European Water 19/20: 37-46, 2007.
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Groundwater quality in Slovenia assessed upon the results of national groundwater monitoring

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Abstract: In Slovenia groundwater is predominant drinking water source. More than 97% of drinking water is abstracted from shallow, unconfined alluvial aquifers and fractured or karstic porosity aquifers. The protection of groundwater quality is therefore of upmost importance for Slovenia. According to the landuse on the recharge areas of shallow alluvial aquifers and their natural vulnerability pollution of groundwater is to be expected. In Slovenia groundwater quality monitoring of 19 alluvial aquifers important for drinking water supply started in 1987 while groundwater quality monitoring of karstic springs has been carried out since 1990. Monitoring network on alluvial aquifers contains 100 observation wells (among them 2 automatic monitoring stations) and 23 springs and wells on fractured- or karstic-porosity aquifers. Two to four times a year about 160 different chemical parameters are analysed, among them 100 different pesticides and their metabolites. Groundwater is polluted mostly by nitrates, pesticides and volatile chlorinated aliphatic hydrocarbons therefore these parameters are most important for groundwater quality assessment. Monitoring results from the year 2004 are statistically treated to represent groundwater quality on individual sampling site. Some characteristic trends are shown.

Key words: aquifer, drinking water, groundwater, pollution, monitoring, groundwater quality assessment, chemical status, trend

1. THE IMPORTANCE OF GROUNDWATER IN SLOVENIA

Slovenia is situated at the transition of alpine region, dinaric chain and pannonian basin. This transitional position together with abundant precipitations enabled amazing variety of geology, geographical shape, karstic phenomena, vegetation, etc. An important issue of this position and precipitations is the abundance of surface- and ground-water. The abundant groundwater resources in Slovenia were known for centuries. First explorer of Slovene groundwater, Valvasor (2004) described Slovene groundwater and karstic phenomena in detail in his extensive book "The Glory of the Duchy of Carniola".

Annual precipitations vary from 800 mm/year in pannonian region up to 3000 mm/year in alpine region (Cegnar, 2000). The ratio between infiltration and run-off estimated upon IDPR index is higher in karstic and alpine compared to pannonian region (Mardhel et al., 2004). The amount of infiltration is responsible for the quantity of dynamic reserves of shallow groundwater. Most abundant groundwater dynamic reserves are therefore expected in regions of high precipitation rate and predominant infiltration.

Most of the rivers flowing across the country with exceptions of Drava, Mura and few smaller streams have springs in Slovenia. Environmental policies and practice in Slovenia, responsible for the water quantity and quality, declared groundwater as high priority strategic resource which quality should be preserved (NEAP, 1999).

In Slovenia groundwater is traditional drinking water resource providing more than 97% of population. About 60% of drinking water originates from intergranular porosity (alluvial) aquifers while 40% from fractured porosity and karstic porosity aquifers.

2. GEOLOGY AND HYDROGEOLOGY OF AQUIFERS IN SLOVENIA

Almost the entire Slovene area is covered by groundwater aquifers. Groundwater in porous media with 3.726 km² of national territory, and groundwater in karst areas with 12.644 km² of national territory form the most important source of drinking water, supplying more than 97% of the entire population.

Major part of Slovenia is covered by sediment rocks with good permeability and intergranular porosity (19.8% of the area), fractured porosity (14.2%) and karst porosity (33.2%). The rest of the area consists of layers with intergranular or fractured porosity with lower conductivity or rocks with poorer porosity (Prestor et al., 2002).

Alluvial aquifers with intergranular porosity are relatively shallow, flat, gravel – sand alluvial deposits of tectonics depressions along major Slovenian rivers. Intergranular porosity appears in alluvial, quaternary, mostly gravel-sand deposits. In the Pleistocene and Holocene of the past two million years of the Earth′s history, surface water deposited great amounts of sediment into tectonic depressions (Uhan and Krajnc, 2003). Alluvial aquifers contribute a vital part to the dynamic reserves of Slovene groundwater (36.8%) (Kranjc, 1995).

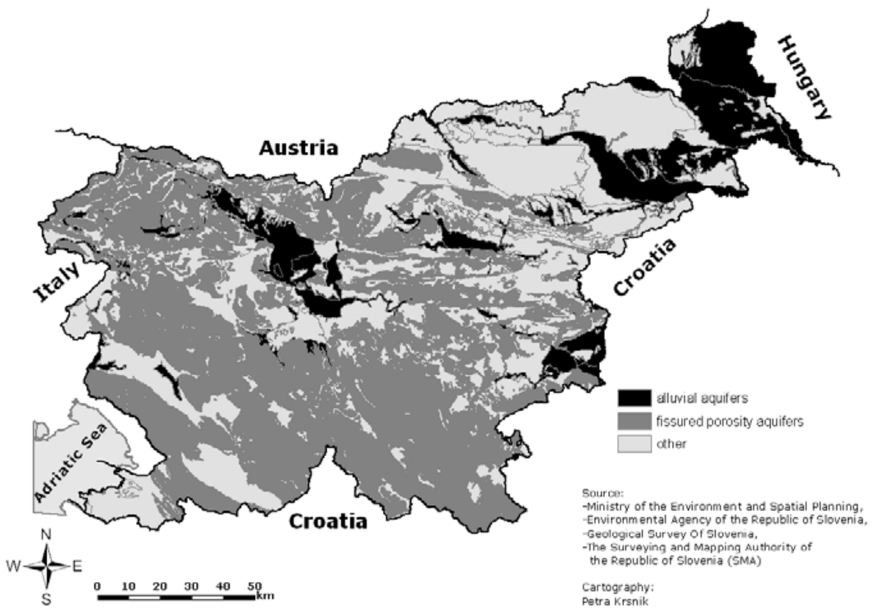
They are recharged mainly from precipitation and by infiltration of water into the ground from rivers and streams. In the effluent parts, groundwater drains back into riverbeds, or resurfaces in the form of plain spring. Some valley spring called »windows« have different characteristics where the groundwater is confined under clay layers and under constant pressure depressions (Uhan and Krajnc, 2003).

Apart from sand and gravel, there are also water bearing layers in limestone, dolomite limestone, sandstone, marl, etc. Karst porosity is typical for the layers of limestone and partly of dolomite, which had been fractured due to the tectonic movements, and were later karstified. For the dolomite layers fractured porosity is characteristic. In fractured porosity and karst porosity aquifers there are 62% of dynamic reserves of groundwater in Slovenia (Kranjc, 1995).

Less abundant groundwater layers in sandstones and marls have poorer permeability and fractured porosity.

Total dynamic reserves in intergranular porosity aquifers in flat river valleys are estimated as 18.8 m^3/s while for karstic and fractured porosity aquifers the dynamic reserves are estimated as 31.6 m^3/s (Kranjc, 1995).

According to data of Geological Survey of Slovenia (GeoS, 2004) on the Slovene territory there are 165 aquifer systems and 21 groundwater bodies (Map 1).



Map 1. Slovenian hydrogeological map and aquifers (161)

3. CHARACTERISTICS OF GROUNDWATER IN DIFFERENT TYPES OF AQUIFERS IN SLOVENIA

The groundwater quality in intergranular porosity aquifers differs substantially from the quality of groundwater in fractured porosity and karstic aquifers.

The vadose zone of intergranular porosity aquifers is the first filter for some pollutants as heavy metals and pesticides. Layers of the unsaturated zone have buffering, adsorption and complexation abilities which prevent to some extent the pollutant entering the groundwater system. On the other hand these layers act as the receptor and reservoir for the pollutants which can be released to the groundwater at changed conditions (Hantush et al., 2000). The slow groundwater flow in intergranular cavities enables groundwater to achieve semi-equilibrium state for various physico-chemical reactions as adsorption, chemisorption, occlusion. Consequently these are also favourable conditions for natural mineralization of groundwater at specific conditions (pH, T, redox potential, oxygen concentration, etc.). Intergranular porosity aquifer is not favourable environment for the growth of microorganisms (Pang et al., 2005). Nonpolluted natural groundwater from shallow alluvial aquifers in Slovenia has excellent characteristics and can be distributed as drinking water without any treatment, even no disinfection. This is most important advantage of this drinking water resource.

The fractured porosity aquifers consist of numerous underground channels of different size. Largest channels were formed in limestone (highly developed karst in southern part of Slovenia). Wide channels enable high groundwater flow and rapid long distance transport of pollutants from the source to the karstic springs. Microorganisms, also pathogenic, survive in these conditions (Dussart-Baptista et al., 2003). Drinking water from karstic springs has to be disinfected and sometimes chemically treated.

4. POLLUTION SOURCES

Shallow unconfined intergranular porosity aquifers in Slovenia, used as drinking water sources, are situated in flat river valleys with intense human activities as agriculture, industry, trade, relatively dense population and traffic infrastructure. All these activities represent potential pollution danger. Due to intense pressures and high vulnerability of shallow alluvial aquifers pollution of groundwater with nitrates, pesticides and chlorinated organic solvents has been stated.

On the other hand the surface above karstic aquifers is naturally protected by forests. Human activities are not as intense and population density is lower compared to flat river valleys. The consequence is lower pollution grade compared to alluvial aquifers. Main problems are high level of microorganisms, even pathogenic, higher organic content, turbidity after heavy precipitations. These parameters produce after treatment with gaseous chlorine or chlorine dioxide harmful organochlorine compounds, among them also trihalomethanes (THM). In sediments of karstic springs heavy metals and polycyclic aromatic hydrocarbons (PAHs) have been detected.

5. PRESENT STATUS OF SLOVENE GROUNDWATER LEGISLATION

Water Frame Directive (2000/60/EC) (WFD, 2000) defines the rules for groundwater bodies identification and requires quality assessment for the bodies.

The Slovene Environmental Protection Act (EPA, 1993) provides a legal basis for groundwater monitoring system. In year 2002 new Slovene legislation for groundwater, harmonized with EU legislation, came into force (Decree 2002, Regulation, 2002). Before 2002 groundwater quality used to be assessed according to the standards for drinking water on individual sampling site (Regulation, 2000). Decree sets different approach to groundwater quality assessment. It defines chemical characteristics of groundwater, limit values for parameters (chemical status parameters), methodology for chemical status determination and trends and criteria for endangered groundwater bodies identification.

More details on groundwater quality monitoring system are laid down in the Regulation on the groundwater imission monitoring (Regulation, 2002) which determines the way and extent of groundwater quality monitoring.

Due to proposed EU Groundwater directive (GWD proposal, 2004) Slovene Decree on groundwater quality is expected to be changed. The proposed Decree (May 2005) on groundwater quality has amendments on methodology of chemical status determination and quality standards.

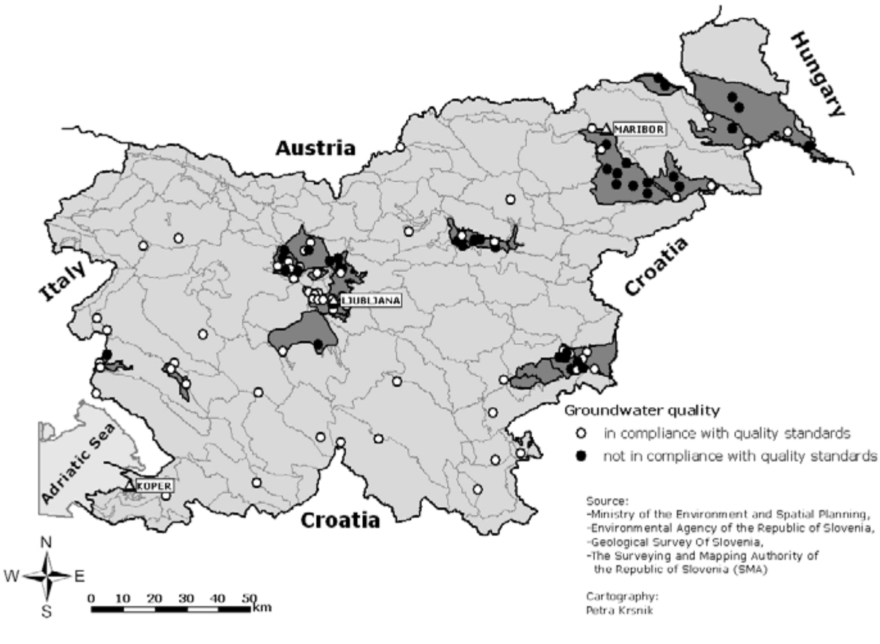
6. NATIONAL GROUNDWATER MONITORING

First measurements of groundwater quantity derive from early 19th century while regular national monitoring of groundwater level and flow started in 1952. First chemical analysis of groundwater were evidenced in 1830 (Kramer, 1905) but systematic groundwater quality monitoring on national level started in 1987.

Groundwater quality in Slovenia is monitored within the framework of national monitoring system by the Environmental Agency of the Republic of Slovenia (EARS) within the Ministry of the Environment and Spatial Planning (MESP). Additionally groundwater quality monitoring programmes are performed on the local level by the local authorities and water supply managements.

Design of existing groundwater quality monitoring is based on following principles:

- Determination of geogene conditions and surveillance of all potential anthropogenic substances in aquifer (parameters are summarized in table 1)
- Surveillance of drinking water resources (actual and potential) and their recharge areas; drinking water resources are mainly shallow unconfined aquifers and karstic aquifers with large recharge areas (monitoring sites on Map 2)
- Surveillance of human activities impact: monitoring the upper part of shallow unconfined alluvial aquifer (1 – 2 m beneath the groundwater table)
- Financial aspect: monitoring is state budget financed, its expenses should remain within approved limits



Map 2. Slovene national groundwater quality monitoring network

Monitoring network on 19 alluvial aquifers important for drinking water supply consists of 100 measuring sites. In the beginning monitoring sites were selected out of existing observation objects.

The structure of monitoring sites is following: 25% drinking water and industrial wells, 39% private wells, 27% boreholes and 9% automatic measuring stations (AMS) (Map 2, Picture 1).

Monitoring network on fractured porosity and karstic porosity aquifers consists of 23 measuring sites among them 17 springs and 6 drinking water production wells (Map 2).

Existing groundwater quality monitoring network covers 38 out of 165 aquifers. The density of monitoring sites is much higher on alluvial aquifers compared to fractured porosity and karst porosity aquifers. Measuring sites on karst aquifers (mostly karstic springs) are representative of larger recharge areas compared to alluvial aquifers (Map 2). The aquifers not covered by monitoring network are of minor importance.

Five years ago a programme of representative national monitoring network construction started. Two automatic measuring stations (AMS) have been in function since 2003. They were financed by PHARE and the Republic of Slovenia. The third AMS will be in function in July 2005. AMS are equipped to monitor on-line following parameters: groundwater level, electrical conductivity, groundwater temperature, pH, oxygen content and nitrate concentration. Every 30 minutes data are transmitted to central computer of the EARS. AMS have multilevel boreholes which enable sampling of groundwater from different horizons (Picture 1).

Picture 1. Automatic measuring station on the alluvial aquifer of Ljubljana

Groundwater from all measuring sites is sampled twice to four times a year and analysed for about 160 different chemical and physical parameters listed in Table 1.

Changes of the list of parameters since 2003 list are indicated in Table 1. According to WFD and Slovene Decree on groundwater quality only chemical status and trends for groundwater bodies have to be determined. There is no legal basis for determination of microbiology, sediment analysis and for parameters which have never been determined above the limit of detection (LOD) since the start of the groundwater quality monitoring. On the other hand the list of pesticides has been extended to new active compounds and their metabolites as well as few dangerous substances.

According to WFD requirements following changes in groundwater quality design are to be expected in future:

- Monitoring network: representativity of monitoring sites for the whole groundwater body
- Increase of parameters mostly from following groups: persistent organic pollutants (POPs), pesticides, dangerous substances
- Differentiation in monitoring schemes: surveillance and operational monitoring

Table 1. Parameters analysed in groundwater samples

Groups of parameters	Parameters / specific groups
Basic parameters	T, pH, electroconductivity, redox potential, oxygen content, turbidity, colour, COD, TOC, Cations: Na^+, K^+, Ca^{2+}, Mg^{2+}, NH_4^+ Anions: NO_2^-, NO_3^-, PO_4^{3-}, o- PO_4^{3-}, SO_4^{2-}, Cl^-, F^-, HCO_3^-
Pollution group parameters	surfactants*, mineral oils, AOX, PCB, cyanides*, phenolic index*
Metals and metalloids	Al, Fe, Mn, As, B, Cu, Zn, Cd, Cr-VI, Cr_{tot}, Ni, Pb, Hg
Pesticides	about 100 active substances and their metabolites; major groups: triazines, OCP, anilines, nitriles, amides, organic phosphates, organic thio-phosphates, chloroacetanilides, phenylurea derivatives, phenoxypropionic derivatives
Volatile halogenated aliphatic hydrocarbons	trichloromethane, tribromomethane, bromdichloromethane, dibromochloromethane, trichloronitromethane, tetrachloromethane, dichloromethane, trichlorofluoromethane, difluorodichloromethane, 1,1-dichloroethane, 1,2-dichloroethane, 1,1-dichloroethene, 1,2-dichloroethene, tetrachloroethene, trichloroethene, 1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane, hexachlorobutadiene
Aromatic compounds	benzene, toluene, xylene, mesitilene, 1,2,3-trichlorobenzene, 1,2,4-trichlorobenzene, 1,3,5-trichlorobenzene
Identification of organic compounds by GC/MSD*	
Microbiological parameters (fractured porosity and karstic porosity aquifers)*	
Sediment analysis in springs (fractured and karstic porosity aquifers)*	

*: analysed up to 2003
T: temperature of groundwater
pH: negative logarithm of H_3O^+ concentration
COD: chemical oxygen demand ($KMnO_4$ method)
TOC: total organic carbon
AOX: organohalogenes adsorbed on active carbon
OCP: organochlorine pesticides
PCB: polychlorinated biphenyles
GC/MSD: gas chromatography coupled with mass-selective detector

7. THE RESULTS OF GROUNDWATER QUALITY MONITORING

The basis for groundwater quality assessment was the proposed Decree on groundwater quality. For all the results from the year 2004 following treatment was applied:

- arithmetic mean of all parameters on individual sampling site
- arithmetic mean of parameters of chemical status for the aquifer
- longterm trends of parameters on individual sampling site: arithmetic mean for twelve years period 1993 – 2004

According to proposed Decree groundwater quality on individual sampling site was assessed to be in compliance if arithmetic means of all parameters were lower or equal to quality standards (Table 2).

Table 2. List of quality standards in the proposed Decree on groundwater quality

Groundwater parameters	Unit	Quality standard
Nitrates	mg NO_3^-/l	50
Individual pesticide or its relevant metabolite	μg/l	0.1
Total pesticides and their relevant metabolites	μg/l	0.5
Amonium	mg NH_4^+/l	0.2
Potassium	mg K^+/l	10
orto-phosphates	mg PO_4^{3-}/l	0.2
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
Sum of volatile halogenated aliphatic hydrocarbons	μg/l	10
Mineral oils	μg/l	10
Chromium	μg/l	30

Groundwater quality is first assessed on individual sampling sites. For each measured parameters arithmetic mean (AM) on sampling site is calculated. If AMs for all parameters are lower or equal to quality standards (table 2), groundwater quality from individual sampling site is estimated to be in compliance with the requirements (pale spots on Map 2). In case that AM of one or more parameters exceed quality standards groundwater quality is estimated not to be in compliance (dark spots on the Map 2). Groundwater quality assessment on individual sampling site is indicated on Map 2. Groundwater is most polluted in alluvial aquifers of NE part of Slovenia, while groundwater of central SE and SW alluvial aquifers is of better quality. Groundwater from karst and fractured porosity aquifers shows good chemical characteristics being in compliance on all sampling sites.

For aquifers yearly arithmetic mean values for all parameters were calculated. According to WFD in future chemical status for groundwater bodies (GWB) shall be determined. In 2004 Slovene GWB were still in process of identification and not officially defined. For aquifers chemical status in 2004 was not determined but compliance with quality standards was stated.

In Table 3 arithmetic means of parameters analysed in 2004 are shown. Only parameters indicating pollution are selected while all those lower or equal to quality standards are omitted. Compliance with quality standards is stated for those aquifers where arithmetic means of all groundwater parameters are lower or equal to quality standards. Groundwater in an aquifer where at least one of groundwater parameters exceeds quality standard is not in compliance.

From Table 3 it can be concluded that 9 out of 38 aquifers are not in compliance with quality standards. All nine aquifers being not in compliance are of alluvial type. Most problematic pollutants are nitrates (4 aquifers), desethylatrazine (6 aquifers), atrazine (1 aquifer), pesticides (2 aquifers), trichloroethene (1 aquifer) and tetrachloroethene (1 aquifer).

According to monitoring results atrazine is in spite of legal prohibition still widely applied on Dravsko polje (aquifer code 32714). For all other alluvial aquifers low ratio atrazine/desethylatrazine indicates that atrazine is not applied elsewhere. Chlorinated organic solvents represent very serious threat to groundwater quality. Numerous spillages of trichloroethene and tetrachloroethene caused degradation of smaller parts of aquifers. The problem can not be seen on a large scale but groundwater in 7 out of 123 sampling points is polluted by those chemicals.

Table 3. Compliance of groundwater in Slovene aquifers: arithmetic mean values of parameters indicating pollution in the year 2004

Aquifer code	NO_3^-	AT	DAT	Pesticides	C_2HCl_3	C_2Cl_4	Compliance
	mg /l	µg/l	µg/l	µg/l	µg/l	µg/l	YES / NO
11320	2.6	0.02	0.02	0.04	0.45	0.25	YES
11512	25.0	0.03	0.04	0.16	0.11	0.05	YES
11513	30.2	0.03	0.06	0.22	0.19	0.74	YES
11711	24.4	0.06	0.07	0.12	0.10	0.05	YES
11712	15.2	0.03	0.05	0.09	0.59	0.93	YES
11713	7.4	0.03	**0.13**	0.16	0.57	0.04	NO
11823	3.8	0.02	0.02	0.04	0.45	0.25	YES
11825	3.8	0.02	0.02	0.04	0.45	0.25	YES
11911	21.3	0.05	**0.11**	0.16	0.37	0.28	NO
12121	3.4	0.02	0.02	0.04	0.45	0.25	YES
12221	4.0	0.02	0.02	0.04	0.45	0.25	YES
12411	26.9	0.02	0.03	0.05	0.45	0.59	YES
12414	30.0	0.03	0.08	0.11	0.45	0.56	YES
12429	8.2	0.02	0.02	0.04	0.45	0.25	YES
12432	3.8	0.02	0.02	0.04	0.45	0.25	YES
12512	**67.1**	0.05	**0.17**	**0.53**	0.11	0.05	NO
12513	**63.4**	0.03	0.07	0.14	0.20	0.81	NO
12524	6.0	0.02	0.02	0.04	0.45	0.25	YES
12528	5.6	0.02	0.02	0.04	0.45	0.25	YES
22921	3.8	0.02	0.02	0.04	0.45	0.25	YES
22927	6.6	0.02	0.02	0.04	0.45	0.25	YES
22930	7.3	0.02	0.02	0.04	0.45	0.25	YES
32713	13.3	0.02	0.02	0.04	0.10	0.05	YES
32714	46.2	**0.22**	**0.14**	0.40	0.35	0.13	NO
32715	**64.2**	0.06	0.08	0.16	0.10	0.05	NO
32722	2.2	0.02	0.02	0.02	0.45	0.25	YES
42811	**68.2**	0.06	**0.13**	0.20	0.10	0.05	NO
42812	15.1	0.02	0.02	**0.67**	0.10	0.13	NO
42813	38.9	0.09	**0.11**	0.23	**10.03**	**30.06**	NO
50521	4.3	0.02	0.02	0.00	0.45	0.25	YES
50621	8.5	0.02	0.02	0.04	0.45	0.25	YES
50721	4.4	0.02	0.02	0.00	0.45	0.25	YES
60129	2.4	0.02	0.02	0.04	0.45	0.25	YES
60221	5.3	0.02	0.02	0.04	0.45	0.25	YES
60222	4.6	0.02	0.02	0.04	0.45	0.25	YES
60313	5.9	0.02	0.02	0.04	0.45	0.25	YES
60321	31.6	0.02	0.02	0.04	0.58	0.31	YES
60421	5.5	0.02	0.02	0.04	0.45	0.25	YES
QS	50.0	0.10	0.10	0.50	2.00	2.00	

NO_3^- nitrate
AT atrazine
DAT desethylatrazine
C_2HCl_3 trichloroethene
C_2Cl_4 tetrachloroethene
QS quality standard

Long term changes from 1993 to 2004 were analysed by regression analysis. In most cases linear regression analysis was applied. Specific parameter has long term trend if:

$R^2 > 0.5$ R^2 coefficient of determination

Analysing long term changes in concentration of major pollutants it can be generally stated that trends for nitrates are pronounced very weakly (Figure 1), while for desethylatrazine and atrazine trends of declining are perceived for most of the alluvial aquifers (Figure 2).

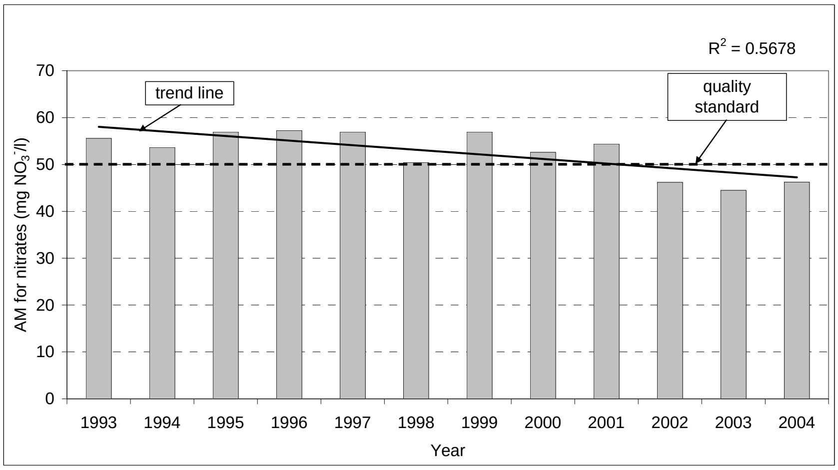


Figure 1. Longterm trends of nitrate concentration in groundwater of Dravsko polje from 1993 to 2004

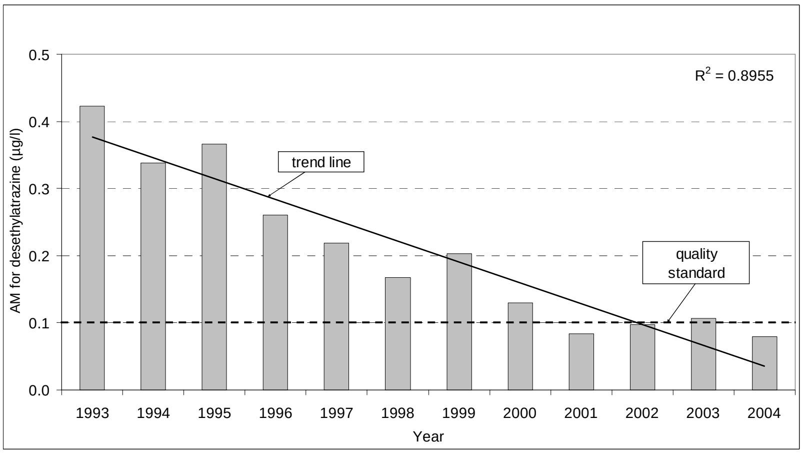


Figure 2. Longterm trends of desethylatrazine concentration in groundwater of Ptujsko polje from 1993 to 2004

Longterm analysis for most of parameters does not give any indication for trend. Annual arithmetic mean values for longer period are scattered ($R^2 < 0.5$).

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