layers being later confirmed or corrected by responsible analysts. After this procedure all data were transferred to central database of ARSO. For the period 1995 – 2010 about 74.000 analytical results and data were collected.

In table 5 there are all individual groundwater samples for the period 2005 – 2010 where parameter concentrations exceeded quality standards (QS) or threshold (TV) values given in Slovene decree for groundwater [1)] (table 4).

Through the national groundwater monitoring pollution was detected in two drinking water wells (Hrastje 1A, Iški vršaj 1Agl), three boreholes of two automatic measuring stations (AMS Mercator V-1 and V-2, AMS Hrastje V-1) as well as boreholes Navje and Stožice. In the table 4 there are only parameters for which QS or TV are given. Considering only those parameters groundwater is most polluted by desethyl-atrazine and tetrachloroethene. Atrazine concentrations declined below QS with the exception of one groundwater sample taken in drinking water well Hrastje Ia in 2010. Sudden increase of trichloroethene concentration in drinking water well Hrastje 1A is a consequence long-distance transport of pollutant from a point source pollution which has been remediated. Tetrachloroethene pollutions sources have not been identified yet. In 2009 sudden tetrachloroethene pollution in borehole Stožice was evidenced. Concentrations in the same sampling site declined below threshold value in 2010.

Additionally in drinking water well Hrastje 1A pollution of groundwater by hexa-valent chromium with long-term upward trend has been detected. At some sampling sites upward trends of chloride, sulphate and sodium were determined.

Table 4: Standards and threshold values for groundwater

Parameter	**Unit**	**Quality standard (QS)**
Nitrate	mg NO_3/L	50
Pesticide or its relevant metabolite	µg/L	0,1
Total pesticides	µg/L	0,5
Parameter	**Unit**	**SI threshold value (TV)**
Dichloromethane	µg/L	2
Tetrachloromethane	µg/L	2
1,2-dichloroethane	µg/L	3
1,1-dichloroethene	µg/L	2
Trichloroethene	µg/L	2
Tetrachloroethene	µg/L	2
Total volatile halogenated alyphatic hydrocarbons	µg/L	10

Table 5: All groundwater samples not in compliance with Slovene decree for groundwater (OJ of RS, 25/2009) in the period 2005 - 2010

Sampling site	Date	Atrazine	Desethyl-atrazine	Tetrachloro-ethene	Trichloro-ethene
		µg/L	µg/L	µg/L	µg/L
QS / TV		0,1	0,1	2	2
AMS MERCATOR V1	18.9.2006	0,04	0,05	2,20	<0,1
AMS MERCATOR V1	13.6.2007	0,03	0,04	3,40	<0,1
AMS MERCATOR V1	18.9.2007	0,1	0,12	3,81	0,50
AMS MERCATOR V1	12.5.2010	<0,02	0,02	4,50	<0,25
AMS MERCATOR V1	16.9.2010	<0,02	<0,02	5,90	<0,25
AMS MERCATOR V2	13.12.2005	0,12	0,13	<0,3	<0,4
AMS MERCATOR V2	13.6.2007	0,10	0,13	4,20	0,30
AMS MERCATOR V2	14.11.2007	0,10	0,15	1,30	0,67
AMS MERCATOR V2	22.5.2008	0,09	0,11	1,84	<0,1
STOŽICE	11.6.2009	0,03	0,04	4,90	<0,25
STOŽICE	25.9.2009	<0,02	0,02	3,40	<0,25
NAVJE-LIMNIGRAF	12.6.2007	0,03	0,04	4,10	0,70
NAVJE-LIMNIGRAF	19.9.2007	0,03	0,04	4,22	0,91
NAVJE-LIMNIGRAF	11.6.2009	0,03	0,05	2,10	0,40
NAVJE-LIMNIGRAF	24.9.2009	0,03	0,04	2,50	0,60
AMS HRASTJE V1	1.6.2005	<0,03	<0,03	3,70	<0,4
AMS HRASTJE V1	21.6.2006	<0,02	0,02	5,13	<0,1
AMS HRASTJE V1	19.9.2006	0,02	0,03	5,00	<0,1
AMS HRASTJE V1	14.11.2006	0,02	0,03	4,04	<0,1
AMS HRASTJE V1	16.4.2007	<0,02	0,03	5,70	<0,1
AMS HRASTJE V1	13.6.2007	<0,02	0,02	9,70	<0,1
AMS HRASTJE V1	17.9.2007	<0,02	0,03	8,46	<0,1
AMS HRASTJE V1	14.11.2007	0,02	0,03	5,10	0,20
AMS HRASTJE V1	22.5.2008	<0,02	0,03	5,62	<0,1
AMS HRASTJE V1	17.9.2008	<0,02	0,02	4,14	<0,1
AMS HRASTJE V1	3.6.2009	<0,02	<0,02	6,50	<0,25
AMS HRASTJE V1	16.9.2009	<0,02	0,02	6,60	<0,25
AMS HRASTJE V1	12.5.2010	<0,02	<0,02	4,30	<0,25
AMS HRASTJE V1	16.9.2010	<0,02	<0,02	3,40	<0,25
HRASTJE (I a) 0344	29.3.2005	0,14	0,15	0,50	3,80
HRASTJE (I a) 0344	1.6.2005	0,15	0,14	1,40	3,80
HRASTJE (I a) 0344	25.10.2005	0,13	0,13	0,40	0,60
HRASTJE (I a) 0344	20.4.2006	0,10	0,11	1,00	1,10
HRASTJE (I a) 0344	22.6.2006	0,10	0,11	1,25	1,13
HRASTJE (I a) 0344	13.9.2006	0,15	0,15	1,70	1,40
HRASTJE (I a) 0344	14.11.2006	0,11	0,12	1,42	1,20
HRASTJE (I a) 0344	16.4.2007	0,09	0,12	0,83	0,81

Sampling site	**Date**	**Atrazine**	**Desethyl-atrazine**	**Tetrachloro-ethene**	**Trichloro-ethene**
		µg/L	µg/L	µg/L	µg/L
QS / TV		0,1	0,1	2	2
HRASTJE (I a) 0344	15.6.2007	0,10	0,13	4,19	1,60
HRASTJE (I a) 0344	17.9.2007	0,09	0,14	3,30	1,70
HRASTJE (I a) 0344	5,6,2009	0,09	0,12	1,1	0,9
HRASTJE (I a) 0344	17,9,2009	0,09	0,11	2,3	1,1
HRASTJE (I a) 0344	13,5,2010	0,11	0,16	1,4	0,7
HRASTJE (I a) 0344	30,9,2010	0,09	0,13	1,1	<0,25
IŠKI VRŠAJ 1Agl	29,3,2005	0,07	0,65	<0,3	<0,4
IŠKI VRŠAJ 1Agl	25,10,2005	0,08	0,67	<0,3	<0,4
IŠKI VRŠAJ 1Agl	27,7,2006	0,07	0,58	<0,1	<0,1
IŠKI VRŠAJ 1Agl	11,9,2006	0,10	0,69	<0,1	<0,1
IŠKI VRŠAJ 1Agl	15,11,2006	0,06	0,46	<0,1	0,19

QS – quality standard; TV – threshold value

3. GROUNDWATER CHEMICAL STATUS FOR INDIVIDUAL YEAR IN THE PERIOD 2005 - 2010

For every sampling site (SS) yearly arithmetic mean (AM) for the period 2005 - 2010 was calculated for all parameters. Yearly AMs are the basis for chemical status assessment.

Chemical status of groundwater in aquifers Ljubljansko polje and Ljubljansko barje (sub-body of groundwater body 1001-Savska kotlina in Ljubljansko barje) was assessed according to the methodology proposed in EC document No, 18 »Guidance on Groundwater Status and Trend Assessment« [2)].

For chemical status assessment following steps have to be applied:

1. For the period 2005 – 2010 yearly AMs of individual parameter on all sampling sites were compared to quality standard (QS) or threshold value (TV) given in Slovene groundwater decree[1)] (table 4). Groundwater quality on sampling site is in compliance with the decree if AMs of parameters are equal to or lower than QS or TV. Results for parameters exceeding QS /TV are shown in tables 6-11.
2. Additional tests:

- the influence of groundwater pollution on chemical status of surface water bodies
- the influence of groundwater pollution on terrestrial ecosystems
- meeting the requirements for drinking water protected areas (WFD, Art, 7 [3)])
- saline intrusion into the groundwater body

Good chemical status for groundwater body [1)] is achieved when:

- Part of polluted groundwater body does not exceed 30%.
- Groundwater body does not deteriorate surface water bodies.
- Groundwater body does not deteriorate terrestrial ecosystems.
- Groundwater pollution does not enhance drinking water treatment.
- There is no evidence of saline or other pollutant intrusion into the groundwater body.

In table 12 summary of applied tests and chemical status are given.

Table 6: AM parameters 2005

Sampling site (SS)	Atrazine	Desethyl-atrazine	Pesticides	Trichloro-ethene	Compliance
	µg/L	µg/L	µg/L	µg/L	
QS / TV	**0,100**	**0,100**	**0,50**	**2,00**	
Podgorica	0,067	0,093	0,16	0,20	YES
Jarški prod	0,015	0,015	0,00	0,20	YES
Brod	0,015	0,015	0,00	0,20	YES
Roje	0,015	0,015	0,00	0,20	YES
Šentvid IIa	0,015	0,045	0,05	0,20	YES
Dekorativna	0,035	0,030	0,06	0,20	YES
AMS Mercator, V1	0,040	0,040	0,10	0,20	YES
AMS Mercator, V2	0,120	0,130	0,25	0,20	NO
Kleče	0,015	0,023	0,01	0,20	YES
Stožice	0,028	0,015	0,02	0,20	YES
AMS Hrastje, V1	0,015	0,015	0,02	0,20	YES
AMS Hrastje, V2	0,015	0,015	0,00	0,20	YES
AMS Hrastje, V3	0,023	0,040	0,05	0,20	YES
AMS Hrastje, V4	0,015	0,015	0,00	0,20	YES
Hrastje Ia	0,140	0,140	0,31	2,73	NO
Elok	0,015	0,015	0,00	0,20	YES
Koteks	0,040	0,015	0,04	0,20	YES
Iški vršaj, 1Agl	0,075	0,660	0,74	0,20	NO
Iški vršaj, 2Agl	0,015	0,100	0,10	0,20	YES
Borovniški vršaj	0,023	0,027	0,04	0,20	YES

Table 7: AM parameters 2006

Sampling site (SS)	Atrazine	Desethyl-atrazine	Pesticides	Tetrachloro-ethene	Compliance
	µg/L	µg/L	µg/L	µg/L	
QS / TV	**0,100**	**0,100**	**0,50**	**2,00**	
Podgorica	0,055	0,080	0,135	0,15	YES
Jarški prod	0,015	0,025	0,043	0,12	YES
Brod	0,010	0,020	0,020	0,05	YES
Roje	0,010	0,010	0,000	0,05	YES
Šentvid IIa	0,028	0,045	0,078	0,11	YES
Dekorativna	0,030	0,037	0,067	0,50	YES
AMS Mercator, V1	0,035	0,043	0,101	1,66	YES
AMS Mercator, V2	0,090	0,100	0,190	1,51	YES
Kleče	0,025	0,035	0,058	0,11	YES
Stožice	0,025	0,025	0,095	0,05	YES
AMS Hrastje, V1	0,015	0,028	0,050	3,77	NO
AMS Hrastje, V2	0,025	0,035	0,070	0,05	YES
AMS Hrastje, V3	0,035	0,040	0,075	0,05	YES
AMS Hrastje, V4	0,010	0,010	0,000	0,05	YES
Hrastje Ia	0,115	0,123	0,328	1,34	NO
Elok	0,020	0,020	0,040	0,17	YES
Koteks	0,035	0,025	0,085	0,58	YES
Iški vršaj, 1Agl	0,060	0,435	0,510	0,05	NO
Iški vršaj, 4Agl	0,010	0,010	0,000	0,05	YES
Borovniški vršaj	0,033	0,035	0,080	0,05	YES

Table 8: AM parameters 2007

Sampling site (SS)	Desethyl-atrazine	Tetrachloro-ethene	Compliance
	µg/L	µg/L	
QS / TV	**0,100**	**2,00**	
Podgorica	0,075	0,10	YES
Dolsko	0,035	0,07	YES
Jarški prod	0,025	0,21	YES
Brod	0,030	0,05	YES
Roje	0,010	0,05	YES
Šentvid IIa	0,045	0,10	YES
AMS Mercator, V1	0,065	2,58	NO
AMS Mercator, V2	0,140	2,75	NO
Kleče	0,043	0,10	YES
Stožice	0,020	0,05	YES
Navje	0,068	2,74	NO
AMS Hrastje, V1	0,028	7,24	NO
AMS Hrastje, V2	0,035	0,05	YES
AMS Hrastje, V3	0,050	0,05	YES
AMS Hrastje, V4	0,010	0,05	YES
Hrastje Ia	0,123	2,48	NO
Elok	0,020	0,05	YES
Koteks	0,025	1,16	YES
Iški vršaj, V7	0,025	0,10	YES
Borovniški vršaj	0,025	0,05	YES
OP-1	0,025	0,10	YES
DBP-10	0,015	0,05	YES

Table 9: AM parameters 2008

Sampling site (SS)	Desethyl-atrazine	Tetrachloro-ethene	Compliance
	µg/L	µg/L	
QS / TV	**0,100**	**2,00**	
Podgorica	0,065	0,05	YES
Dolsko	0,015	0,05	YES
Jarški prod	0,025	0,05	YES
Brod	0,025	0,05	YES
Roje	0,015	0,05	YES
Šentvid IIa	0,035	0,05	YES
AMS Mercator, V1	0,035	0,38	YES
AMS Mercator, V2	0,110	1,84	NO
Kleče	0,035	0,05	YES
Stožice	0,015	0,05	YES
Navje	0,070	0,98	YES
AMS Hrastje, V1	0,025	4,88	NO
AMS Hrastje, V2	0,030	0,05	YES
AMS Hrastje, V3	0,040	0,05	YES
AMS Hrastje, V4	0,010	0,05	YES
Hrastje Ia	0,090	1,13	YES
Elok	0,015	0,05	YES
Koteks	0,025	0,38	YES
Iški vršaj, V8	0,050	0,05	YES
Borovniški vršaj	0,025	0,05	YES
OP-1	0,025	0,05	YES
DBP-10	0,010	0,05	YES

Table 10: AM parameters 2009

Sampling site (SS)	Desethyl-atrazine	Tetrachloroethene	Compliance
	µg/L	µg/L	
QS / TV	**0,100**	**2,00**	
Podgorica	0,090	0,21	YES
Dolsko	0,015	0,13	YES
Jarški prod	0,015	0,21	YES
Brod	0,020	0,13	YES
Roje	0,015	0,13	YES
Šentvid IIa	0,040	0,13	YES
AMS Mercator, V1	0,045	1,65	YES
Kleče	0,030	0,13	YES
Stožice	0,030	4,15	NO
Navje	0,045	2,30	NO
AMS Hrastje, V1	0,015	6,55	NO
Hrastje Ia	0,115	1,70	NO
Elok	0,015	0,21	YES
Koteks	0,020	0,90	YES
Iški vršaj, V8	0,050	0,13	YES
Borovniški vršaj	0,025	0,13	YES
OP-1	0,090	0,13	YES

Table 11: AM parameters 2010

Sampling site (SS)	Desethyl-atrazine	Tetrachloroethene	Compliance
	µg/L	µg/L	
QS / TV	**0,100**	**2,00**	
Podgorica	0,075	0,21	YES
Dolsko	0,010	0,13	YES
Jarški prod	0,010	0,21	YES
Brod	0,010	0,13	YES
Roje	0,010	0,13	YES
Šentvid IIa	0,010	0,13	YES
AMS Mercator, V1	0,015	5,20	NO
Kleče	0,010	0,13	YES
Stožice	0,010	0,90	YES
Navje	0,010	1,30	YES
AMS Hrastje, V1	0,010	3,85	NO
Hrastje Ia	0,145	1,25	NO
Elok	0,010	0,13	YES
Koteks	0,010	0,90	YES
Iški vršaj, V8	0,010	0,13	YES
Borovniški vršaj	0,010	0,13	YES
OP-1	0,095	0,13	YES

Table 12: Sampling sites "not in compliance", tests and chemical status for the period 2005 - 2010

Year	No, of SS "not in compliance"	Total no, of SS	Percentage of SS "not in compliance"	Deterioration of surface water bodies	Enhancement of DW treatment	Chemical status of GWsub-body
2005	3	17	18	NO	NO	GOOD
2006	3	20	15	NO	NO	GOOD
2007	5	22	23	NO	NO	GOOD
2008	2	22	9	NO	NO	GOOD
2009	4	17	24	NO	NO	GOOD
2010	3	17	18	NO	NO	GOOD

SS – sampling site; DW – drinking water; GW - groundwater

For chemical status assessment of sub-body of groundwater body Savska kotlina in Ljubljansko barje following tests have been carried out (table 12):

- Percentage of sampling sites not in compliance with QS or TV: for the period 2005 – 2010 < 30%
- Deterioration of surface water bodies: all associated surface water bodies had good chemical status
- Enhancement of drinking water treatment: according to the drinking water supplier no increased drinking water treatment has been applied in the period 2005 – 2010. Due to pollution of drinking water source in Iški vršaj by desethyl-atrazine a drinking water well 1Agl was disconnected from the drinking water supply
- Saline water intrusion: no evidence

Methodology for chemical status assessment according to Slovene decree on groundwater status[1)] is based only on parameters for which quality standards or threshold values are given (table 4). Other parameters with concentrations above the natural state are discussed in section 4 (long-term trends).

Yearly chemical status of groundwater sub-body Ljubljansko polje and Ljubljansko barje was good for the observed period 2005 – 2010 (table 12).

Nitrate concentrations in groundwater of Ljubljansko polje and Ljubljansko barje range from about 10 – 36 mg NO_3/L and are on all sampling sites of national monitoring (table 2) lower than quality standard 50 mg NO_3/L.

In the period 2005 – 2010 following pesticides were detected above LOD (Limit of Detection): atrazine, desethyl-atrazine, metholachlor, desisipropyl-atrazine, terbutrin, bromacyl, 2,6-dichlorobenzamid, diuron, metazachlor, bentazon. Atrazine and desethyl-atrazine exceeded quality standard 0,1 µg/L in AMS Mercator, Hrastje Ia and Iški vršaj 1Agl.

Groundwater is polluted by trichloroethene and tetrachloroethene in AMS Mercator, Stožice and Hrastje Ia.

4. LONGTERM TRENDS

The WFD [3)] and GWD [5)] require Member States to identify any significant and sustained upward trend in concentrations of pollutants, groups of pollutants or indicators of pollution found in groundwater bodies or groups of bodies identified as being at risk (WFD Annex V 2.4.4 and GWD Article 5). If parameter concentration reaches 75% of quality standard (QS) or national threshold value (TV) measures have to be taken in order to reduce groundwater pollution.

Methodology for trend evaluation was following:

- Sampling sites (SS): national monitoring network
- Time sequence for trend evaluation has to be at least 6 years.
- For SS yearly arithmetic mean (AM) for the period 1995 - 2010 was calculated for all parameters. Yearly AMs are the basis for trend assessment.
- AM of individual parameter: results <LOQ (Limit of Quantification) or <LOD (Limit of Detection) were treated as 0,5 LOQ or 0,5 LOD respectively
- Calculation of group parameters (total pesticides, volatile halogenated aliphatic hydrocarbons): results of individual parameter <LOQ (Limit of Quantification) or <LOD (Limit of Detection) were treated as 0.
- Statistical treatments: Excel, statistically significant trend $R^2 > 0,5$

Significant and sustained long-term trends were determined only for sampling sites with time sequence longer than six years. This condition was not fulfilled for Dolsko, Navje, automatic sampling station (AMS) Mercator V2, OP1 and DBP-10.

Graphs of all detected trends on individual sampling sites are in Appendix B.

4.1 Significant and sustained upward trends on sampling sites

Significant and sustained long-term upward trends are summarized in table 13.

Table 13: Significant and sustained upward trends on Ljubljansko polje and Ljubljansko barje

SS	Period	Parameter	R2	AM
Podgorica	1995 - 2010	Chloride	0,7767	14,6 mg/L
Jarški prod	1995 - 2010	Chloride	0,8090	14,0 mg/L
Dekorativna	1995 – 2006	Nitrate	0,8755	32,6 mg/L
	1995 – 2006	Sulphate	0,7289	35,4 mg/L
	1995 – 2006	Chloride	0,8230	53,7 mg/L
Šentvid IIa	1995 - 2010	Chloride	0,6539	22,3 mg/L
AMS Hrastje V2	2003 - 2008	Chloride	0,9004	16,9 mg/L
	2003 - 2008	Chromium tot.	0,7100	3,0 µg/L
AMS Hrastje V3	2003 - 2008	Nitrate	0,9598	20,5 mg NO_3/L
	2003 - 2008	Chloride	0,9976	17,0 mg/L
Hrastje 1a	1995 - 2010	Sodium	0,8554	13,8 mg/L
	1995 - 2010	Chloride	0,9225	42,5 mg/L
	1995 - 2010	Chromium-VI	0,8083	17,0 µg/L
	1998 - 2010	Chromium tot	0,6775	18,0 µg/L
Iški vršaj 1Agl	1995 – 2006	Desethyl-atrazine	0,5882	0,44 µg/L

SS sampling site; AM arithmetic mean in the last year of the period

Chloride and sodium concentrations are mostly increasing but are still lower than 75% of standards for drinking water [4)]. The source of this pollution has to be investigated yet. Upward chloride trend was detected on seven SS (three drinking water wells, two industry wells and two boreholes of deeper groundwater layers in AMS Hrastje – V2 and V3). Sodium upward trend was observed only in drinking water well Hrastje Ia.

Nitrate upward trend was determined for two SS: Dekorativna and deeper borehole in AMS Hrastje V3. AMs at last year of observations were on both SS lower than 75% of quality standard (QS).

The source for upward trend of desethyl-atrazine in drinking water well Iški vršaj 1Agl (VD Brest-1a) is investigated in A.2.8. and A.4.1.

Chromium upward trend was evidenced in V2 of AMS Hrastje and in Hrastje Ia. Of highest concern is upward trend of toxic hexa-valent chromium in drinking water well Hrastje Ia where concentrations increased to 17 μg/L.

4.2 Significant and sustained downward trends on sampling sites

Significant and sustained long-term downward trends are summarized in table 14.

Table 14: Significant and sustained downward trends on Ljubljansko polje and Ljubljansko barje

SS	Period	Parameter	R2	AM
Podgorica	1995 - 2010	Nitrate	0,5239	18,8 mg/L
	1995 - 2010	Atrazine	0,8983	0,025 μg/L
	1995 - 2010	Desethyl-atrazine	0,8832	0,075 μg/L
	1995 - 2010	Trichloroethene	0,6723	0,23 μg/L
Kleče	1995 - 2010	Atrazine	0,6265	0,01 μg/L
Roje	1995 - 2010	Nitrate	0,5608	6,7 mg NO_3/L
Šentvid IIa	1995 - 2010	Atrazine	0,5868	0,01 μg/L
AMS Hrastje V4	2003 - 2008	Chloride	0,7041	1,6 mg/L
	2003 - 2008	Sodium	0,5679	1,6 mg/L
Hrastje 1a	1995 - 2010	Atrazine	0,7325	0,10 μg/L
Elok	1995 - 2010	Nitrate	0,6276	9,0 mg NO_3/L
	1995 - 2010	Sulphate	0,7843	12,0 mg/L
Koteks	1995 - 2010	Sulphate	0,7559	15,4 mg/L
	1995 - 2010	Atrazine	0,8520	0,01 μg/L

SS sampling site; AM arithmetic mean in the last year of the period

Concentrations of nitrate, sulphate, atrazine and its metabolite desethyl-atrazine are in most cases declining. This effect is achieved due to restrictions (prohibition of atrazine application) as well as to better agricultural practice. For volatile halogenated aliphatic hydrocarbons (LHCH) significant and sustained long-term trends are rarely observed.

Nitrate downward trends are determined for industry wells Podgorica and Elok as well as for the borehole Roje.

Atrazine declined under QS 0,1 µg/L in two drinking water wells Kleče VIIIa and Šentvid IIa as well as in industry wells Podgorica and Koteks. In drinking water well Hrastje Ia downward trend is observed but the concentrations are still at the allowed limit of QS. No upward trend for atrazine or desethyl-atrazine

For volatile halogenated aliphatic hydrocarbons (LHCH) significant and sustained longterm trends are rarely observed. In Podgorica downward trend for trichloroethylene is determined.

Downward trend of sulphates is indicated in industry wells Elok and Koteks. Sodium and chloride is declining in the deepest groundwater layer in AMS Hrastje.

5. AUTOMATIC MEASURING STATIONS - BOREHOLES IN DIFFERENT GROUNDWATER LAYERS

Two automatic measuring stations (AMS) on Ljubljansko polje are equipped with boreholes in different groundwater layers. In AMS Hrastje there are four boreholes while in AMS Mercator two boreholes each one of them having filter in different groundwater layer (table 15). Layers are presumed to be separated partly by impermeable layers (clay or conglomerate) preventing water flow in vertical direction. It is expected to detect stratified layers of groundwater with contamination mostly in the upper layer and groundwater quality reflecting mostly natural background in deeper layers. In AMS Hrastje data collection started in 2003 and in Mercator 2005. First year of operation was not used for data analysis.

Table 15: Characteristics of boreholes in different groundwater layers in AMS Hrastje and Mercator

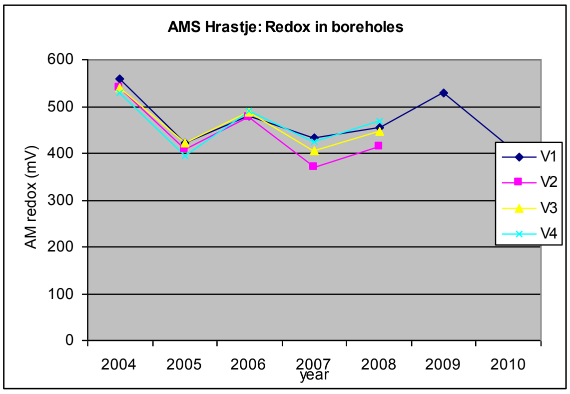
Sampling site	**X**	**Y**	**Average GW level**	**Depth of the borehole**	**Filter position**
			meters above the sea level	meters	meters
AMS Hrastje V1	5103453	5465865	274,50	27,8	17,9 - 27,8
AMS Hrastje V2	5103449	5465862	274,50	39,8	32,9 - 39,8
AMS Hrastje V3	5103445	5465866	274,50	57,0	47,0 - 56,9
AMS Hrastje V4	5103449	5465869	274,50	82,6	61,7 - 79,6
AMS Mercator V1	5104845	5459827	278,28	64,0	44,0 - 60,0
AMS Mercator V2	5104843	5459831	278,28	93,2	73,2 - 91,2

5.1 AMS Hrastje

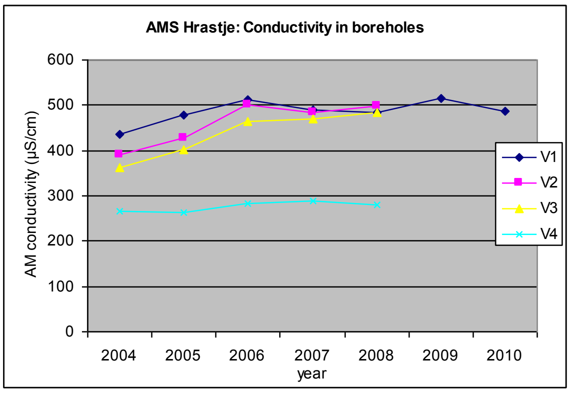
Behaviour of selected basic parameters in boreholes in different groundwater layers of AMS Hrastje V1 (the upper groundwater layer), V2, V3 and V4 (the deepest groundwater layer) in the period 2004 – 2010 is shown in graphs 1-7.

Redox potencial is comparable in all four layers up to 2006, small differencies are noticed later (graph 1). Mineralization as expected is lowest in the deepest groundwater layer V4 while comparable in upper layers V1-V3 (graph2).

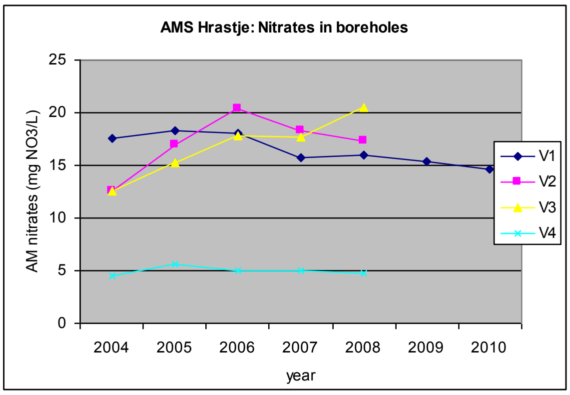
Nitrate and sulphate concentrations are the lowest in the deepest layer V4, the differencies in upper layers (V1, V2 and V3) are smaller (graphs 3 and 4). The only clear stratification in the period 2004 – 2008 is evidenced for sodium and potassium (graphs 6 and 7).



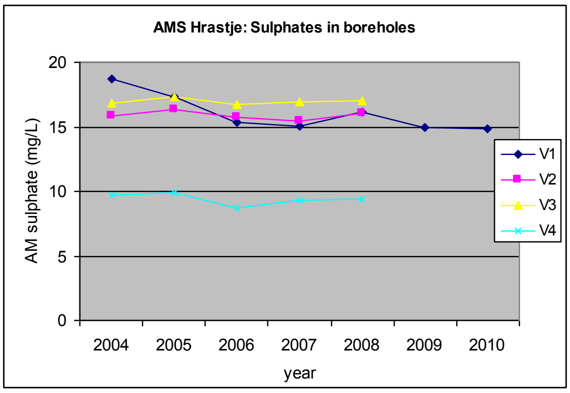
Graph 1: Redox potencial in AMS Hrastje



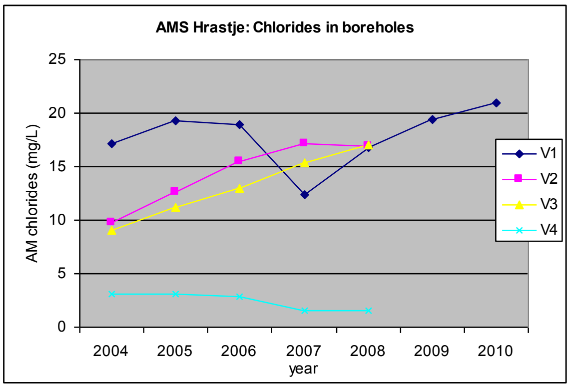
Graph 2: Conductivity at 20°C in AMS Hrastje



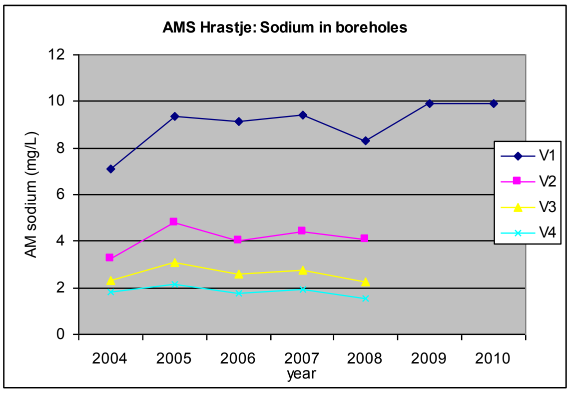
Graph 3: Nitrates in AMS Hrastje



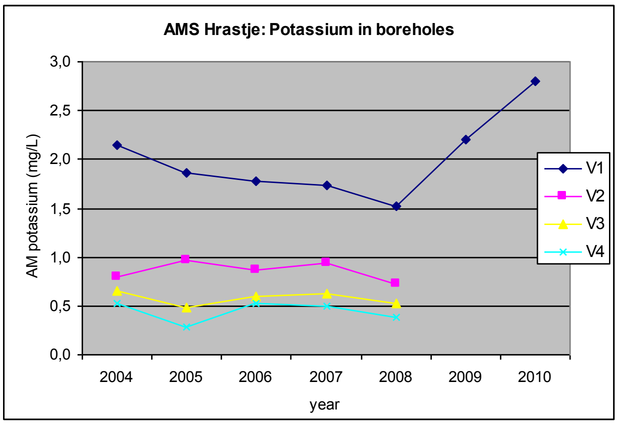
Graph 4: Sulphates in AMS Hrastje

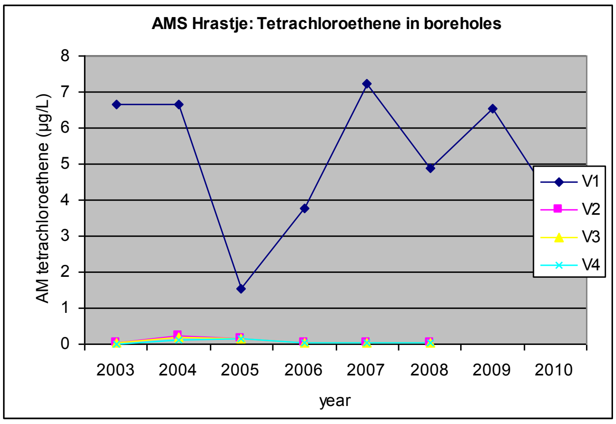


Graph 5: Chlorides in AMS Hrastje



Graph 6: Sodium in AMS Hrastje





Graph 7: Potassium in AMS Hrastje

Graph 8: Tetrachloroethene in AMS Hrastje

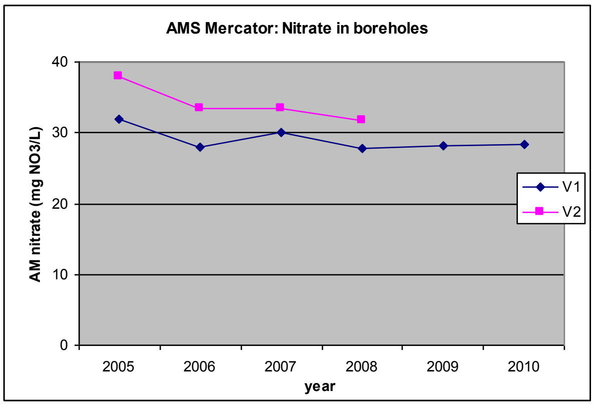
Groundwater in AMS Hrastje was polluted mostly by tetrachloroethene in the upper layer V1. The highest yearly mean value was 7,24 µg/L in 2007 (graph 8). Pollution with pesticides was minor. In groundwater atrazine, desethyl-atrazine and bentazon were occasionally analysed in concentrations up to 0,05 µ/L.

5.2 AMS Mercator

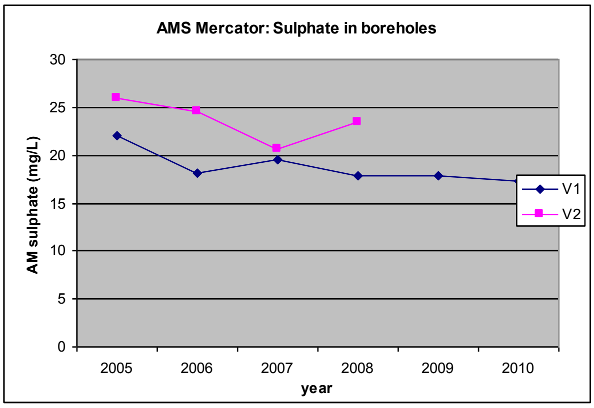
Variation of selected parameters in boreholes AMS Mercator V1 (the upper groundwater layer) and V2 (the deeper groundwater layer) in the period 2005 – 2010 is shown in graphs 9-16. Piezometric groundwater level in both boreholes is practically the same.

Concentrations of all four basic parameters (nitrate, sulphate, chloride and sodium) are higher than natural background and are consequence of minor pollution. Nitrates did not exceed quality standard for groundwater neither was sulphate, chloride or sodium concentration higher than the standard for drinking water.

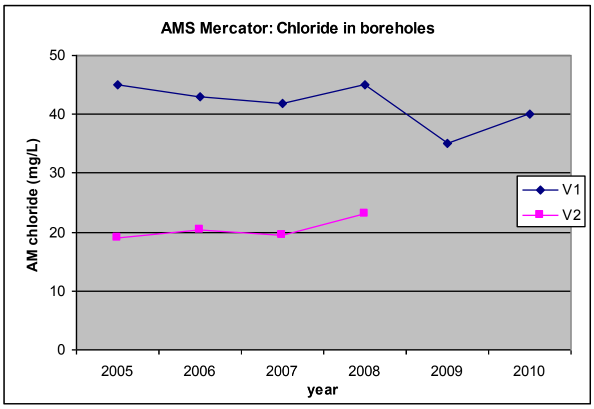
Stratified concentrations are evident for all four basic parameters. The most important difference between them is that for nitrate and sulphate concentrations are higher in deeper layer (V2) while quite in contrary for chloride and sodium in upper layer (V1). The mechanisms of pollution which are presumed to be different for nitrate and sulphate in comparison to chloride and sodium are objects of further investigations.



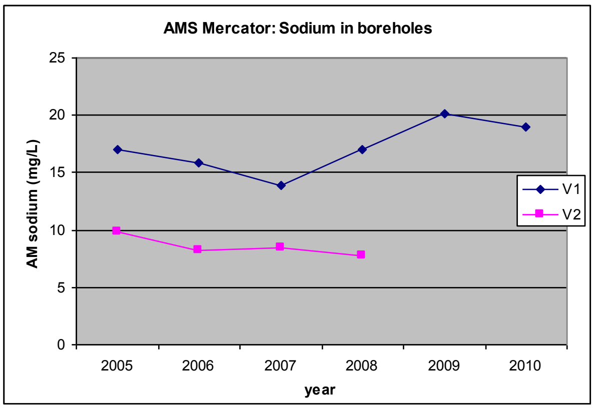
Graph 9: Nitrate in AMS Mercator



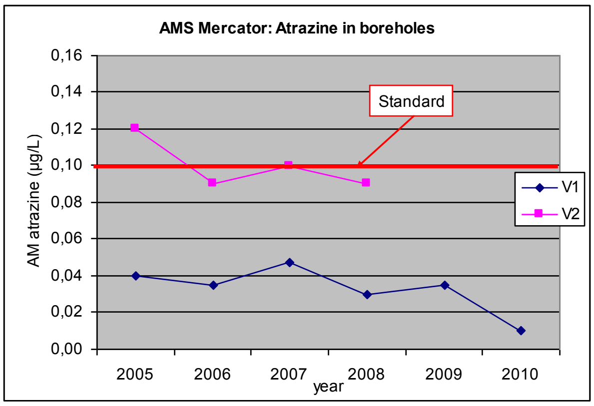
Graph 10: Sulphate in AMS Mercator



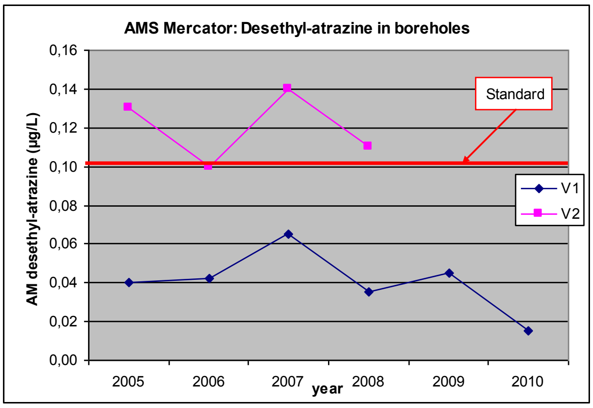
Graph 11: Chloride in AMS Mercator



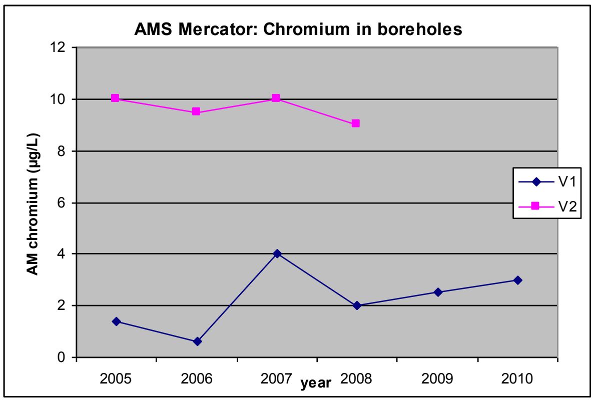
Graph 12: Sodium in AMS Mercator

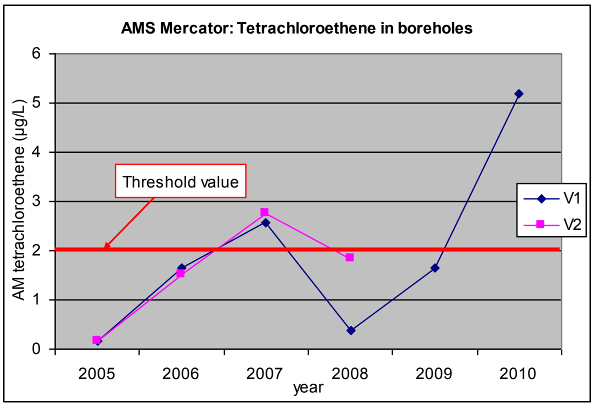


Graph 13: Atrazine in AMS Mercator



Graph 14: Desethyl-atrazine in AMS Mercator





Graph 15: Total chromium in AMS Mercator

Graph 16: Tetrachloroethene in AMS Mercator

Groundwater in AMS Mercator was found to be polluted also by atrazine and desethyl-atrazine. Concentrations in deeper layer V2 are higher compared to upper layer V1 and often exceeded quality standard (graphs 13 and 14). Of concern is the pollution of deeper groundwater layer V2 with chromium predominantly in hexa-valent form (graph 15). In 2010 an increase of tetrachloroethene over the quality standard was evidenced (graph 16).

6. CONCLUSIONS

Groundwater in aquifers Ljubljansko polje and Ljubljansko barje achieved good chemical status for the period 2005 – 2010.

In the period 1995 – 2010 significant upward trends were detected for chloride (7 sampling sites), nitrate (7 sampling sites) as well as for sulphate, sodium, hexa-valent chromium and desethyl-atrazine (1 sampling site each). Of great concern is long-term upward trend of toxic hexa-valent chromium in drinking water well Hrastje Ia. Groundwater quality standards (QS) for parameters having upward trend were exceeded for desethyl-atrazine in Iški vršaj (year 2006). Nitrate in Dekorativna reached 65% of QS (50 mg NO_3/L). For other parameters having upward trends neither QS nor threshold values (TV) are given in the groundwater decree. Comparing AMs of the last year with standards for drinking water [4)] chloride reached from 6 to 21 % of the standard (250 mg/L), sulphate 14 % of the standard (250 mg/L), sodium 7 % of the standard (200 mg/L) and chromium 36 % of the standard (50 µg/L). In the year 2010 drinking water resources were with the exception of desethyl-atrazine in Iški vršaj not endangered due to pollutants in table 13. Upward trend of hexa-valent chromium has to be reverted.

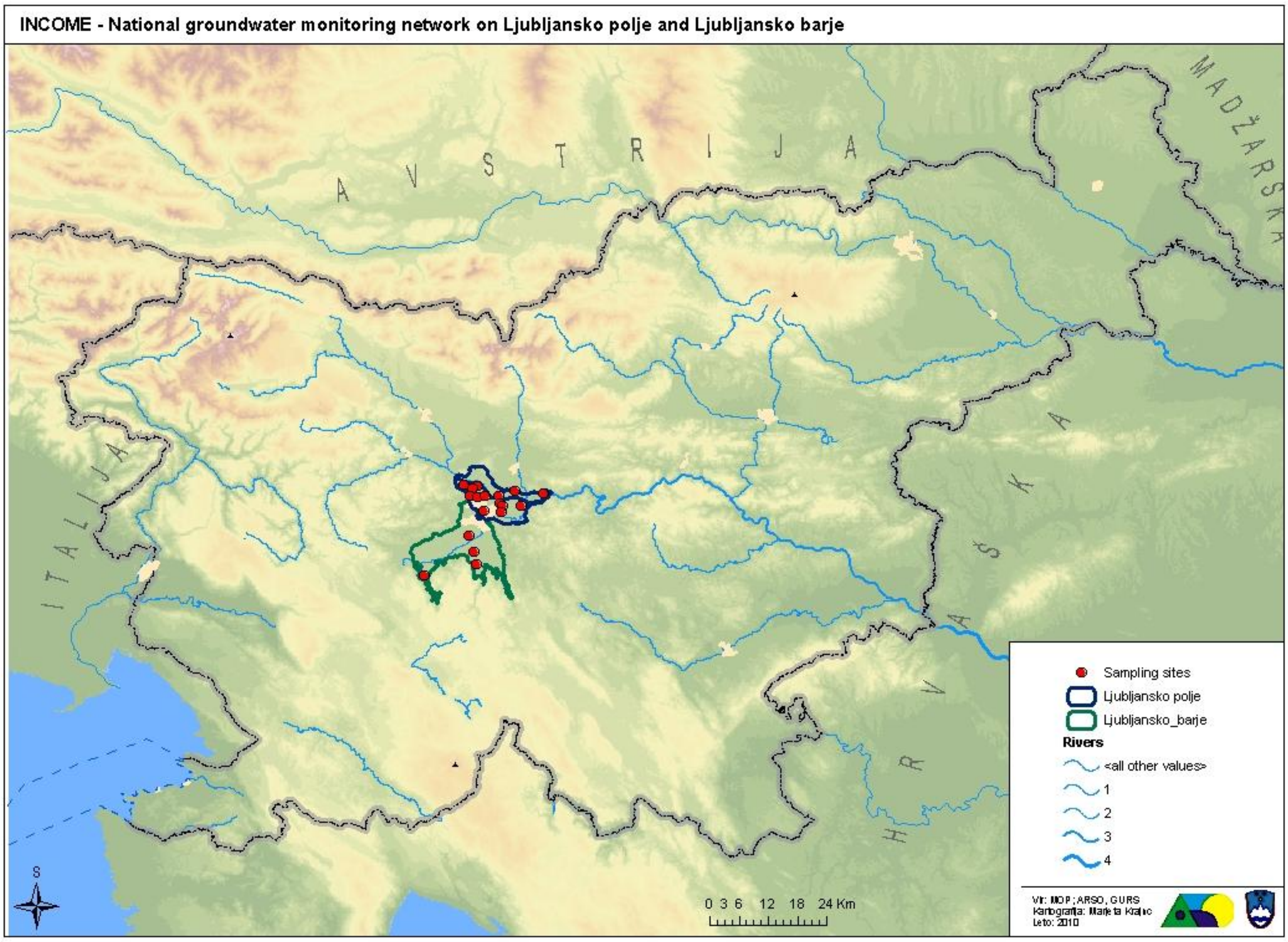
Tetrachloroethene concentrations in groundwater of the shallow piezometer of AMS Hrastje V1 have been constantly exceeding threshold value 2 µg/L. The source of the pollution has not been identified yet. Concentrations in the period 2003 – 2010 did not show significant trend, their maximal value being 15,4 µg/L. This pollution represents constant threat to drinking water resources in Hrastje.

Analysis of long-term results of groundwater in different layers at automatic measuring stations Mercator and Hrastje gave suggestions for further hydrochemical investigations. Pollution was expected mainly in upper layers. For AMS Mercator pollution by hexa-valent chromium, atrazine and desethyl-atrazine, nitrate and sulphate is predominantly found in deeper layer V2. On the other hand higher concentrations of chloride and sodium were analysed in upper layer V1.

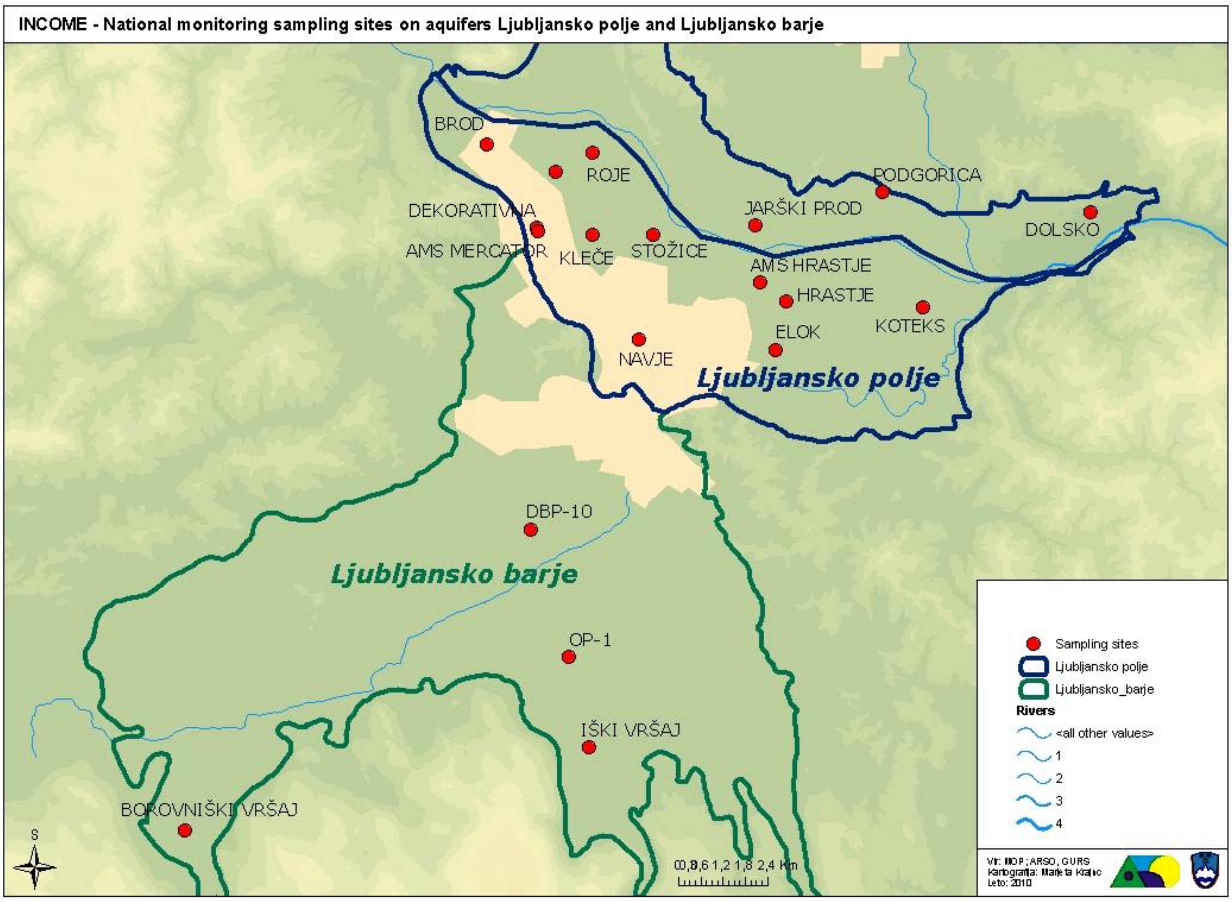
REFERENCES:

1. Slovene decree on groundwater status, OJ RS, 25/2009.
2. Guidance Document No, 18 "Guidance on Groundwater Status and Trend Assessment".
3. Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy.
4. Regulation on drinking water, OJ RS, 19/2004.
5. Directive 2006/118/EC of the European Parliament and of the Council of 12 December 2006 on the protection of groundwater against pollution.

APPENDIX A: Maps of national groundwater monitoring network



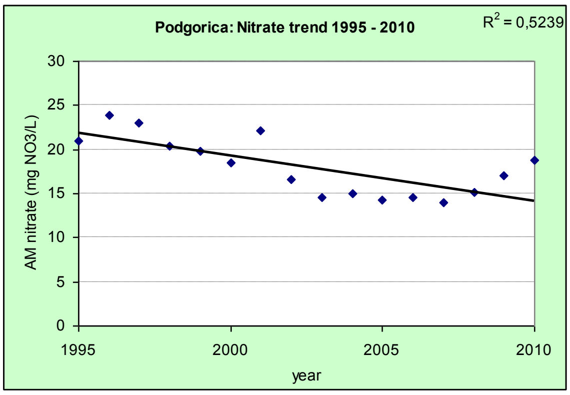
MAP 1

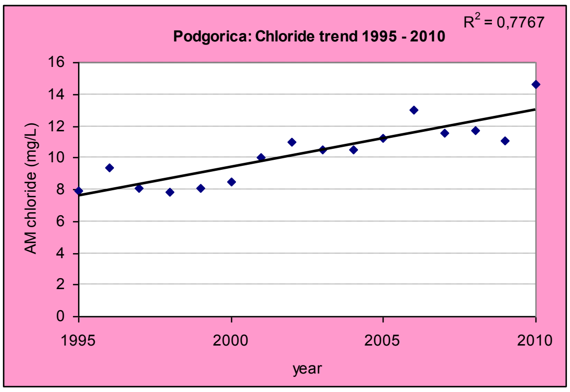

INCOME - National monitoring sampling sites on aquifers Ljubljansko polje and Ljubljansko barje
BROD
ROJE
PODGORICA
JARŠKI PROD
DOLSKO
DEKORATIVNA
AMS MERCATOR
KLEČE
STOŽICE
AMS HRASTJE
HRASTJE
KOTEKS
ELOK
NAVJE
Ljubljansko polje
DBP-10
Ljubljansko barje
OP-1
IŠKI VRŠAJ
BOROVNIŠKI VRŠAJ
S
Sampling sites
Ljubljansko polje
Ljubljansko_barje
Rivers
<all other values>
1
2
3
4
Vir: MOP; ARSO, GURS
Kartografija: Marjeta Krajnc
Leto: 2010

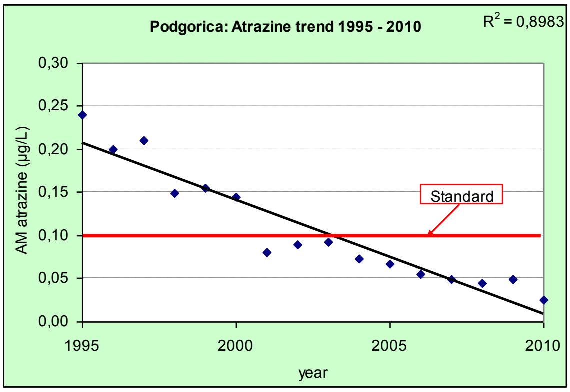
MAP 2

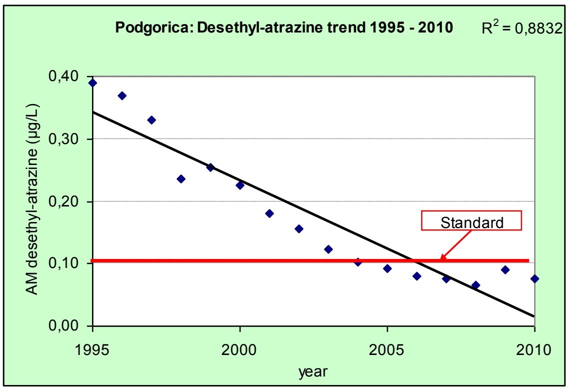
APPENDIX B: Graphs of significant long-term trends 1995 - 2010

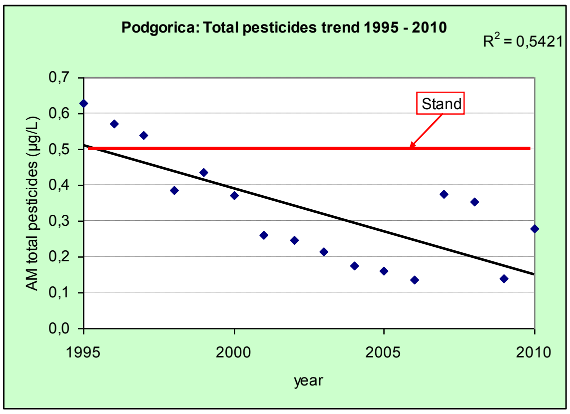
PODGORICA

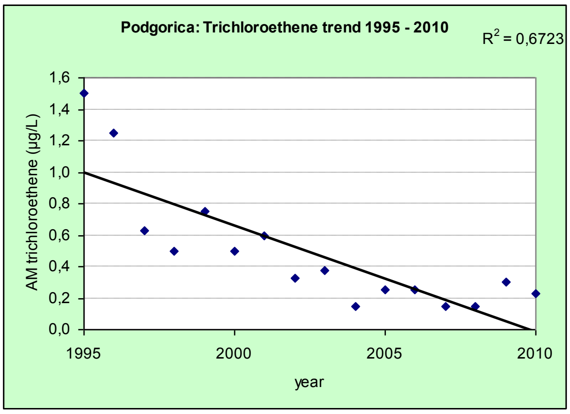




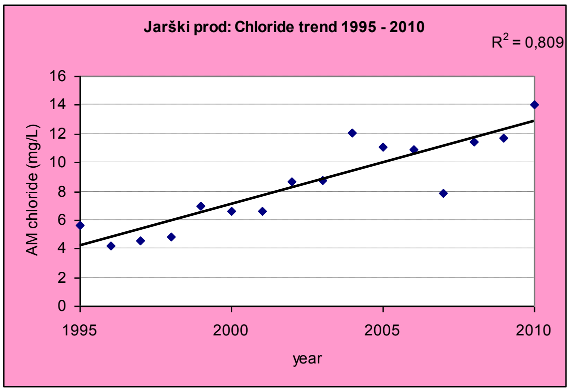




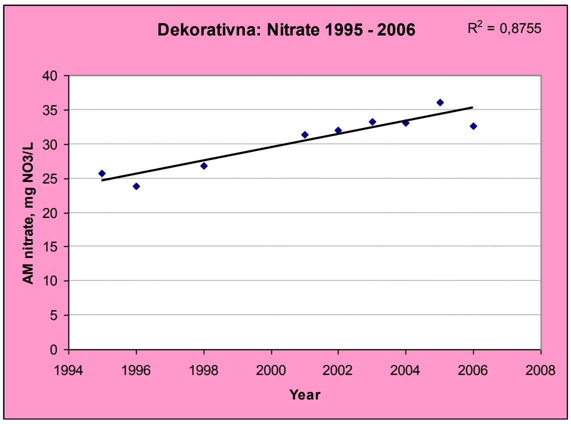


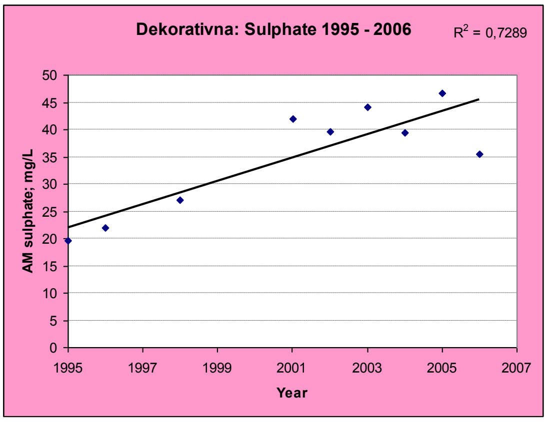


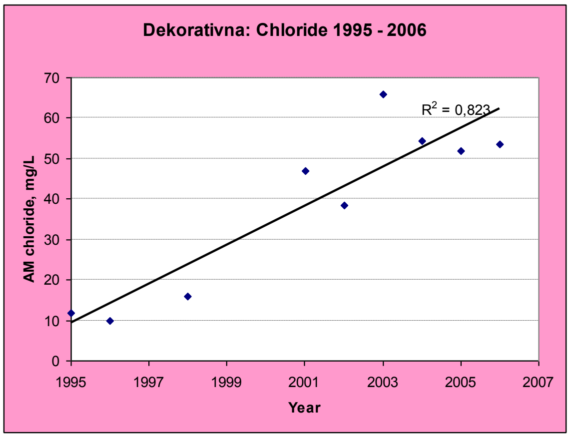
JARŠKI PROD



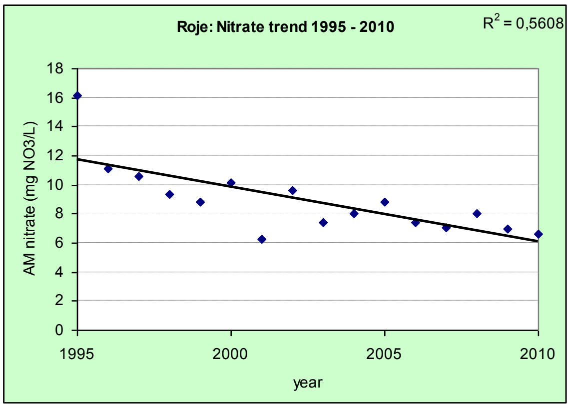
DEKORATIVNA



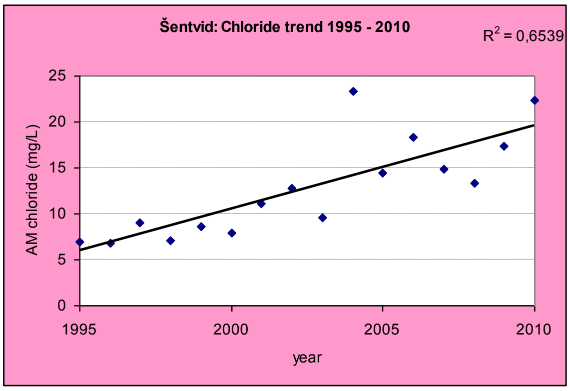


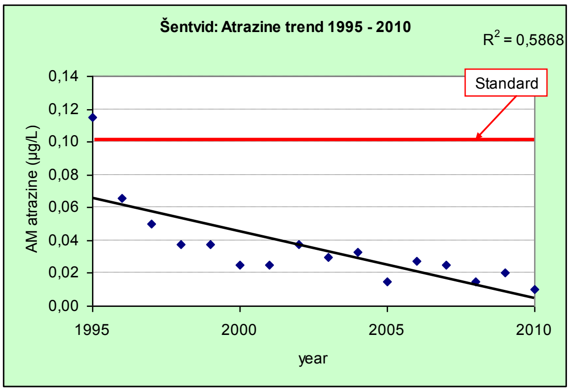


ROJE

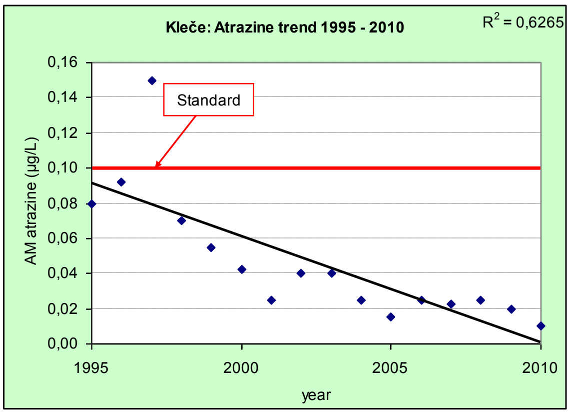


ŠENTVID IIa

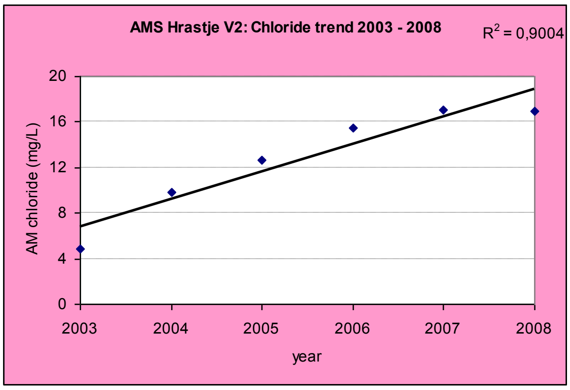


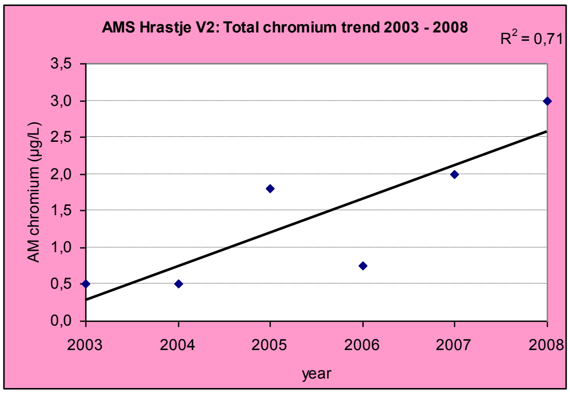


KLEČE VIIIa



AMS HRASTJE V2





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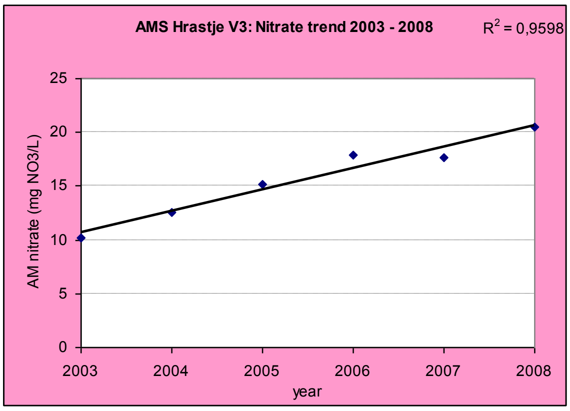
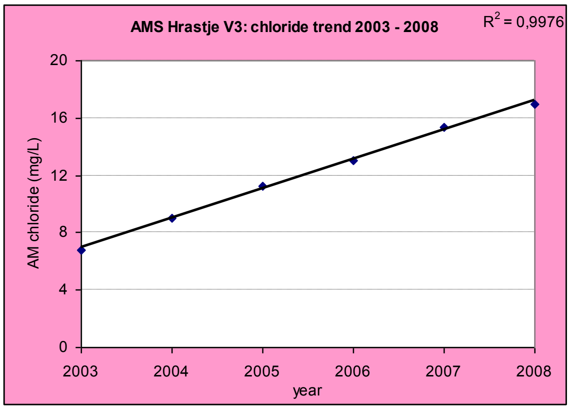
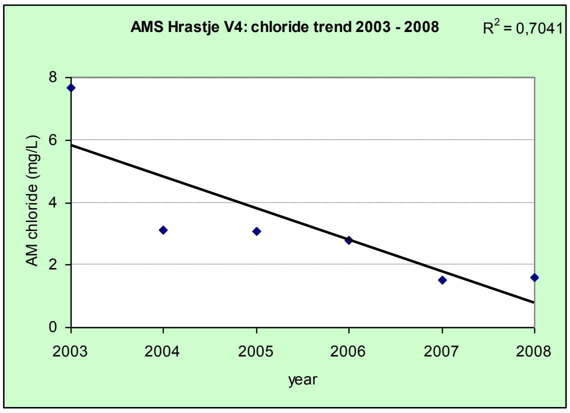
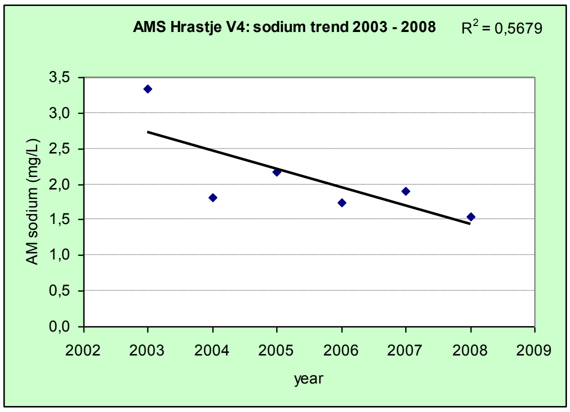


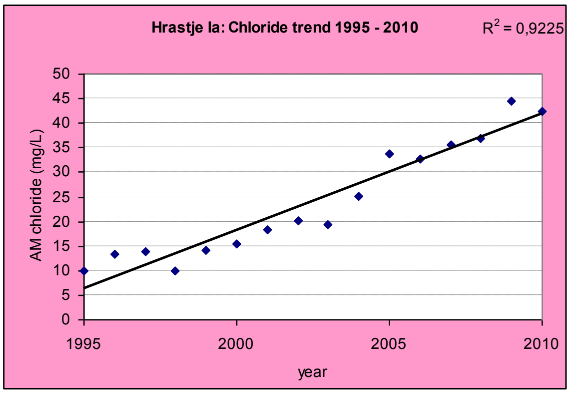


AMS HRASTJE V4

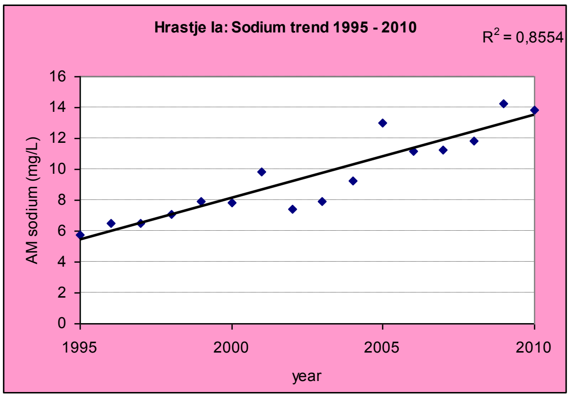




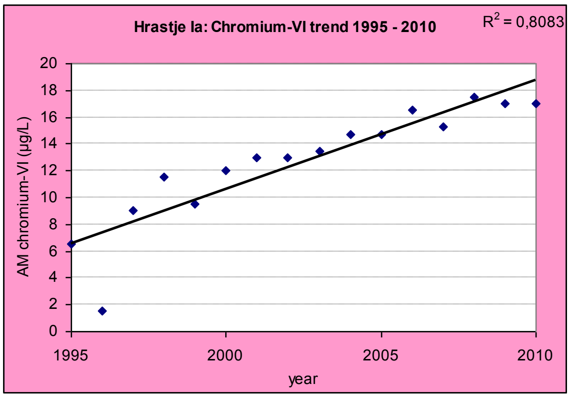
HRASTJE 1A



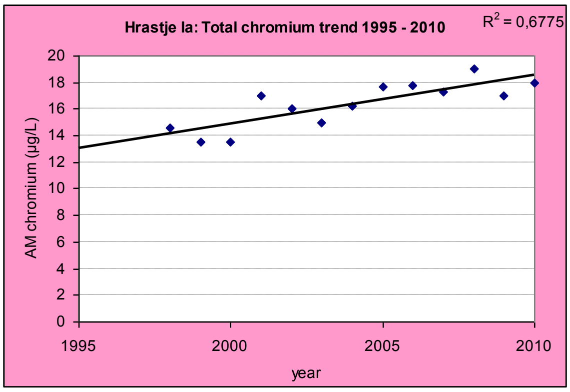
Hrastje Ia: Chloride trend 1995 - 2010
R^2 = 0,9225
AM chloride (mg/L)
year



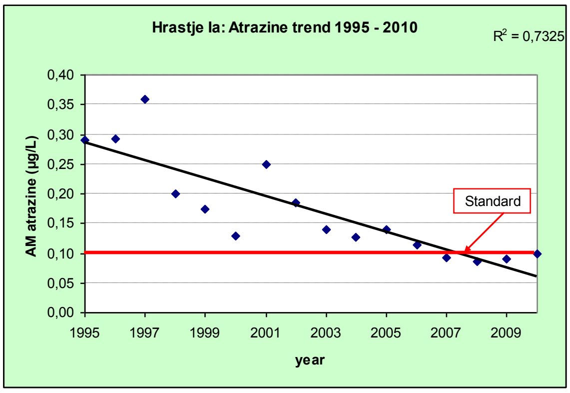
Hrastje Ia: Sodium trend 1995 - 2010
R^2 = 0,8554
AM sodium (mg/L)
year



Hrastje Ia: Chromium-VI trend 1995 - 2010
R^2 = 0,8083
AM chromium-VI (µg/L)
year

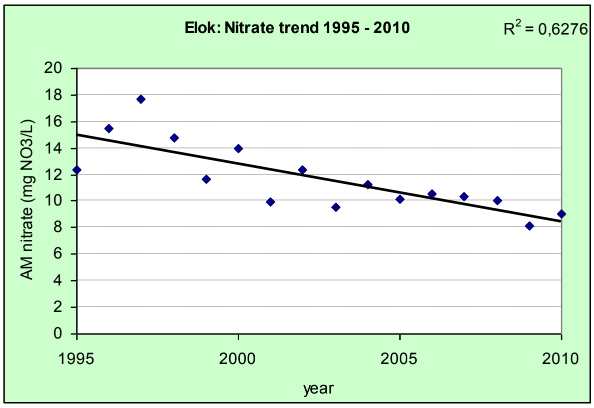


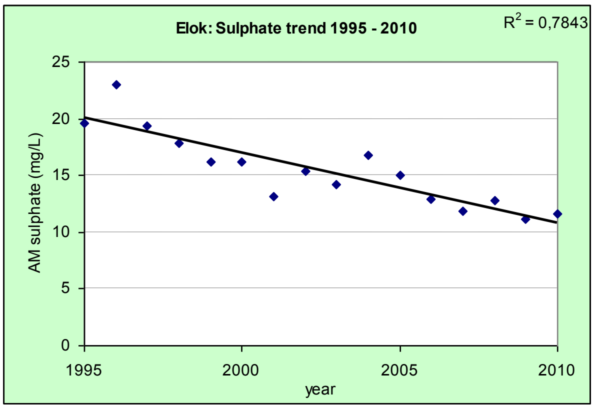
Hrastje Ia: Total chromium trend 1995 - 2010
R^2 = 0,6775
AM chromium (µg/L)
year



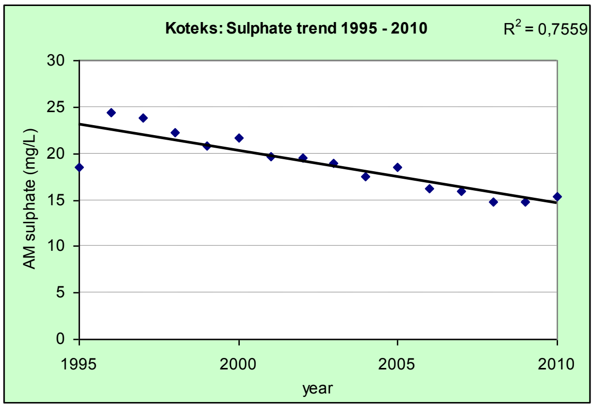
Hrastje Ia: Atrazine trend 1995 - 2010
R^2 = 0,7325
AM atrazine (µg/L)
Standard
year

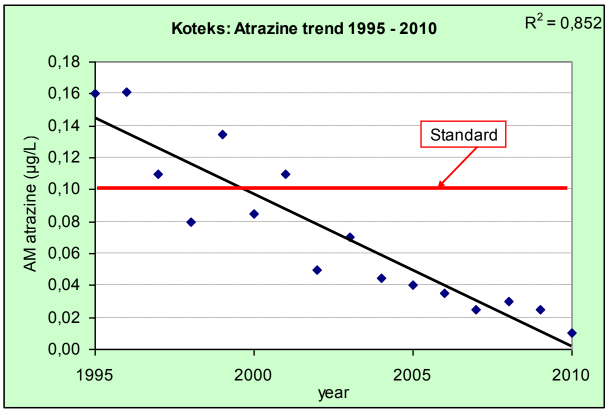
ELOK





KOTEKS





IŠKI VRŠAJ 1Agl