Water quality analysis and trends on Isonzo river alluvial plain pilot area – Friuli Venezia Giulia Region, Italia

> AcegasApsAmga (LP) jointly with DMG - UNITS

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Lead Author/s	Chiara Calligaris, Franco Cucchi
Lead Authors Coordinator	
Contributor/s	
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2



1 Introduction

The present report focuses on water quality trends and data analysis on the pilot area of Isonzo river alluvial plain (Northeastern Italy) chosen as test site area in the framework of DRINKADRIA project.

The Isonzo Plain, about 170 km², is located in the eastern side of the Friuli Venezia Giulia Region. It holds a significant phreatic aquifer and many rich artesian aquifers that represents an important natural wealth, in terms of quantity, quality and ease of supply. The aquifers are used for different purposes: drinking, household, industrial, agricultural and farming. They serve more than 350.000 inhabitants.

Water analyses are based on reports and data published on the subject since 1960 and updated by recent studies realized in the framework of ITA-SLO INTERREG Projects in the period between 2010 and 2014: GEP and ASTIS (**GEP** - Joint Geo-Information System (GIS) for Emergency Protection of Drinking Water - <u>http://www.gepgis.eu/;</u> **ASTIS** - Groundwater and Transition Isonzo/Soča).

The Isonzo-Soča Plain (Figure 1) is almost made entirely by quaternary alluvial deposits of Isonzo/Soča, Torre, Judrio, and Versa rivers. It is divided in two areas: the High Plain to the North and the Low Plain to the South. The High Plain at its North edge has the Collio Hills, made up by marlstones and sandstones of the Eocene Flysch. To the South are present instead the cretaceous limestone reliefs of the Karst Plateau. Coarse and very permeable deposits that hold a well-developed phreatic aquifer mainly constitute the High Plain. The rivers have an influent character with respect to the High Plain; for this reason, Torre and Judrio rivers remain dry most of the year. Isonzo/Soča River loses about 25% of its discharge. The river losses, together with effective infiltration, run-off waters coming from the hills and karst waters, actively recharge the phreatic aquifer of the High Plain. Proceeding towards the Low Plain from North to South, the phreatic aquifer joins into a multi layered aquifer system characterized by alternating gravel-sand and clay-silt deposits. Due to the southward permeability decrease, the High Plain phreatic waters outflow in correspondence to a NW-SE wide area displayed as a resurgence belt. Here waters are rising creating an outflow that can be identified as a water quantity and quality indicator.

For a year, every 15 days, during the ASTIS Project, the phreatic aquifer in the High Plain has been monitored. 46 wells/piezometers have been monitored on the Italian side. These data allowed the elaboration of several maps where the obtained results are summarized. *In primis* the phreatic aquifer was analyzed and different isophreatic scenarios were elaborated (high water regime, low water regime) obtaining the groundwater flow directions and the water table fluctuations, Figure 2 is one example of the obtained results.





Figure 1: DRINKADRIA pilot area (in red), the Isonzo/Soča River plain.

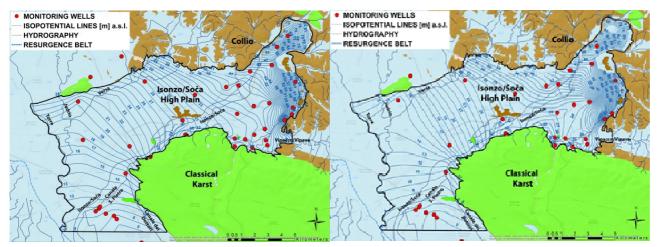


Figure 2: A) Isophreatic map during a period of very high level (first decade of February 2014); isophreatic map during a period of minimum level (8th August 2013). Red dots are the monitored points. Blue lines are the isophreatic lines. The numbers are expressing the water level in m a.s.l.

The thickness of the alluvial deposits is changes from site to site according to the different places in which it is calculated. It varies from few meters in proximity of the reliefs to hundreds of meters in correspondence of the depressions complicating the bedrock morphologies.



The bedrock consists of sandstones and marls, Eocene in age to the North, and limestones of Cretaceous age-Paleocene to the South. The shape of the case where flood deposits are contained is complex. It is characterized by valleys and mountains generated by erosional and tectonical processes. South of Gorizia is present a depression: here the bedrock drops of approximately 100 meters. The deepening starts in Mariano municipality (-50 m) reaching, in the surroundings of Villesse area, the depth of -350 m b.g.l.

The isopach map elaborated for the Quaternary deposits, obtained by subtracting from the Digital Elevation Model the values of the isobaths, shows that the thickness of the deposits reaches 100 m in correspondence of the depression south of Gorizia and 75 m in the area between Farra and Medea. The thickness of the deposits, in the test area, reaches its maximum at Villesse (-350 m).

In part of the test site area, the water table level was monitored manually and automatically. This allowed the reconstruction of the water table, its fluctuations (Figure 2) and the identification of the main groundwater flow directions. The isophreatic maps highlight a general groundwater flow partially guided by the presence of the different rivers that flows from East toward West. In the surroundings of Sagrado, the flow is veering toward South. In particular, from the maps, it is possible to identify two contributions: one due to the Isonzo/Soča and Vipacco rivers and the other derived from the hills around runoff. In the western part of the investigated area, the presence of the Torre River is also recognized: its contribution is the one that trigger and accelerate the southern veering of the groundwater flow.

South of Gorizia, part of the groundwaters are drained by the karst hydrostructure contributing with approximately 10 m³/s to the Timavo spring discharge area (Zini et al. 2011, Cucchi et al., 2015).

2 Pilot areas and tested water quality parameters

In the area of the Isonzo Plain, to integrate and update the hydrogeological data collected within the time, in correspondence of the phreatic aquifer, a series of qualitative monitoring surveys were realized seasonally. During the surveys, water samples were collected and sent to the laboratories in order to analyze the main physico-chemical, geochemical and isotopical parameters. All these activities were realized by the researchers of the Department of Mathematics and Geosciences of the Trieste University in the framework of ASTIS Project (<u>www.astis.ung.it</u> - Acque Sotterranee e di Transizione Isonzo/Soča).

During the DRINKADRIA Project, the available data were collected, studied and later rielaborated.

From the analysis of the previous reports emerges that in the test area, the prevailing hydro chemical facies is the bicarbonate calcium and/or magnesium with more or less meaningful concentrations of sulfates. The facies is consistent with the lithologies present in the recharge areas that are mainly limestone and dolomite. The distribution of the nitrate concentrations, as the one of other minor elements, shows that the groundwater along the river Isonzo/Soča is poor in elements due to the dilution caused by the influent character of the river. Distancing from the river course instead, the concentrations are higher highlighting an enrichment. This is visible not only



through the analysis of the EC (Electrical Conductivity), but especially on the maps elaborated for specific parameters as the ones related to the sulphate (Figure 3) and the nitrates (Figure 4).

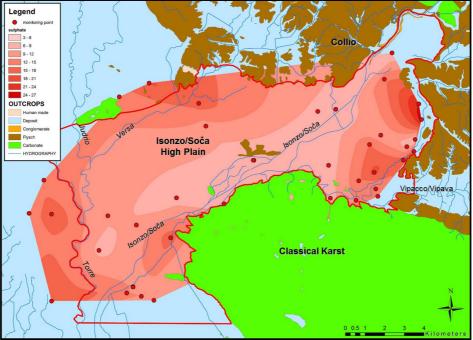


Figure 3: Map of the sulphates [mg/l] for the period July 2013 in the High Plain of the Isonzo/Soča River. Red dots correspond to the monitored points during the INTERREG "ASTIS" Project.

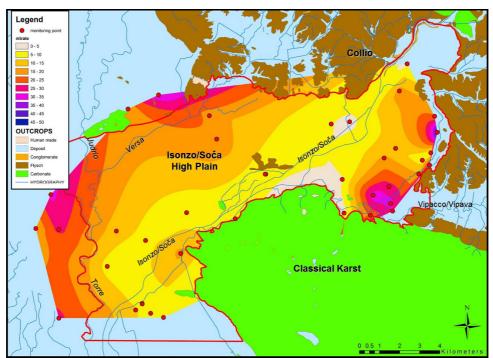


Figure 4: Map of the nitrates [mg/l] for the period July 2013 in the High Plain of the Isonzo/Soča River. Red dots correspond to the monitored points during the INTERREG "ASTIS" Project.



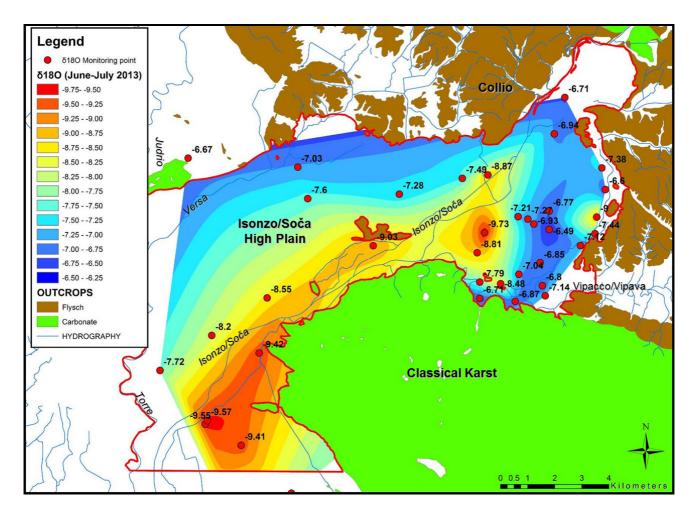


Figure 5: Map of the δ^{18} O for the period June-July 2013 in the High Plain of the Isonzo/Soča River. Red dots correspond to the monitored points during the INTERREG "ASTIS" Project.

Similar considerations to the ones expressed for the ion nitrate and sulphate can be applied to the spatial variability of the isotopic values δ^{18} O and ²H. Isotopical ratio in fact, acts as natural tracers and allowed, together with the isophreatic maps, to better define the groundwater flow direction and the role of the Isonzo/Soča River with respect to its influent character on the phreatic groundwaters.

In correspondence of the Isonzo/Soča River are present the most negative values, while on its hydrographic left and especially on its right, the phreatic groundwaters have less negative values. Isonzo/Soča waters that originate from a catchment in which the precipitations occur at high altitude, have a very high negative values. The precipitations over the plain instead, present δ^{18} O values less negative.



3 Test results and trends

In the test area, several are the water points that were analyzed in the past and that can be considered as good quality monitoring points also for the future. These are pumping wells, piezometers, rivers and springs. For some of them as Timavo and Sardos springs and the monitored point on the DN2000 pipe, the AcegasApsAmga has a routine check up on specific parameters. The DN2000 point is a sampling point on the pipe DN2000 located in the Randaccio aqueduct building (Figure 6). Until 5 years ago, this sampling point was at the end of the tunnel close to Sablici channel, but later on it has been moved making the sampling easier.

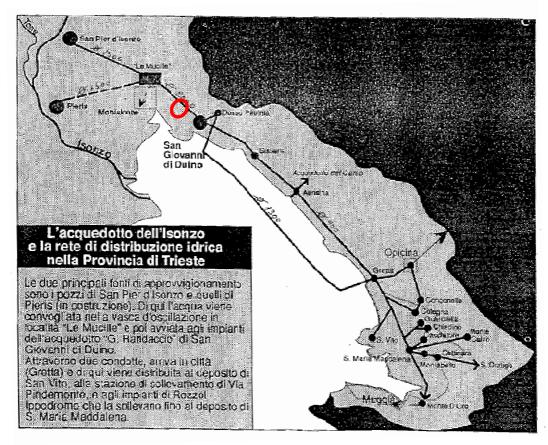


Figure 6: In red, the sampling point from the pipe DN2000. It actually correspond to a tap in the Randaccio building. San Pier d'Isonzo and Pieris represent instead two aqueduct lines: the line North and the line South respectively.

Each month:

- Organoleptic parameters: color and odor
- Chemical-physical parameters: UV absorption at 254 nm, electrical conductivity (EC), pH, temperature, turbidity;
- Chemical parameters: ammonium, residual disinfectant (only on the distributed waters), total hardness, Oxidability;



- Bacteriological indicators: total coliforms, fecal coliforms and/or Escherichia Coli, fecal streptococci (enterococci) the number of bacteria at 37 °C;
- Major ions: *anions:* fluoride, chloride, bromides, sulfates, phosphates, nitrates, brominated, chlorinated, chlorited; *cations:* calcium, sodium, potassium, magnesium;

Every three months:

- some metals (arsenic, cadmium, chrome, iron, manganese, lead, copper, zinc);
- Chlorinated Solvents 1,2-dichloroethane, tetrachloroethylene, Trichloroethylene, trihalomethanes THM;
- Herbicides Triazine (atrazine, desethylatrazine, terbuthylazine, desetilterbutilazina, simazine, propazine);
- Other microbiological parameters: Clostridium perfringen, Pseudomonas aeruginosa, Pathogenic staphylococci.

Once a year:

- Other Chemical parameters: benzene, cyanide, Acrylamide (b), Vinyl chloride, Epichlorohydrin;
- Other Metals: Aluminum, boron, antimony, mercury, nickel, selenium, vanadium;
- Pesticides: chlorinated herbicides (aldrin, dieldrin, heptachlor, heptachlor epoxide);
- Polycyclic aromatic hydrocarbons PAH: (Benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(ghi)perylene, indeno (1,2,3-cd) pyrene).

Despite the large amount of available data, it has not been possible to elaborate trend analysis for all the previously mentioned parameters. This is due to the data out coming from the analysis. What is important for the company is to guarantee good quality waters to the users. Good quality means waters having chemical and microbiological data that never exceed the legal limits fixed by the Italian legislations (D.Lgs 31/01 - National standard reference for water devoted to human consumption). The public water supply water quality standards for drinking water are regulated by D.Lgs 31/01 and D.Lgs 152/06, implemented of the European directive 98/83/CE and 2000/60/CEE. This licensed that in a water sample it is not important the effective concentration and the fluctuations of the elements, what is important is not to exceed the legal limit. For this reason, for most part of the parameters it is impossible to realize a trend analysis due to the lack of values. What we know is that the values constantly remained and remain below the limit.

For some parameters instead, as ion concentrations, values were defined within the years and trends are here calculated.

Regarding the frequency of monitoring, in the study area, two are the options taken into account:

1) Through two INTERREG projects (ASTIS and GEP), there has been the possibility to start to monitor the piezometers and the surface waters in an area not jet investigated. During the three-year project, were monitored 7 superficial water points (3 in Italy and 4 in Slovenia). For the groundwaters, almost 70 water points (piezometers and wells) were investigated (the most part in Italy and only a small amount in Slovenia, 12). The surveys occurred according to the seasonality.



2) On the pumping wells present in the southern part of the test site area, exploited by AcegasApsAmga company, the monitoring occur on 13 wells (12 Linea Nord + P16 Dobbia) once a year as previously described.

To realize the trends, were evaluated the data collected from the 13 pumping wells exploited by AcegasApsAmga (Figure 7). The waters are analyzed once a year with a complete analysis based on D.Lgs. 31/01 in collaboration with the ASS n°1 Triestina. Analysis were available since 1973, drilling date, but good quality data are available since 2000.

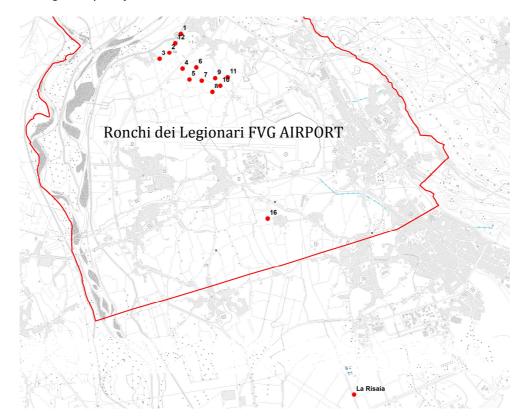
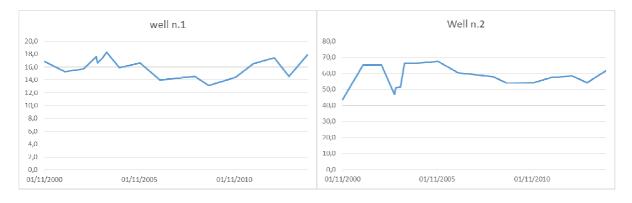


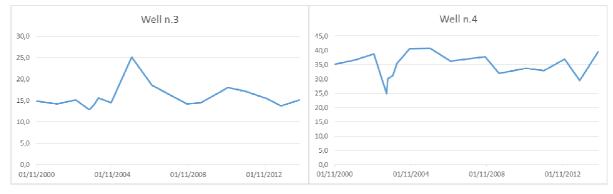
Figure 7: Location of the AcegasApsAmga pumping wells and La Risaia well. Most part of the pumping wells are located north of FVG Ronchi dei Legionari airport. At present, of the line South the only exploited well for drinking purposes is the number 16.

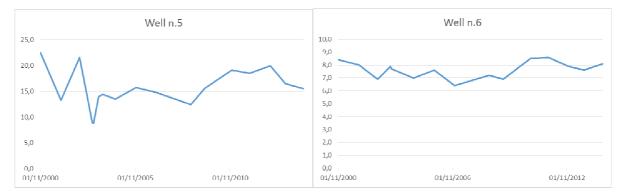
3.1 Physical and chemical composition

Basic physical-chemical and geo-chemical properties of piezometers do not show significant deviations except the normal annual fluctuations depending on the hydrological conditions of the basin. Concerning the AcegasApsAmga wells, one example of the available data is given by the Chlorides analysis (Figure 8).









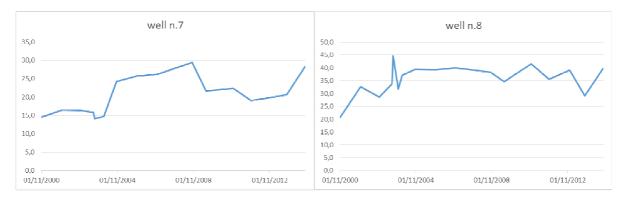






Figure 8: Chloride [mg/l] analysis in the AcegasApsAmga wells 2000-2014. However in line with what is actually available, even if not so accurate are the data from 1974. Nevertheless, seen that values that are more accurate are available since 2000, for the present work was decided to realize the trend analysis only on the more reliable data. La Risaia, n.10 and n.11 wells have a very low Chloride value (less than 8 mg/l). Higher values are reached by 45mg/l in the Well.8 and by the 35 mg/l of the well 4. The chlorides in the water derives from the composition of the soil, from industrial and municipal discharges, from the use of salts to melt ice on the roads. In the analyzed wells where the exploitations occur at considerable depths the just mentioned causes of chloride increase are not present.

3.2 Nitrates

Groundwater nitrate levels may be high in areas where land use activities increase the rates of leaching losses from the soil or where there are large or multiple discharges of wastewater to land.



In the pilot area, large changes occurred in recent years concerning the land use but if we look at the trends on the AcegasApsAmga pumping wells (Figure 12), the impact on the exploited groundwater is very small, small enough to be considered insignificant. The origin of the nitrate can be due to artificial fertilizers used to increase soil fertility or by discharges containing elevated nitrogen concentrations (such as wastewater discharges).

Over recent years has increased the potential cumulative effects of the nitrates on groundwater quality, particularly related to groundwater nitrate concentrations.

Nitrate content on AcegasApsAmga pumping wells, within the years, had always quite low concentrations (<15mg/l) over a legal limit of 50 mg/l. Only one well (Well n.16) had in the past, before the exploitation phase, high values of nitrates (max 21 mg/l) but in 2006 when the company started to withdraw waters, the concentration of the ion dramatically dropped reaching and later maintain constant values in the range of 10mg/l. All the other analyzed wells (Well n.2, 11 and 12 – Figure 12) always show values between 5 and 10 mg/l. If we look at the areal distribution of the nitrates (Figure 4), taking into account all the wells analyzed within the framework of the GEP and ASTIS projects, it is interesting to note that there is a polluted area in Slovenia, and more precisely at the border with Italy where the nitrates concentration exceeds the legal Italian limit. When the waters reach the Italian territory, the nitrates concentration, thanks to the diluting capacity of the Isonzo/Soča waters reach low, admissible values.

3.3 Microbiological parameters

Is known that microbiological contamination is present on all water sources and the concentrations varies in association to the hydrological conditions in the watersheds. High values are linked to the occurrence of torrential waters and increased amounts of silt which is entering in the aquifers. Due to turbulent flow of water, the move of the internal sediment occurs and then result with the appearance of turbidity.

Higher concentrations of total number of microorganisms and microorganisms of fecal origin can be observed also on all water sources (at least occasionally). The source of these organisms can be wild animals or livestock which move in the recharge areas, but mostly the main sources are the untreated urban waste waters from settlements. For the considered test site area, in the analyzed AcegasApsAmga pumping wells, all the analyses carried out within the years always showed a complete absence of any kind of microorganisms. This result depends from the long residence times that the groundwaters have within the confined systems of aquifers (Zini et al., 2011; Environment Southland State of the Environment Groundwater Quality Technical Report, 2010).

3.4 Metals

Once a year, AcegasApsAmga analyse the concentration of the heavy metals on the 13 pumping wells. All the recorded values are definitively below the LOQ, so no trends are able to be elaborate.



3.5 Chromium

The average concentration of chromium in rainwater is in the range 0.2–1 μ g/l. Natural chromium concentrations in seawater in the amount of 0.04–0.5 μ g/l have been measured. In the North Sea, a concentration of 0.7 μ g/l was found. The natural total chromium content of surface waters is approximately 0.5–2 μ g/l and the dissolved chromium content 0.02–0.3 μ g/l. Most surface waters contain between 1 and 10 μ g of chromium per liter. In general, the chromium content of surface waters reflects the extent of industrial activity. In surface waters in the USA, levels up to 84 μ g/l have been found; in central Canada, surface water concentrations ranged from 0.2 to 44 μ g/l. In the Rhine, chromium levels are below 10 μ g/l, and in 50% of the natural stream waters in India the concentration is below 2 μ g/l (World Health Organization, 1996; Mattuck et al., 1996).

In general, the chromium concentration in groundwater is low (<1 μ g/litre) against an Italian legal limit of 50 μ g/l. In the study site area, for the period 2006-2014, in the exploited wells, the max reached value was 1.2 μ g/l, in 2006 and 2007 in the Well 1. In all the analyzed wells the trend is anyway decreasing with values less than 0.8 μ g/l (Figure 9).

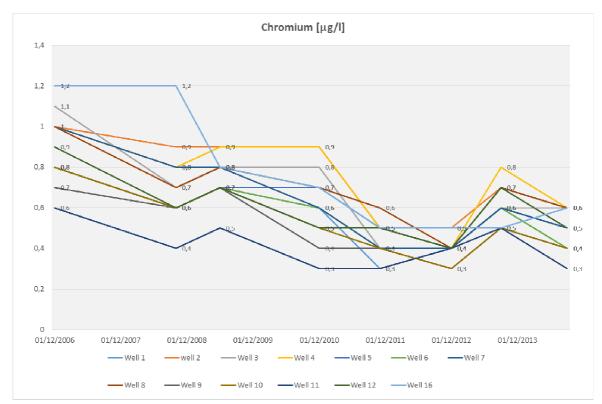


Figure 9: Total chromium values analyzed in the exploited wells, within the period 2006-2014.



3.6 Trends in water quality

Analyzing all the collected data, the only elements that show a variation in their concentrations are chlorides, sulphates, nitrates and tetracloroethylene evaluated in the wells 2, 6, 11, 12, 16 and in the La Risaia well. The data used to realize the trends are part of the archive data of the AcegasApsAmga. They are dated back to 1973 and are collected every year since then.

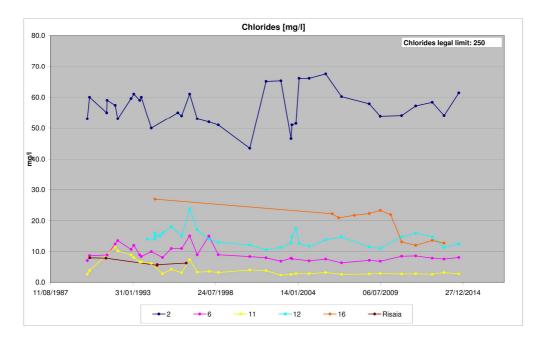


Figure 10: Chloride trend. The general trend is quite constant, slightly decreasing within these last years. Only well no. 2, is showing a higher concentration of chlorides with average values of 60 mg/l.



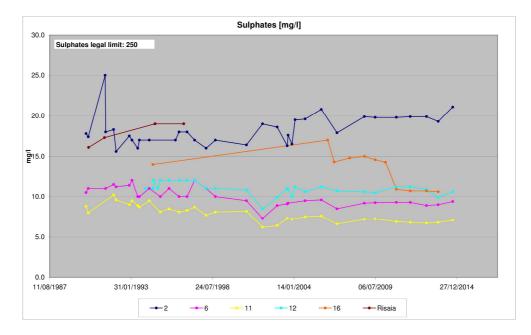


Figure 11: Sulphates trend. The general trend is quite constant, slightly increasing within these last years for the wells 2 and La Risaia. All the values anyway remain definitely below the legal limit being lower by one order of magnitude.

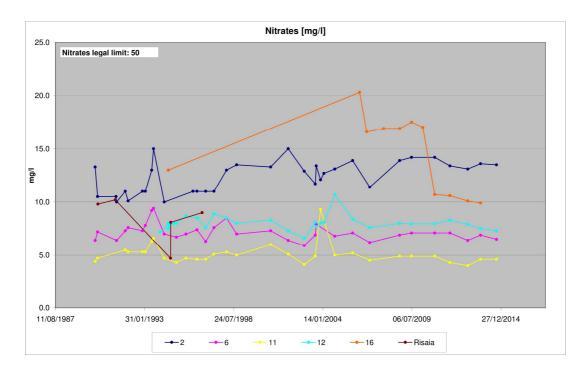


Figure 12: Nitrates trend. The general trend similar to the sulphate ones, quite constant within the years for the wells 6, 11 and 12. The values identified in well 2 and in the La Risaia show instead a slight increase while remaining well below the legal limit (max 20mg/l on a limit of 50 mg/l). Well 16 show a rapid decrease in correspondence of the exploitation started in 2006.



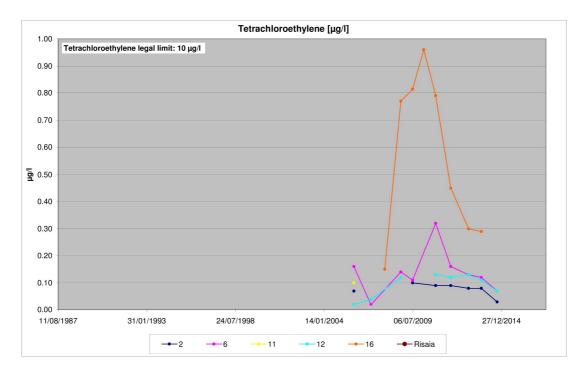


Figure 13: Tetracloroethylene trend. This parameter has been measured only since 2006. It shows a similar behavior in the wells 2 and 12. In the well 6 a peak was measured on 2011. The well 16, belonging to the south line of the aqueduct, showed a huge increase in 2011 but later, during the following years, the values went back on more reasonable numbers. Anyway, all the measured values are well below the legal limit being this last one one order of magnitude higher than the measured values.

4 Salt water intrusion

One of the sources of pollution, in addition to organic matter, pathogens and microbial contaminants, nutrients, acidification (precipitation and runoff), heavy metals, toxic organic compounds and micro-organic pollutants, silt suspended particles, that impact water resources at local scale, is the salinization due to salt water intrusion. The natural balance between freshwater and saltwater in coastal aquifers is disturbed by groundwater withdrawals and other human activities that lower groundwater levels, reduce fresh groundwater flow to coastal waters, and ultimately cause saltwater to intrude coastal aquifers.

The chloride concentration of groundwater samples has been the most commonly used indicator of saltwater occurrence and intrusion in coastal aquifers (Reilly and Goodman, 1985; Bear et al., 1999). In the study site area, the wells close to the coast areas were analyzed to face this problem. Chlorides were taken into account and the results are visible on Figure 9.





Figure 14: Chloride concentration evaluated for the surface and groundwaters. The red line represents the maximum ingression of the salt wedge measured in correspondence of the surface waters (rivers and channels).



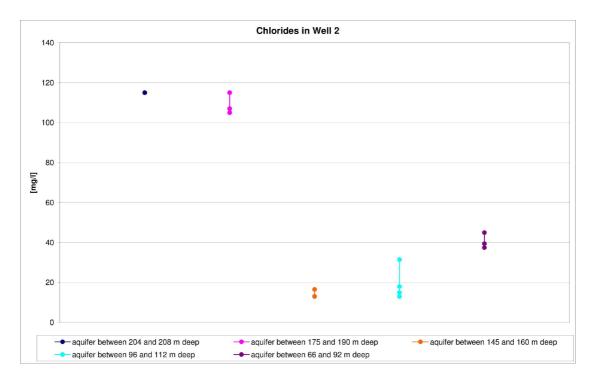


Figure 15: Well 2, chlorides concentration measured while drilling. Values correspond to the different exploited aquifers.

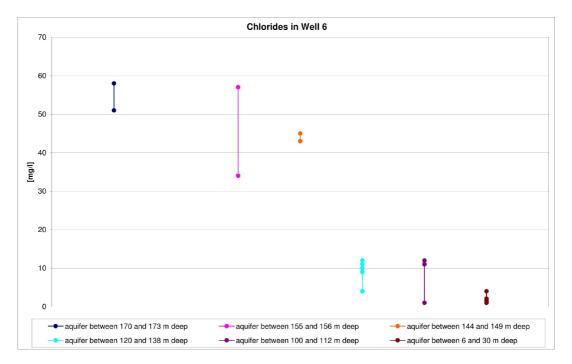


Figure 16: Well 6, chlorides concentration measured while drilling. Values correspond to the different exploited aquifers.



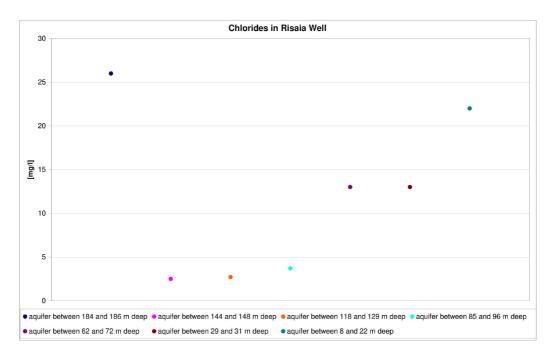


Figure 17: La Risaia well, chlorides concentration measured while drilling. Values correspond to the different exploited aquifers.

To understand if in the study area there can be the evidence to face with salt water intrusion problems, were taken into account the data coming from the deepest wells and the ones were chemical analyses for each single different aquifer were available.

Analyzing singly the different exploited wells, emerges that in the Well 2 the higher chloride concentrations are identified at depths higher than 170m with values greater than 100 mg/l. The other aquifer among 60 and 170m presents values ranging between 10 and 50 mg/l.

In the Well 6, have been measured values ranging between 30 and 60 mg/l at depth of 140-180m. The shallower part (6 - 140m) presents instead always lower values of about 15mg/l.

The La Risaia well, located in the area where the salt wedge is present (Figure 17), has "high" chloride values of 20-30 mg/l in the shallower (8 - 22 m) and in the deeper (184 - 186 m) exploited aquifer. All the other aquifers present values lower than 15 mg/l.

The three wells reach approximately the same depths and the same aquifers, so the data are comparable. They indicated that in the area is clear that the southern well has definitively lower chloride values than the northern ones (2 and 6). The higher recorded values were found within the limestones at depths exceeding the 200m. Is known (Petrini et al., 2013) that a fossil marine aquifer is present in the depths in the carbonates. This aquifer supplies the Monfalcone thermal springs and has been exploited also at Grado (Grado-1 well) beneath 700m (Cimolino et al., 2010). Therefore the high chloride values identified in the northern well (2 and 6) can be linked to this resource and not to the salt water intrusion. This contamination interests only the deeper aquifers and not the shallower ones (Figures 8 and 10).



5 Impact of existing Land Uses on water quantity and quality according to water quality data

The spatial analysis and the proposals for a different environment management of the study area (Isonzo/Soča Plain) required the application of GIS techniques integrated to assessment systems for the estimation of environmental pressure and to decision support systems. The tool used is the ArcGIS 10.2 software. Within the framework of GEP INTERREG project (A.A.V.V., 2014), a specific study started for a part of the actual study area and a specific methodology was used in order to assign to the different soil categories a different score resulting from human activities that may produce potential impact on the quality of the aquifer.

The groundwater pollution, in space and time, is connected in almost all cases, directly or indirectly to human activity. The pollution sources are in fact associated with a wide range of industrial, agricultural, commercial and domestic activities. Land use activities having the potential to impact on groundwater quality are described as either point or non-point source discharges (Figure 18 and 19).

Point source discharges can be defined as discharges from specific and identifiable sources (such as pipes or drains) concentrated at a given point, whereas non-point source discharges can be described as water contamination derived from diffuse sources where there is no single identifiable discharge point. Point source discharges can include tanks, offal holes, silage pits, landfills, leaking effluent ponds, underground storage tanks and wastewater application systems.

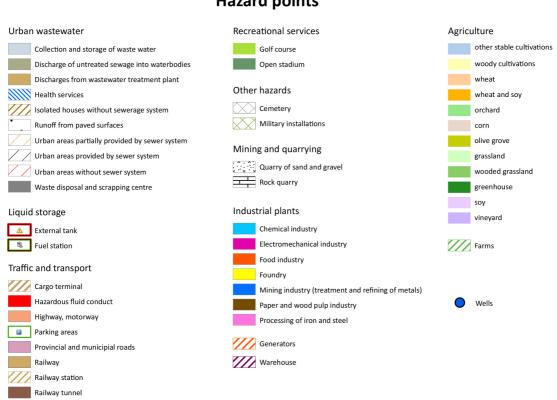
Non-point source discharges relate to the infiltration of water over a widespread area are often associated with agricultural or horticultural land use. Contaminants applied to land, including animal wastes and fertilizers, can leach through the soil profile to groundwater. The potential magnitude of non-point source discharges can also be exacerbated by land management practices such as the timing of soil cultivation. The effects of point source discharges on groundwater quality are typically localized but may be of significant magnitude and can involve a range of potential contaminants depending on the nature of the specific discharge.

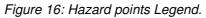
For the project, within the test site area, was carried out the continuation of the analysis done for the GEP project. Were therefore collected and digitized point and non-point discharge areas. In particular: civil waste waters, urban solid waste, liquid storage, traffic and transportation, recreational services, mining operational and abandoned, industrial plants, electric power generators, industrial warehouses, animal husbandry, agriculture and other generic hazards.

The mapping provides an updated overview of the hazard points assessing the hazard of each hazard point in order to evaluate its compatibility with the protection of the groundwater resources.

Among the available different methods relative weight assignment scoring systems were used. These methods offer a quick preview of the scenario that can be caused by a pollution point source (Trevisan et al., 1998; Civita & Zavatti, 2006).







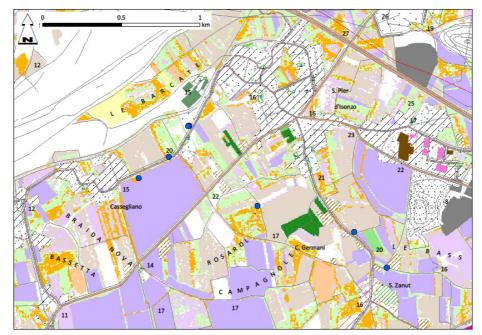


Figure 17: Sketch of the hazard points digitized in the study area. The map focused on the AcegasApsAmga pumping wells of the northern line (blue dots). Vineyards and corns are the more prevalent cultures in the area.



Hazard points

6 Future water safety regarding changing land uses

The dominant climate drivers for water availability are precipitation, temperature and evapotranspiration caused by net radiation at the ground, atmospheric humidity and wind speed, and temperature. Projected changes in these components of the water balance are described in the previous report on Climate Change in the pilot area. In short, more intense rainfall events will lead to an increase in suspended solids (turbidity) in rivers, lakes and reservoirs due to soil fluvial erosion (Leemans and Kleidon, 2002) and pollutants will be introduced (Booth and Zeller, 2005; Fleury et al., 2005; Nicholls, 1999; Committee on the Environment and Natural Resources National Science and Technology Council (2008). The projected increase in precipitation intensity is expected to lead to a deterioration of water quality, as it results in the enhanced transport of pathogens and other dissolved pollutants (e.g., pesticides) to surface waters and groundwater and in increased erosion, which in turn leads to the mobilization of adsorbed pollutants such as phosphorus and heavy metals. In addition, more frequent heavy rainfall events will overload the capacity of sewer systems and water and wastewater treatment plants more often. An increased occurrence of low flows will lead to decreased contaminant dilution capacity, and thus higher pollutant concentrations. In particular, in the study area, the occurrence of this scenario will take a while to verify due to the huge amount of available water (Zini et al. 2011), even if the path we are on is the one just described. In the Isonzo/Soča Plain area, the analyzed chemical trends remain always well below the legal limits with not worrying fluctuations. What is worrying instead, is the increased precipitation variability that may decrease the groundwater recharge due to the decreased effective infiltration capacity of the soil being exceeded more often. Anyway, the hydrologic changes associated with climate change cited thus far will all impact freshwater availability from both groundwater and surface water sources even in an area like the study site where freshwaters are abundant. Shifts in stream height will affect aguifer levels more significantly than changes in temperature and precipitation levels seeing a decreased groundwater aquifer recharge. Shallow, unconfined aquifer levels will be impacted most drastically. These aquifers tend to have good quality water for drinking. This is a general consideration, but in the study area, due to the presence of an international agreement that guarantee the minimum amount of water (Siché and Arnaud-Fassetta, 2014) the global amount is nearly constant. What will change will be the effective infiltration on the Italian territory that will be added as recharge contribution.

7 Measures to improve the quality of drinking water

Fresh water is essential for human life and in general, it is an essential input to human production and to the economic development. Unfortunately, in many countries around the world, some drinking water supplies become polluted and the deteriorated quality is becoming a grave issue. Water pollution is not only a serious environmental issue but also an economic and human health problem. So this requires a monitoring adaptation based on **community-based monitoring programs.** This will play a central role in keeping communities abreast of the state of their waters. Information gathered from monitoring water (this could include water quality parameters, water levels) can be used in source water protection plans and water management decision-making



at local, regional and national levels. Community-based water monitoring programs have the potential to provide essential localized information to support community decision-making and community participation in regional watershed governance partnerships. They will often require initial training and capacity support to ensure quality control, maintain complete community data collections, and a usable database up-to-date.

Water quality monitoring data collected regularly throughout the year, over a number of years will contribute to reveal seasonal water quality fluctuations and trends over time. This pays an important role in the development of more effective contextual community water treatment regimes and source water protection plans. Monitoring water quality and quantity parameters over the long-term will make communities more conscious on the ongoing changes. Such information provides powerful leverage to support decision-making in favor of water stewardship.

Community outreach and education will be required to support watershed stewardship initiatives and to raise overall awareness not only of climate change impacts but also on land use changes impact so that community members clearly understand the importance of water conservation in the broader attempt to nourish watershed health.

Surface water, groundwater and precipitations of the Isonzo plain were monitored thanks to a monitoring network realized in collaboration with the Italian and Slovenian partners in the framework of GEP and ASTIS projects, according to the different realities existing over the territories. The aim of this monitoring network has been the one to monitor the surface and groundwaters from a quantitative and qualitative point of view. This means that were analyzed the water levels within the water level devices and qualitative through geochemical and isotopical analysis. In Italy were used and joined the network of the Servizio Idrografico Regionale, the one of the ARPA FVG and some other points. In Slovenia were used some points of the Slovenian Geological Survey and some made available by ARSO. An important issue is the **monitoring network maintenance** in order to verify, in the foreseen years, the changes in quantity and quality of the exploited waters.



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Water quality and trends

Water quality analysis and trends on ATO 3 Test Area, Italy

Lead Author/s	Daniele Nardi
Lead Authors Coordinator	
Contributor/s	Simona Mercuri
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1 Introduction

This report concerns water quality data and trends referred to ATO 3 Test Area, Marche Region, Italy, within DRINKADRIA project. Water quality data are based on reports issued by Marche Region Environmental Protection Agency and on analysis and information obtained from Water Utilities, collected in the last 10-15 years.

The observations refer to the most important water resources used in water supply systems of ATO 3 Area and to those additional natural resources which can be included in such supply systems in cases of need.

Water sources represent the starting point of any water supply system. Their quality, relating monitoring activities and protection measures largely influences the character of the entire water supply system, especially in case of water intended for human consumption, also determining operational costs and investment, maintenance needs and development of the system. In addition, observation of quality of water sources enables detecting and preventing problems concerning water quality, which can occur within the water supply system.

Water sources must comply with a large number of limits and constraints, including sanitary and hygienic conditions, economic, social, cultural and technological conditions, all of which finally referring to two basic indicators: quality and quantity of water.

Quality standards for public drinking water supply in Italy are defined by Legislative Decree no. 31 of 2 February 2001, concerning the implementation of EU Drinking Water Directive 98/83/EC on the quality of water intended for human consumption.

Local Health Unit is responsible for sampling water from the water supply and distribution systems, while Environmental Protection Agency (regional) carries out chemical and bacteriological analysis.

In the specific case of ATO 3 Test Area, Environmental Protection Agency of Marche Region (ARPAM, Agenzia Regionale per la Protezione Ambientale delle Marche) is responsible for collecting information of interest to the public, concerning water quality and water bodies classification, made available through press, television and modern information technologies.



2 Test Area and water quality parameters

ATO 3 Test Area is characterized by a very complex hydrogeological background, with the most important aquifers located in the mountain area and in the valleys, with water mostly belonging to "calcium bicarbonate" family.

Chemical contamination is mainly due to the presence of nitrates, whose distribution is primarily connected to the intensive agriculture practices; just in rare cases other parameters exceed the concentration limits and doesn't match law requirements, mostly because of chemicals (magnesium sulfate, iron, ...) having a natural origin.

Spring water, mostly available in the mountain area, is characterized by electric conductivity values between 200 and 400 μ S/cm at 20 °C and hardness between 10 and 20 French degrees. Chemical contamination can be considered actually non-existent, with Nitrate concentration below 5 mg/l NO₃, which would make this water suitable to be bottled. Bacteriological contamination, on the other hand, is frequent in the small water sources that are in many cases obsolete and not well maintained.

In the central, medium-low hill area, most of the water supplied for drinking purposes comes from springs or drainage systems, and it is characterized by electric conductivity values between 400 and 800 μ S/cm at 20 °C and hardness between 20 and 40 French degrees. Nitrates concentration is comprised between 5 and 40 mg/l NO₃ and chemical contamination is mostly referable to and caused by greater agricultural activity, sometimes even resulting in exceeding the limit of 50 mg/l NO₃ required for drinking water. Bacteriological situation is similar to that of mountain springs.

In the valley areas water intended for human consumption is drawn from wells dug into the alluvial mattress of major rivers, with groundwater that have electric conductivity values between 800 and 1300 μ S/cm at 20 °C. Nitrates concentration often exceeds the limit of 50 mg/l NO₃ and in areas characterized by high human activity and intense agricultural activity, it can be greater than 100 mg/l. Bacteriological contamination is much less frequent.

Water drawn from wells dug in the alluvial mattress in the coastal area shows chemical characteristics similar to the one abstracted in the valleys. In some cases, intense exploitation of wells located next to the sea and their overuse has produced saline ingression phenomena. High Nitrate concentrations and bacterial contamination are less frequent, but a progressive deterioration of groundwater quality has been registered since

1980's because of contamination caused by industrial activity (Tetrachloroethylene, Trichloroethane).

The progressive deterioration of groundwater quality and increased drinking water demand have led, since the early 1980's, to abandon the poorest sources of supply, to be replaced by the use of treated surface water or, whenever possible, by new mountain water resources.

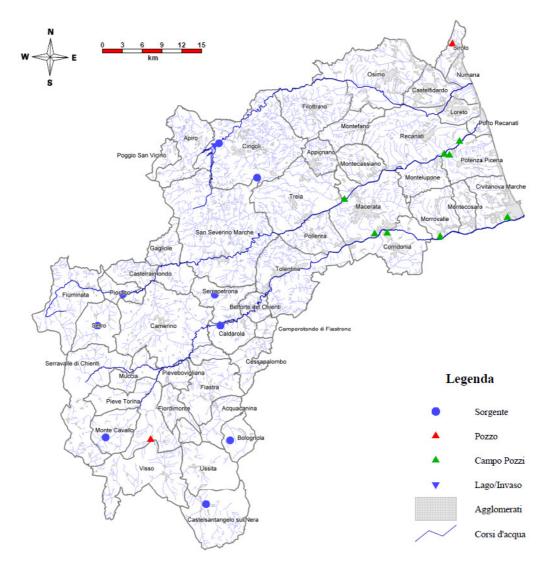


Figure 1: the most important Water Resources in use in ATO 3

Cases of "non-compliance" with law requirements at the point of compliance (users' taps) currently involve less than 5% of the population and are mostly due to temporary



drawbacks in treatment or disinfection plants and distribution network or can be connected with natural causes. Prolonged and heavy precipitation or long periods of drought producing variations of springs natural flow or changes in water quality and quantity (flow rates) affecting treatment and disinfection plants effectiveness, may result in temporary supply of water not complying with law requirements thus forcing competent Authorities to inform the population with "not drinking water" warnings.

Cases of non-compliance with bacteriological requirements and limits are very rare in the largest water supply systems, while they are common in the small distribution networks of mountain areas.

The minimum frequency of sampling and analysis for water intended for human consumption supplied from a distribution network is set by the Legislative Decree no. 31/2001, depending on the volume of water supplied by a distribution network: ARPAM Provincial Department of Macerata examine around 7.000 samples of water each year in ATO 3 Area, some of which taken at the production sites and the rest in specific sampling points representing the distribution network situation and the quality of water supplied to final users.

To be highlighted that, despite groundwater can be affected by nitrates contamination, water supplied to final users, thanks to mixture with higher quality water in order to ensure perfect compliance with law requirements, is suitable for drinking purposes.

In ATO 3 Test Area, as in many other Italian regions, groundwater represents the major source of "water intended for human consumption". Deep groundwater resources, well protected by natural filters, can guarantee wholesome and good quality water and a safe supply. Safeguard measure are anyhow very important as the extensive and, often, unplanned land use could represent a serious danger. Pollution by organohalogen compounds (Trichloroethane and, later, tetrachloroethylene, used as solvents in the industrial cycle of footwear production - polyurethane soles - by local factories) in the lower Chienti River Valley aquifer, affecting Montecosaro and Civitanova Marche drinking water supply, since 1992, is a clear example of that.

Another problem, also connected with human pressure on natural resources, are the eutrophic phenomena, with the presence of toxic *Planktothrix rubescens* cells in Castreccioni lake, an artificial reservoir used for drinking water production, detected starting from January 2011, with increasing concentration of algae in the lake water, up to 4 Million cells per liter.



The recovery of such situations involves the use of significant economic, human and technological resources, sometimes implying negative environmental side effects.

The following quality parameters are generally taken into account, according to the Legislative Decree no. 31/2001 set:

- Organoleptic properties of water (color, smell, taste);
- Microbiological parameters: Coliform bacteria, Escherichia Coli, Enterococci, colony count at 22 °C and 37 °C;
- Physical and chemical parameters: temperature, pH, alkalinity, total hardness, electric conductivity, dry residue at 180 °C, turbidity;
- lons: fluoride, chloride, sulfate, sodium, potassium, calcium, magnesium, dissolved silica, total cyanides;
- Nutrients: nitrogen compounds (ammonia, nitrites, nitrates) and phosphorus compounds (total phosphorus);
- Organic matter: total organic carbon (TOC), pesticides/herbicides, polycyclic aromatic hydrocarbons (PAH), ;
- Heavy metals: arsenic, aluminum cadmium, copper, zinc, iron, manganese, total chromium, lead, mercury, nickel, etc.;

3 Test results and trends

3.1 Physical and chemical composition

In ATO 3 Test Area cases of non-compliance with parametric values set by Legislative Decree no. 31/2001 are almost not existing, in relation to chemical properties. Mean values detected for the most commonly used physical and chemical parameters are shown in the following charts.



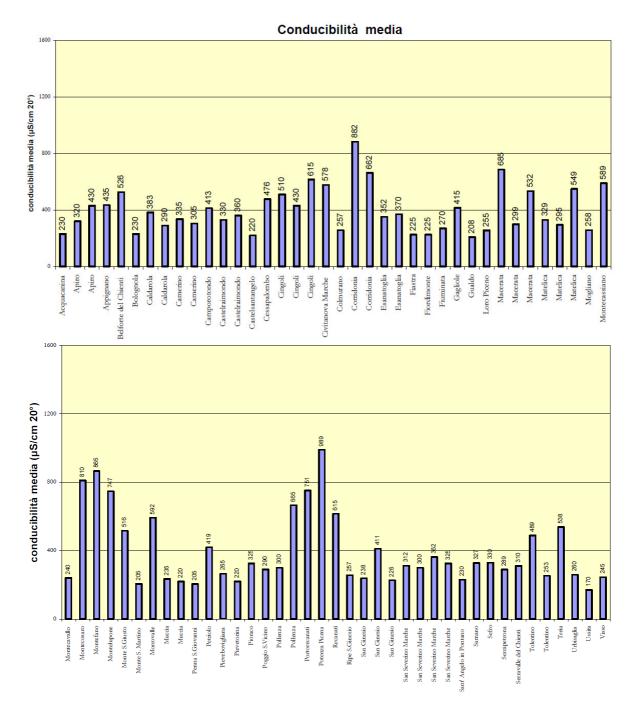
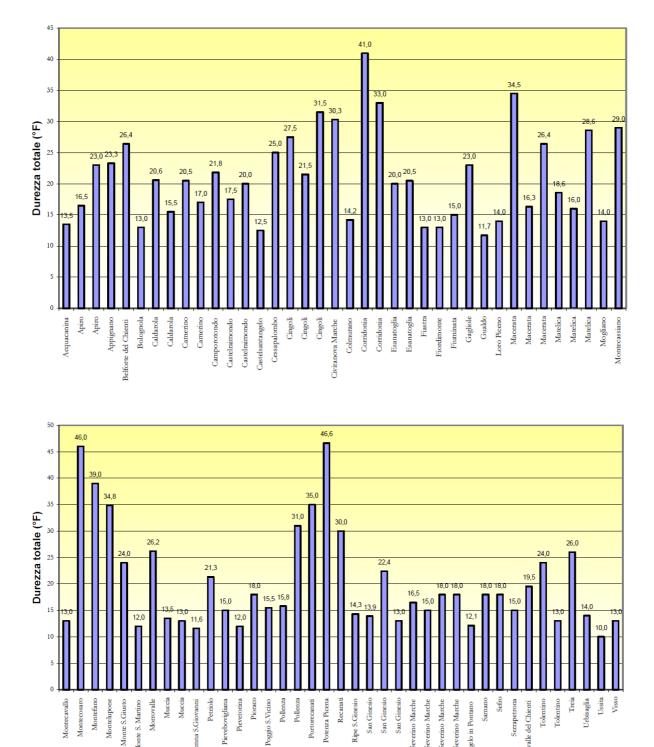


Figure 2: electric conductivity mean values for different WSS.



Durezza media



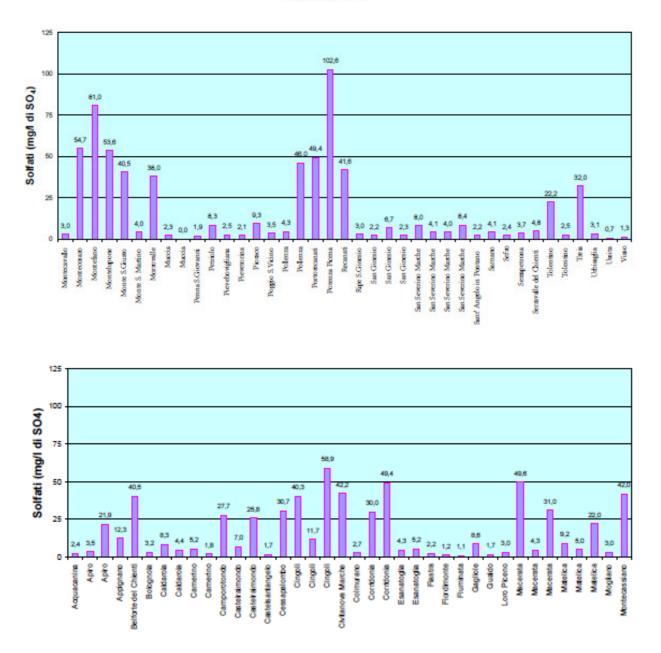
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Figure 3: total hardness mean values for different WSS.



3.2 lons

Among the lons taken into consideration to assess the quality of the water distributed for drinking purposes, the most relevant are sulfate ions and chloride. The concentrations of these ions remain relatively low compared to legal limits except for some rare cases as evidenced in the following charts.



Solfati media

Figure 4: Sulfate concentration mean values for different WSS.



Cloruri media

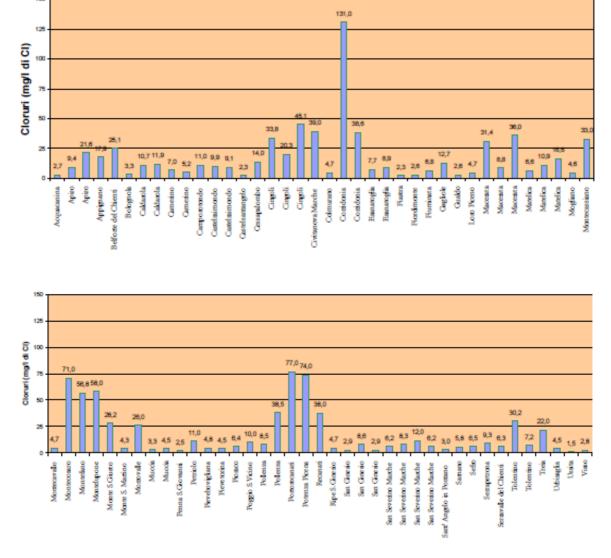


Figure 5: Chloride concentration mean values for different WSS.



3.3 Nutrients

Nutrients are compounds of nitrogen and phosphorus. For all water sources in use in ATO 3 Test Area phosphates and total phosphorus are very low.

The most important Well fields are located in proximity of watercourses and the wells in use are those abstracting groundwater with the lowest concentration of Nitrates and electric conductivity values. Where higher Nitrate concentrations are detected Utilities are equipped with reverse osmosis treatment plants.

Mean values detected for Nitrogen (as NO₃) are shown in the following charts.



Nitrati media

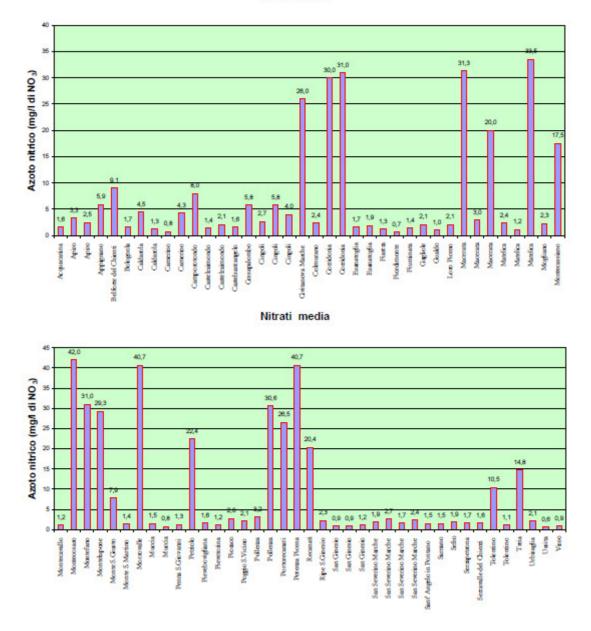


Fig. 6: Nitrates concentration mean values for different WSS.

3.4 Microbiological parameters

Most of the cases of non-compliance to the parametric values set by Legislative Decree no. 31/2001 is connected to Microbiological contamination, present on many of the water sources in use in the mountain area. The contamination of water supplied by the



distribution network may derive directly from the source contamination, if this is poorly protected and superficial, the facilities are obsolete, and they lack adequate buffer zones, or from the network itself, when the pipes are too old and when lacking adequate maintenance of tanks. The determining factor of the non-compliance is generally due to the presence of bacteria, related to poor maintenance of pipelines, not yet existing Drinking Water Protected Areas (DWPAs) and disinfection treatment carried out just occasionally.

3.5 Metals

Just few cases of non-compliance to parametric values have been detected in the last 10 years, due to the high concentration of Iron - phenomenon linked the too old pipes still in use - and to the high concentration of Aluminium, used as coagulant factor in one of the treatment plant dedicated to the potabilization of surface water.

3.6 Organic compounds

In the spring waters are not detected measurable concentrations of organic compounds (generally hydrocarbons of mineral origin, volatile hydrocarbons, polyaromatic hydrocarbons, organochlorine pesticides, some organophosphorus pesticides) and other tested chemicals as phenols, cyanides, anionic and nonionic surfactants.

In very rare cases Trihalomethanes and Pesticides have been detected in groundwater abstracted by wells in the ATO 3 Area valleys.



4 Water quality evaluation

Water quality evalution is conducted according to Legislative Decree no. 31/2001 specification by Local Health Units, supported by regional Environmental Protection Agency (laboratory activity).

According to the check monitoring activity carried out by competent Authorities, the cases of non-compliance to the parametric values set by Legislative Decree no. 31/2001 are very few, as shown in the following chart.

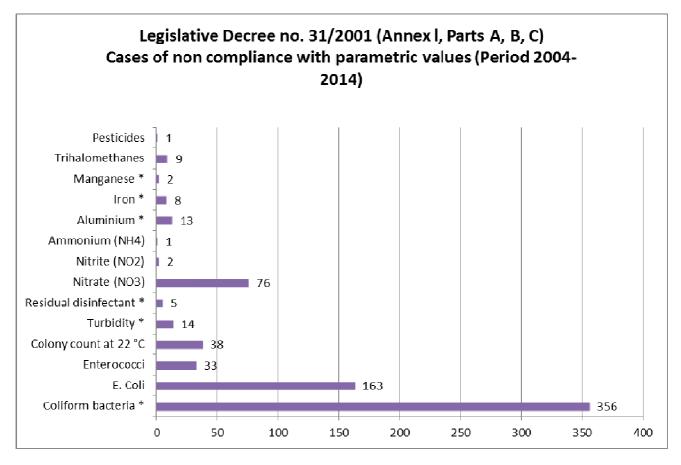


Figure 7: Cases of non-compliance with parametric values (Period 2004-2014)

Particularly referring to Nitrate concentration, specific trends can be detected with regard to the riverbed aquifers where the most important well fields in use are located. The following charts refer to Potenza and Chienti valley well fields (Data provided by the involved Utilities: ASTEA Spa and APM Spa).





Figure 8: Nitrates concentration (2001-2014) and trends in Potenza riverbed aquifer (ASTEA Spa well fields)

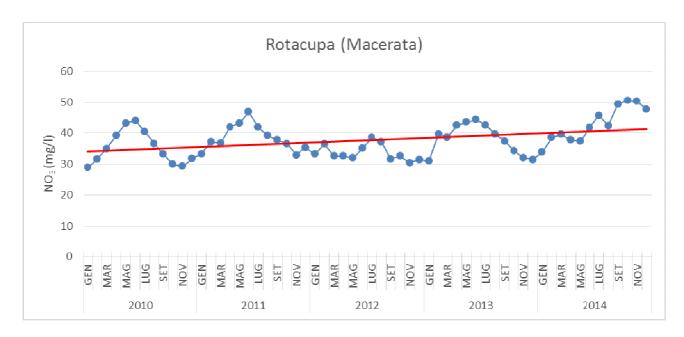
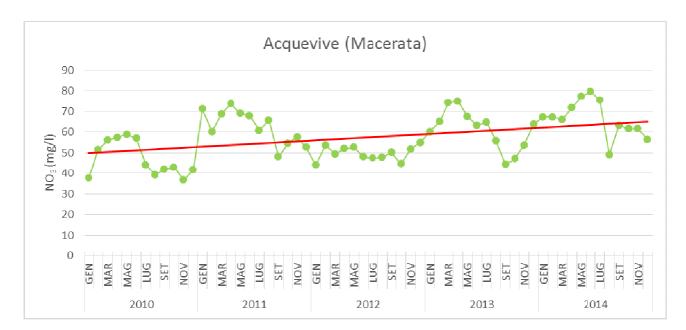


Figure 9: Nitrates concentration (2010-2014) and trends in Potenza riverbed aquifer (APM Spa well field)





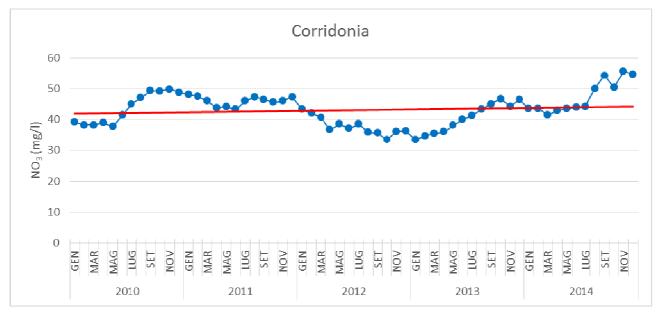
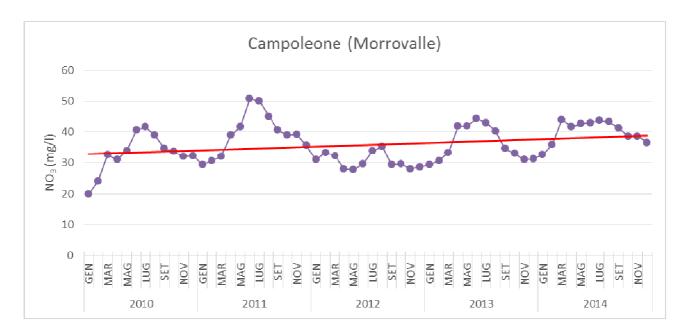


Figure 10.a: Nitrates concentration (2010-2014) and trends in Chienti riverbed aquifer (APM Spa well fields)





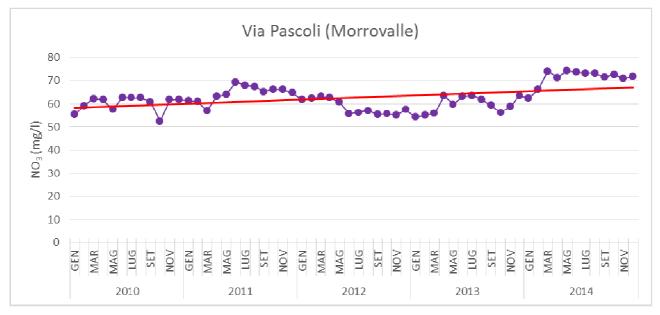


Figure 10.b: Nitrates concentration (2010-2014) and trends in Chienti riverbed aquifer (APM Spa well fields)



5 Conclusions

ATO 3 Test Area can be divided into two zones, a mountain area and a foothill area, including medium-high hilly and flat-coastal zones.

The mountain area is very rich in terms of aquifers, potentially providing large volumes of good quality water. The numerous sources in use for drinking water production have a chemical composition characterized by a low salt content (0,1 - 0,3 g/l); consequently, these waters have low values of specific electric conductivity, hardness, chlorides, nitrates and sulfates. Available data indicate that the waters of the mountain area are generally safe. The risk of chemical pollution is particularly low, as these water resources are located in an area characterized by just few small human settlement, with scarce presence of industrial activities and limited agricultural activities.

Moving from the mountain area to the valleys (medium-high hilly area and flat-coastal zone), a progressive worsening of water quality features can be detected: electric conductivity is between 600 and 1400 μ S / cm, dry residue is generally between 0,3 and 0,8 g/l, with an increase of the hardness, reaching values higher than those recommended (maximum recommended value: 50 French degrees). These features are a result of the slow underground movement and of the lithological nature of soils (presence of sand with gravel, mainly limestone elements). The significant increase in the concentration of the nitrates, which may exceed the maximum admissible concentration of 50 mg/l for water intended for human consumption, is a result of the use and abuse of fertilizers in agriculture. A relevant number of wells are used for irrigation, for industrial water supply and for drinking water supply to the largest urban centers and private country houses in this area, so determining a significant pressure on the natural resource.



6 References

[1] White paper on potable water (Macerata Province), 2003 – Environmental Protection Agency of Marche Region (<u>www.arpa.arche.it</u>).





Water quality and trends – Macerata 30.04.2015





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WP4.3. Report:

Present and future water safety and risk for drinking supply at Ostuni test area (Apulia, Italy)

FB3 CNR-IRSA

Bari, April 2015

Lead Author/s	Costantino Masciopinto	
Lead Authors Coordinator	Costantino Masciopinto	
Contributor/s	S. Liso and F. Visino	
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1. INTRODUCTION

The Apulia region with more than 4 million inhabitants has been exposed to a sequence of prolonged droughts in the past decades, which caused a general decrease in water supply and an increase of demand for irrigation. Moreover, in the past decade the region has been recognized as being among those at the highest risk of desertification in Europe, due to the observed climatic trends and intensified agricultural practices.

The Pilot Area is 1991 km², with a maximum length of 53 km, maximum width of 50 km. The area covers 24 municipalities of the Apulia region, which are in 3 provinces: Brindisi, Taranto and Lecce.

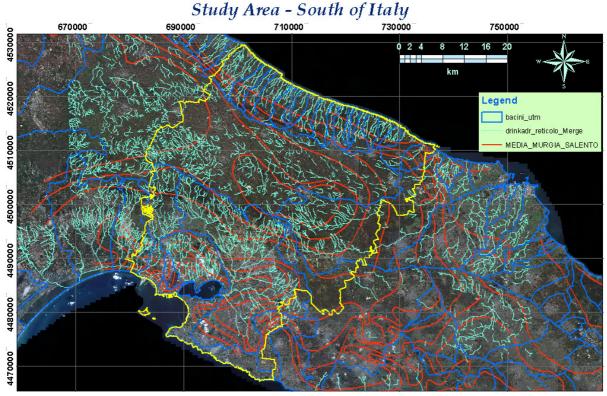


Figure 4.3.1. Ostuni pilot area and stream basins of the Salento peninsula (Apulia region, Southern Italy).

The climate is markedly Mediterranean, with mild wet winters and hot dry summers (the coldest month is January and the warmest is July). Climate variables and rainfall in particular, exhibit a marked inter-annual variability which makes water availability a permanent threat to the economic development and ecosystem conservation of the region. In addition, rainfall has also experienced a declining trend, on average, over the past four decades.



Due to the dominant carbonate nature of rocks (high substrate permeability and infiltration of rainwater), the region has almost no rivers, except in its northern part, where the presence of alluvial materials is favorable to shallow groundwater and permanent (or seasonal) rivers. Instead, in the karst area some basins related to a fossil hydrographical network, present a superficial flow only during intense events. The region is mainly dominated by agriculture that is a vital economic resource for the region, with more than 70% of the total area occupied by cropped land.

1.1. Actual drinking water deficit

The water balance of drinking water resources has been estimated on the basis of the specific standards for water requirement of different types of drinking consumers (see Table 3).

Total polulation (P) of munipality	Drinking wate	Drinking water STANDARD (L/inhab/d					
	PRGA (1967)	PS14 (1981)	Update PRGA (1998)				
Single huose	80	150	170				
P < 5,000	120	150÷170	170				
5,000 < P < 10,000	150	160÷235	170				
10,000 < P < 50,000	200	170÷340	250				
50,000 < P < 100,000	250	270÷340	300				
100,000 < P	300	340	340				
Province	350	375÷445	375				
Principal town (Bari)	350	480	420				
Tourists in hotels	100	350÷500	500				
Tourists not in hotels	100	100	200				
Workers in industries		150	100				
Extra (nonresident) daily population	100	150	100				

Table 4.3.1.	Comparison	of	water	requirement	standards	proposed	by	different
Master Plans	in Italy.							



The total water requirement is then defined when the future trend of population, industry and tourists. The difference between the water demand and the actual water resource availability defines the water deficit in drinking water. The actual estimated value of the deficit of the region is 53 Mm³, including water losses of 15%, which will be covered by including new artificial lakes.

The drinking water supply information at the 24 municipalities of the Ostuni pilot area has been reported in the following table 4.3.2.



COMUNE	PROV	nod e	Flow rate supplie d L/s	Population 01/01/2013 (ISTAT)	Non Residen t	Tourists in hotel	Tourist not in hotel	Workers in industri es	Actual drinking demand	Actual deficit	Demand (L/s) for Tourist
SAN MICHELE SALENTINO	BR	131	16.3	6359	138	0	1096	492	23	7	2
FRANCAVILLA FONTANA	BR	134	137.7	36908	2372	42	11056	2126	199	61	14
CAROSINO	TA	354	14.0	6963	135	0	138	193	24	10	1
ROCCAFORZATA	TA	6111	5.3	1797	24	18	123	88	6	1	0
MONTEPARANO	TA	6111	5.3	2410	25	0	83	145	8	3	0
PULSANO	TA	6111	61.3	11221	468	405	15975	460	69	7	12
FASANO	BR	128	183.3	39431	2578	1603	29270	2736	227	44	30
OSTUNI	BR	130	178.6	31709	2068	2148	40259	4365	197	19	39
LOCOROTONDO	BA	129	50.2	14258	581	44	5120	2057	78	28	7
CISTERNINO	BR	129	44.9	11678	499	124	4078	936	63	18	5
MARTINA FRANCA	TA	129	205.5	48958	2970	350	33280	3874	277	72	32
CAROVIGNO	BR	130	66.0	16187	670	98	13844	1183	93	27	12
SAN VITO DEI NORMANNI	BR	131	77.6	19494	1349	121	5358	1322	105	28	8
CEGLIE MESSAPICO	BR	131	81.1	20089	1343	22	8285	1254	110	29	10
LATIANO	BR	358	57.2	14919	17504	0	700	3031	113	56	39
CRISPIANO	ТА	347- 348	45.5	13646	585	0	861	831	71	25	3
VILLA CASTELLI	BR	132	21.0	8965	181	0	1594	384	32	11	2
GROTTAGLIE	TA	133	116.7	32544	2062	14	1162	1547	169	52	7
MONTEMESOLA	TA	350	8.8	4037	50	0	111	235	14	5	0
TARANTO	TA	349	1093.8	198728	22178	2269	0	44301	1763	669	96
MONTEIASI	TA	352	12.3	5530	123	0	65	129	19	7	0
SAN GIORGIO JONICO	TA	6111	51.9	15480	681	32	181	880	80	28	2
FAGGIANO	TA	6111	8.8	3558	42	0	84	114	12	4	0
LEPORANO	TA	6111	27.4	7873	141	210	12899	704	37	9	10
TOTAL			2570.5	572742	58767	7500	185622	73387	3789	121	9 330

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The estimation of the drinking water demand was based on the drinking water standards (Table 4) by considering the seasonality of 60 days for tourists and a worker presence of 200 days per year. Thus we have

Average water demand = \sum (Water standard x Population x seasonality/365)/86400 x Water losses coefficient (=1.15)

and

Maximum (or actual) water demand = Average water demand x Coefficient of water demand fluctuation (=1.5)

Table 4.3.2. Water requirement for tourists (330 L/s), which is approximately 9% of the total drinking requirement. This means that 9% of the actual drinking water, i.e. 224 L/s is provided from actual water resources, whereas the actual deficit for tourists is about 106 L/s. A fraction of this flow rate, i.e. 76 L/s may be provided by groundwater, along the Ostuni coast. The remaining deficit of 30 L/s may be easily supplied by replenishments and successive pumping from the Ionian coastal groundwater, by using effluent of nearby municipal wastewater plants of (Taranto, Monteiasi, San Giorgio Ionico, Faggiano, Leporano, Carosino, Roccaforzata, Pulsano and Monteparano) after appropriate water treatments).

1.2. Recovery of water losses

The recovery of water by reducing losses from pipelines should be considered a very priority from drinking water communalities. Technology can assist (see for instance georadars) operators in the ducting break and pipe failures or leakages from joints. An experimental study carried out from Apulia communality [1] for water supply on a sample of 25 municipalities of region has shown a percentage of water losses ranging from 10%-15% in large city to 30-35% in small towns. This because there are important water losses that are probably localized on the main pipelines that supply the distribution network. These produce the majority of water leakage and, subsequently the water loss volume is reduced in percentage, when the total volume provided for supply is higher. The mean water losses of the Apulian municipalities were estimated to be 16.08% of the total volume supplied.



2. Analysis of actual land use on test area

Actual land use on test area (Ostuni, Southern Italy) has been depicted in the following Figure 4.3.2.

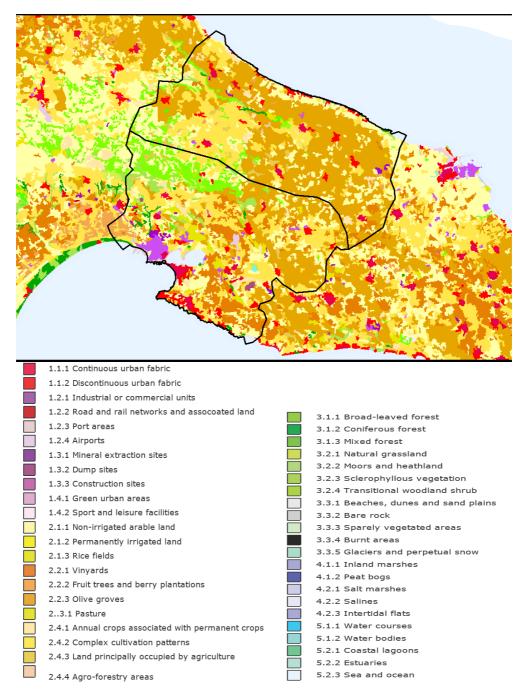


Figure 4.3.2. Actual land use at the Ostuni test area (Southern Italy), (Corinne, 2012; http://www.eea.europa.eu/data-and-maps/indicators/ecosystem-coverage-1/assessment-1).



Irrigation areas are supplied by ARNEO communality and by private wells.

The ARNEO communality area takes in municipalities in the provinces of Lecce, Brindisi and Taranto and covers 249 thousand hectares. Within the area as a whole it is possible to identify – on the basis of the crops grown there – three distinct homogeneous zones:

- A northern, Adriatic coastal zone, which takes in the north-western part of the communality area and some municipalities in the Province of Brindisi, where about 40% of usable land is given over to seed crops;
- A central zone, which comprises the middle part of the communality area straddling the three provinces, where about three quarters of the cultivable land is devoted to growing olives and vines;
- A southern, Ionian coastal zone, which includes the municipalities of Lecce that overlook the Ionian Sea (Porto Cesario, Nardò, Galatone, Sannicola), where 50% of crops are arboreal (olives and vines) and herbaceous.

The table below shows the figures for the irrigated areas within the communality's ambit.

Facility management	Area		bed area na)	Irrigated area (ha)		
	(ha)	Total	In operation	Total	Irrigated/ in operation (%)	
Managed by the Communality		15.3	3.7	553	15	
Managed by the Region		4.4	4.4	574	17	
TOTAL	249.4	18.7	7.1	1,127	16	

Table 4.3.3. Irrigated areas surfaces by ARNEO communality



The main source of water withdrawal is the groundwater, which is derived from wells.

Table 4.3.2 shows the amount of water taken from the sources and the type of use made of it.

	Overall	Withdrawal volumes (Mm ³)				
Type of water supply	available volume at the source (Mm ³)	Total	Drinking water	Irrigation		
Spring waters	0.3	0.1		0.1		
Apani spring	0.3	0.1		0.1		
Surface waters	704	50	50			
Pertusillo dam	250	25	25			
Monte Cotugno dam	450	25	25			
Cillarese dam	4					
Groundwater	27.5	23.3	21	2.2		
Communality wells	4	0.9		0.9		
Puglia Region wells	2,5	1.3		1.3		
AQP wells	21	21	21			
Overall communality resources	731.8	73.4	71	2.3		
Private wells (irrigation use)		86		86		

Table 4.3.4. Water resources supplied per year by ARNEO communality

It is not possible to provide reliable amount of the overall volume of water supplied from groundwater due to numerous private wells, often illegals. In the following there is an estimation of private wells supply.



	Volume for irrigation						
Type of water supply	(Mm³)						
Type of water suppry	Availability	Abstraction	Actual				
	Availability	ADSILACION	use				
Spring waters	0.3	0.1	0.1				
Apani spring	0.3	0.1	0.1				
Groundwater	6.5	2.2	1.5				
Communality wells	4	0.9	0.9				
Puglia Region wells	2.5	1.3	0.6				
Overall communality	6.8	2.3	1.6				
resources	0.0	2.5	1.0				
Private wells		86	86				

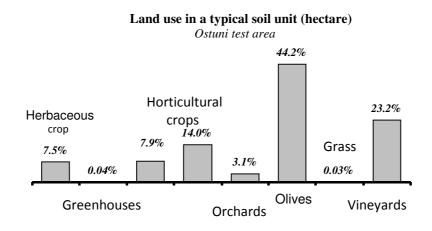
Table 4.3.5. Water groundwater supply per year in the communality area.

The main types of crops and the relative annual water requirements are shown in the tables below.

ARNEO COMMUNALITY

Crop type	Irrigated area	%	Annual net irrigation demand
	[ha]		[m³/ha]
Herbaceous crops in open fields with spring-summer cycle	5798.5	7.5%	2,200
Greenhouse crops	28	0.04%	5,000
Vegetables crops with summer-autumn and spring cycle	6098.9	7.9%	2,800
Vegetables crops with spring-summer cycle	10866.8	14.0%	4,800
Orchards	2439.1	3.1%	3,250
Irrigated olive groves	34334.4	44.2%	1,400
Permanent meadows	23.0	0.03%	3,000
Irrigated vineyards	18051.2	23.2%	2,750
ΤΟΤΑΙ	77640.2	100.0%	





Irrigated surface /in operation surface	26.5%	
Annual net irrigation demand per average irrigated hectare	2,419	m³∕ha
Annual net irrigation demand for the communality	49.8	Мт³
Efficiency of transport and distribution of water	90%	
Efficiency of the irrigation systems	75%	
Annual gross irrigation demand per average hectare	3,584	m³∕ha
Annual gross irrigation demand for the communality	73.7	Мт³



3. Impact of land use on water quality

During DRINKADRIA activity the partner FB3 has carried out several water sampling in order to monitor groundwater and surface water the OSTUNI test area.

In particular were selected three sampling locations into a channel and three wells for groundwater monitoring.



Figure 4.3.2a. Monitoring: Sampling locations at the Ostuni test area.

At each sampling site we have collected two liters of water in a sterile container to detect *Salmonella* spp., one liter to detect the indicators of faecal contamination and a third sample of twenty liters to detect somatic coliphage viruses. The coliphages will be determined after concentration to 50-100 mL of water sample by tangential ultrafiltration (VIVAFLOW 200 with 10,000 MWCO PES, *Sartorius*).

Furthermore the IRSA has defined sampling procedure in order to collect water samples from the OSTUNI wells and standard and bimolecular methods that must be used for microbiological analyses during DRINK ADRIA project at the Ostuni pilot area. In particular sampled water will be analyzed for total bacterial count (TBC) at 22° and 37°, coliforms, *Escherichia coli*, spores of sulphate-reducing clostridia, somatic coliphages, and *Salmonella* spp., and physico-chemical constituents, such as ammonia, nitrates, chemical oxygen demand (COD). The presence and abundance of antibiotic resistance genes (ARGs) will be also determined by q-PCR and large volumes of 5-120 L and 200-250 L will be sampled for the protozoa and virus analyses, respectively. For Enteroviruses determination, the groundwater will be filtered on electropositive



cartridges (Virasorb CUNO MK/Cuno, Sanford, FL). Cartridges will be eluted with a meat extract solution (elution buffer 0.05 M glycine in 0.3% meat extract pH9.5) and viruses will be further concentrated by precipitation with PEG6000 and centrifugation. Finally viral particles will be quantified by cultivations on cellular systems or by bimolecular methods. Cysts and oocysts will be concentrated by filtration in IDEXX foam filters, purified by means of immune-magnetic separation (*Dynabeads*® Crypto-Combo) and stained with fluorescently labelled monoclonal antibodies (*MERIFLUOR*® *Crypto & Giardia* kit, Meridian Bioscience, Europe). *Giardia* and *Cryptosporidium* cysts and oocysts will be finally enumerated by epifluorescence microscopy (Olympus BX-51) and phase contrast observation.

Microbial and chemical constituent results during the first sampling period of the DRINK ADRIA project, have been reported in the following Table 4.3.6, whereas the *Salmonella* was below detection limit of the proposed microbiological method (q-PCR).



	D'Antelmi Mouth			Channel 1		
Water constituents	19/11/2014	13/01/2015	17/02/2015	19/11/2014	13/01/2015	17/02/2015
рН	7.2	6.9	7.5	7	7.2	7.4
Electrical conductance (µS/cm)	1808	1721	1872	1288	1773	1817
COD (mg/L)	64	35	28	41	38	29.6
N-NH4 (mg/L)	<0.4	8.86	4.5	<0.4	11	5.68
N-NO3 (mg/L)	7.2	8	3.8	7.2	6.7	4.33
N-NO2 (mg/L)	0.01	3	1	0.026	2.3	1.2
Microbiological indicators						
E. Coli (MPN/100mL)	2240	31	135	6490	240	137
Total Coliforms (MPN/100 mL)	32550	3450	4160	48800	9210	9606
Spores of C.Perfrigens (CFU/100 mL)	3000	3000	2000	2000	3200	1800
Somatic Coliphages (PFU/100 mL)	300	2400	1300	1000	2800	2000
Enterococci (MPN/100 mL)		218	185		2420	161
HPC 37°C (CFU/mL)		3550	4200		6900	6500
HPC 22°C (CFU/mL)	390	850	680	795	980	840

	Channel 2		Well	We	ll 1	Well 2	Well 3	Well 4	Well 5
19/11/2014	13/01/2015	17/02/2015	13/01/2015	19/11/2014	17/02/2015	13/01/2015	17/02/2015	17/02/2015	17/02/2015
7.5	7.7	7.3	6.9	7.2	7.4	7	6.9	7.2	7
1845	1696	1888	9180	1977	3850	687	8500	2700	4000
48.6	44.4	30	21.2	56	8.8	4	20.6	7	8.5
<0.4	8.66	4.2	0.56	<0.4	0.5	0.12	1.3	0.5	<0.4
7.3	5.6	3.29	3.2	2.5	2.24	1.9	1.3	5.5	1.2
0.016	1.5	0.6	0.22	0.04	0.013	0.01	0.01	0.014	0.004
2183	41	47	<1	67	<1	<1	2	<1	<1
14000	3076	3088	260	30800	2419	50	345	387	1
1000	4500	2430	800	200	400	200	0	1500	0
500	1900	1200	0	0	0	0	0	0	0
	866	44	100		10	2	48	8	0
	4500	2900	800		324	100	311	248	260
475	520	600	350	85	155	450	300	185	110

Table 4.3.6. Surface water and groundwater quality sampled at Ostuni test area.

		ITALIA D. Lgs 31/01
Parameter		Limit Value
рН		6-9.5
Electrical conductance (µS/cm)		2500
Oxidability (mg/L O ₂)		5
N-NO3 (mg/L)		11.3
N-NO2 (mg/L)		0.15
N-NH4 (mg/L)		0.4
E. Coli (number/100 mL)		0
Total Coliforms (number/100 mL)		0
Enterococci (number/100 mL)		0
Spores of C.Perfrigens (number/100 mL)		0
HPC 22°C (number/mL)		Without abnormal changes
HPC 37°C (number/mL)		Not expected
LEGEND		
Prudentino	Well	
Narducci	Well 1	
Guarniero	Well 2	
Soleti	Well 3	
D'Amico	Well 4	
Lobbene	Well 5	
Ex-Caseificio	Channel 1	
Ponte Fontanelle	Channel 2	

3.1. Climate change impact on groundwater discharge: local sea-level rise effect on test area

Considerable work has been published about the impact of climate change on local sealevel rise (LSLR). However, the estimation of its impact on human health and hydrological stress in coastal regions has, surprisingly, not been sufficiently investigated. Focus has been mostly concentrated on direct impacts of sea level related disasters. The impact of LSLR on human health [2] and on groundwater volume reduction has not yet been fully investigated [3], especially in fractured aquifers. Even if there are many challenges relating to predicting and projecting future LSLR, a small increase in sea-level may have a severe impact on many coastal environments. There are many effects potentially caused by LSLR that can affect human health and water availability in various ways. Sea storms amplified by LSLR would also lead to severe impacts on wastewater treatment plants. Furthermore, the reduction of groundwater outflow increases the intrusion length by producing a serious reduction of groundwater volume. This may be very significant in coastal regions, where groundwater is the main source for irrigation and drinking. The sea intrusion problem is truly global in proportion. In Spain, the most severely affected areas by seawater intrusion are the Mediterranean and South-Atlantic coastlines and seawater intrusion is currently one of the main causes of groundwater pollution of about 60% of coastal aguifers. In the world, the most affected areas include Mexico's Pacific and Atlantic coastlines [4], Chile, Peru and Australia. The situation is particularly acute in the Mediterranean, the Yucatan peninsula in Mexico, the Middle East, the SE and SW United States as well as on many islands with arid to semi-arid climates, such as Cyprus.

The aim of our investigation is an experimental evaluation of the LSLR impact during the 21^{st} and 22^{nd} centuries on the Salento peninsula (Southern Italy). Here, the fractured aquifer supplies 80% of the total population's drinking requirements (of about 1 million inhabitants) with 126 million m³/y of water.

The evaluation has been carried out by generalizing the annual rate of LSLR from the best-fit of ultrasonic tide-gauge sea level measurements recorded at three tide-gauge stations on the Salento coast. Then, the Ghyben-Herzberg formula for fractured aquifers has been inverted to determine the progressive reduction of Salento's groundwater volume during the 21st and 22nd centuries. The new proposed formula highlights the reduction of annual groundwater discharge, which corresponds to the sea inland advancement due to LSLR and can be applied in any coastal fractured groundwater (at a regional scale) in order to evaluate the impact of climate change on local water resources.



3.1.1. The OSTUNI study area

The Salento peninsula was selected among the Mediterranean regions because it is one of the driest areas, with an average rainfall of less than 600 mm/y. Here, similarly to other Mediterranean regions (Greece, Cyprus, Lebanon, Egypt, Tunisian, Spain, etc.) the economy largely depends on farming, leading to mainly agricultural land use with a large share of irrigated crops due to low precipitations. The total water consumption in Apulia is estimated to be about 2400 Mm³/y, where 58% (1400 Mm³/y) [5] is consumed by agriculture, 18% (430 Mm³/y) by industry and 24% for drinking use (580 Mm³/y). Furthermore, according to other studies [6], the Mediterranean region is expected to undergo particularly negative climate change consequences over the next decades. These effects, combined with the anthropogenic stress of natural resources, make the Salento one of the most vulnerable areas in Europe. The anticipated negative impacts are mainly related to possible extraordinary heat events (especially in summer), increased frequency of extreme storms and reduction of total annual precipitation.

As the Salento peninsula does not have any relevant surface water sources, groundwater has traditionally been the main source of water supply in the region. Moreover, natural recharge does not refill the aquifers sufficiently, and overexploitation, with consequent seawater intrusion into groundwater, is a critical problem at many locations. The number of private wells (often illegally drilled) is around 140,000. The main problem at the Salento peninsula is related to the increase of groundwater salinization due to groundwater over-abstraction and subsequent seawater intrusion. Here, data (specific conductivities) were collected from 120 wells during the winter of 2009 at a depth ranging from 5 to 10 m below the water table, and were fitted by Surfer (v. 11, Golden Software Inc., Colorado, USA). At several places along Salento's coast, groundwater salinity already exceeds 7 g/l.

In Salento's subsoil, groundwater flows under low pressure inside karstic fissures of carbonate (limestone) aquifers at a depth ranging from 5 to 100 m from the soil. The natural recharge of rocky aquifers occurs via both existing vertical karst fractures and by sinkholes replenished by small ditches (i.e., *lame*) with runoff and, sometimes, [7] with treated effluents derived from municipal plants.

The protection of water resources from seawater intrusion may include several measures to preserve global groundwater balance, considering not only limitations of water supplies and dynamic barriers, but also potential new sources (i.e. reclaimed water) for groundwater replenishment by artificial recharge [8].

3.1.2. Method: Tide-gauge measurements

Many intensive studies have been recently published about global and local sea level forecasting during the 21st and 22nd centuries. Among them, the global rate of sea level



rise during the 20th century is generally agreed to be 1–2.5 mm/y, and many authors concur that sea level data series available for the Mediterranean show a sea level rise of a similar rate. However, other authors [9] noted that, from 1990 onward, the sea level recorded in most Mediterranean tide-gauges indicates a rise in sea level at a rate 5–10 times higher than the 20th century mean rate. In addition, Milne et al. [10] have noted a tenfold increase in the sea level rise rate that can be attributed to climate change through glacier melting and ocean water thermal expansion.

Sea-level rise may significantly differ locally and globally due to variations in the ocean circulation as part of variable climate patterns, the isostatic adjustment of the Earth's crust, past and ongoing changes in polar ice masses and continental water storage [11]. In particular, the LSLR spatial variability may also arise for heat content and salinity changes in seawater [12], for vertical geological layer displacement due to tectonics, groundwater reservoir (and hydrocarbon deposit) exploitations, natural sediment consolidation [13] and subsidence. According to Stammer et al. [14], currently, regional sea level changes seem to be primarily caused by natural climate variability.

In the present study, ultrasonic measurements of three tide-gauge stations on the Salento peninsula, from 2000 to 2014, have been fitted using Microsoft Excel [15]. The data are available on the ISPRA website [16]. Measurements are available at intervals of 10 min and were resampled in order to have one measurement per hour. All measurements refer to sea level on January 1, 2000. When, due to device malfunctioning, measurements were missing, no values were considered for replacements, i.e. series have been plotted with missing values. This is because missing data had no influence on the evaluation of the rate during the long period of 14 years, with 129,039 measurements per station (Figure 4.3.3). The straight-line trends of the Bari and Taranto stations have the same rate, i.e. the increasing LSLR is 10⁻⁴ cm/h (or 8.76 mm/y), while the rate is 0.5×10^{-4} cm/h or 4.38 mm/y (i.e., half) at the Otranto station. Bari and Taranto trends perfectly agree with global sea level (GLS) rise projection as defined by Kopp et al. [17] (see Figure 4.3.3d). They consider 90% (very likely) of probability under representative concentration pathway 8.5 [18], i.e. corresponding to scenarios with usual industrial emissions until the end of the simulation, under maximum radiative forcing (i.e., > 8.5 W/m² by 2100) [19]; IPCC AR5 WG1 [20]) and without greenhouse gas mitigation.

It should be considered that this GLS rise accounts for the melting of both Greenland (about 20%) and Antarctica's (10%) ice sheets, thermal expansion (40%), melting of glaciers and ice caps (25%) and the reduction of land water storage (5%). The Bari and Taranto LSLR trends match with the global rise forecast, as defined during the 2100 by IPCC in the fifth assessment report (AR5 WG1 2013) [20] under representative concentration pathway 8.5 and with estimations carried out by Klein and Lichter [9] in the Mediterranean area for decades after 1990.



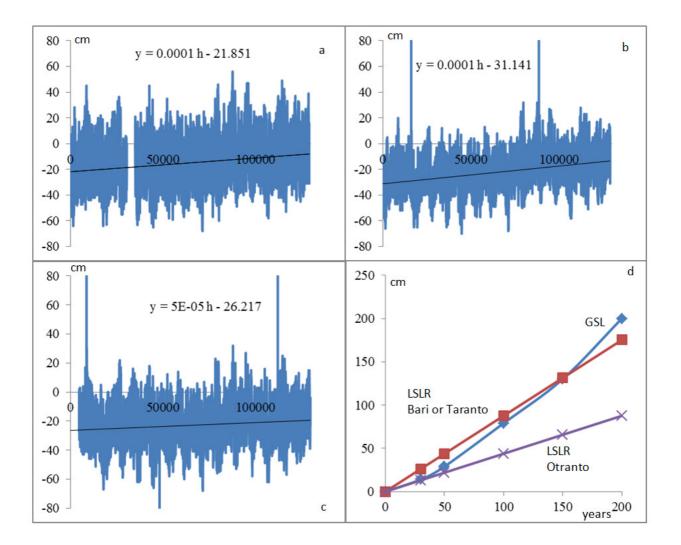


Figure 4.3.3. Tide-gauge measurement trends in (a) Bari, (b) Taranto and (c) Otranto stations from 2000 to 2014, and (d) LSLR trends compared to global level rise projections given by Kopp et al. [17] under representative concentration pathway 8.5 (i.e., 90% very likely).



3.1.3. The coastal salinity map

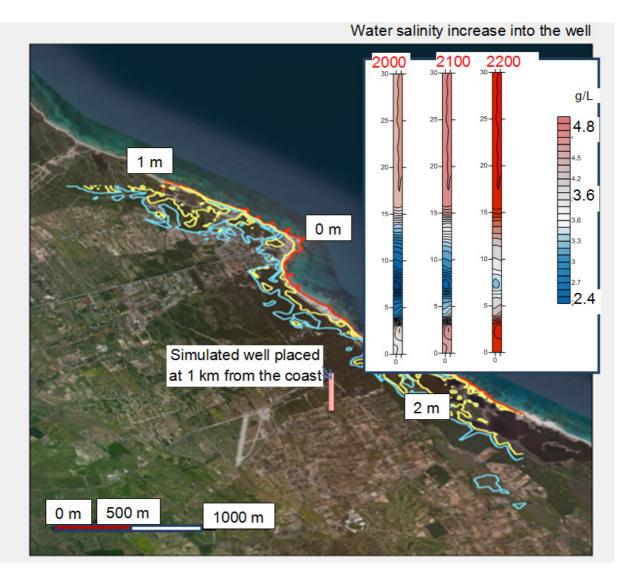
The sea-level rise may produce inland sea advancements, which depend on the coast morphology. Considering a maximum increase of 2 m until 2200, the Salento sea advancement extension due to this LSLR is below 220 m, on average. This distance was estimated to be in a range from 43±30 m to 781±400 m along the Salento ArcGIS according to elaborations made peninsula coastline. bv (http://www.esri.com/software/arcgis) of the coast digital elevation model (http://www.sit.puglia.it) at 8 m of grid size. This average sea advancement is lower than the value of 700-1200 m determined along the same lonic coast by other authors Romanazzi et al. [21]. Figure 4.3.4 shows the advancements (contour lines) of the sea line determined during the 21st (yellow) and 22nd (blue) centuries compared to the coastline during 2000 (red) along the Lecce's coast (Italy) using ArcGIS. In the same figure is shown in a separate window the groundwater salinity progression in an apparent (i.e. fictitious) borehole placed 1 km from the actual coastline. For this purpose, a second interpolation using TableCurve2D (http://www.sigmaplot.com) has provided the best fit (correlation coefficient of 0.92) between groundwater salt concentrations measured in coastal wells and the modeled distance (d) of each borehole from the freshwater/saltwater Ghyben-Herzberg sharp interface,

$$C_{salt} = C_{s0} + A_s \left[\exp\left(-\frac{d}{D_s}\right) \right]$$
(1)

which is a function of the best-fit constants: $C_{s0}=1.54$ g/L, $A_s=12.02$ g/L and $D_s=592.65$ m. For this interpolation, the observed salt concentrations at 1–1.5 m of water depth in 25 wells have been fitted versus the corresponding distances (*d*). Applying equation (1) to the Salento aquifer, we determined into the wells close to the new sharp interface position, a water salinity increase due to LSLR ranging from 7 to 14 g/L. Salinity maps, reconstructed in an apparent well under different LSLR scenarios, corresponding to the years 2000, 2100 and 2200 (Figure 4.3.4), have been determined using d = 1000 m, 850 m and 700 m, respectively.

The overall LSLR impact is very far from the catastrophic hypothesis suggested by Andrew Thaler (http://www.weather.com/news/science/environment/drownyourtown-sea-level-rise-your-city-20131219?pageno=4), showing how the Vatican and St. Peter's Square in Rome (Italy) will look with LSLR of 20, 30 and 45 m. The resulting LSLR of 4.4–8.8 mm/y in the present study and consequent average sea advancement (~220 m) are not negligible when compared with anthropogenic effects, such as over-pumping [22], and surely cannot be neglected in future groundwater volume balances and water management actions. In a previous study at the Ostuni area [23], we showed how stopping the artificial injection of 62 L/s of reclaimed water, it was caused during 1998 a seawater intrusion of about 200 m along 3 km of the coast. This led to a water salinity





increase from 2 to 6 times into the wells within 1.5 km from the coastline

Figure 4.3.4. Sea line advancement (contour line) during the 21st (yellow) and 22nd century (blue) compared to the coastline location in 2000 (red) along Lecce's coast on the Salento peninsula (Italy), using ArcGIS and groundwater salinity progression, in a borehole placed at 1 km from the current coastline.

By defining groundwater outflow at Q_0 when sea water intrusion is absent (i.e. $L_d = L$), is

$$Q_0 = K \frac{B^2 - H_s^2}{2\delta_{\gamma} L_d}$$
(2)



Moreover by defining Q $[L^2/t]$ as the groundwater discharge when the seawater intrusion is present (i.e. $L_d < L$), is

$$L - L_{d} = K \frac{B^{2} - H_{s}^{2}}{2\delta_{\gamma}Q} - L_{d} > 0 \rightarrow Q = K \frac{B^{2} - H_{s}^{2}}{2\delta_{\gamma}[(L - L_{d}) + L_{d}]}$$
(3)

and it can be defined the groundwater discharge reduction (per unit of the coast length)

$$\Delta Q = Q_0 - Q = Q_0 - K \frac{B^2 - H_s^2}{2\delta_{\gamma} [(L - L_d) + L_d]}$$
(4)

which is due to a sea advancement equal to L-L_d. Furthermore, in a fractured aquifer, by replacing the aquifer conductivity given by Equation (2) we obtain

$$\Delta Q = Q_0 - n \frac{b_i^2}{3} \frac{\gamma_f}{\mu_f} \frac{B^2 - H_s^2}{2\delta_{\gamma} [(L - L_d) + L_d]}$$
(5)

It should be noted that, in equation (4) or (5) when the intrusion length is zero, ΔQ must be set zero, i.e. Q=Q₀. Conversely, by increasing the intrusion length, Q will approach zero, and ΔQ will be close to Q₀.

Equation (4), for *K* (0.0037 m/s or 320 m/d), *B* (15 m), L_d (1400) and ϕ_0 = 1 m, provides ΔQ = 9.89×10⁻⁷ m³/s/m, for Bari groundwater in Bari along the coast, by imposing L-L_d = 157 m. Evaluating a coastline length of about 80 km, the substantial groundwater availability reduction due to the LSLR will be 2.5 Mm³/y until 2200, i.e. 9.7% (or 79 L/s) of Murgia's current groundwater withdrawal (813 L/s) for drinking purposes (Figure 4.3.5).

The same estimation was performed along Brindisi's coast, where K= 0.0037 m/s (or 320 m/d), B=15 m, L_d =1250 m and L-L_d = 125 m, estimating a groundwater reduction of 2.5 Mm³/y, i.e. 3.2% (or 77 L/s) of current withdrawal (2500 L/s) for drinking, measuring a coast length of 77 km. On Lecce coast, we have K= 0.008 m/s (or 691 m/d), B=15 m, L_d =2800 m and L-L_d = 480 m, and we obtained a total reduction of 9.25 Mm³/y, i.e. 11.9% (or 293 L/s) of current withdrawal for drinking, measuring a coast length of 189 km. Along the same coast, if we consider the rate of 4.8 mm/y until 2200, L-L_d is close to 220 m and we will have a total groundwater volume reduction of 4.6 Mm³/y, i.e. 5.9% of actual withdrawal for drinking.

Finally, along Taranto's coast (about 116 km), we have K= 0.0008 m/s (or 69 m/d), B=15 m, L_d =2500 m and L-L_d = 190 m, estimating a groundwater source reduction of 0.3 Mm³/y, i.e. 1.2% of Murgia's current groundwater withdrawal for drinking purposes.

These estimations can be carried out with equation (5), even on a local scale, considering effective local piezometric heads along the coast and effective fracture apertures, such as those derived from well pumping tests. In this way, a more appropriate evaluation of groundwater discharge reduction due to the LSLR can be determined, also considering local coast morphology.



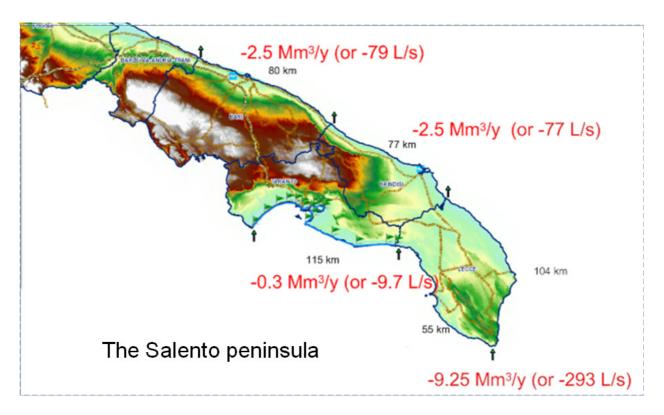


Figure 4.3.5. Groundwater discharge reduction during the 22nd century due to LSLR (over exploitations have not been included) at the test area (Southern Italy).



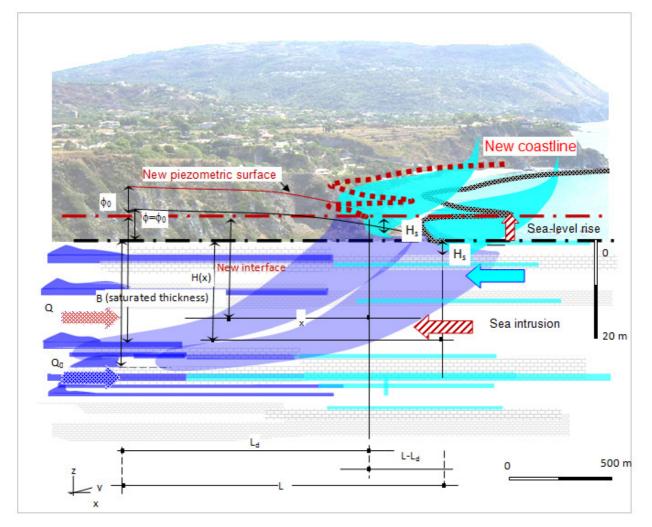


Figure 4.3.6. Sea-level rise and corresponding coastline displacement (red line) can significantly alter the freshwater/saltwater interface leading to a groundwater salinity increase in a very wide zone (shaded area).

3.2. Sea water intrusion problem: theory

Following some authors [24] the variation of groundwater discharge after a LSLR highly depend on the inland boundary conditions. Theoretical studies carried out by same authors suggests two conceptual models to study the impact of sea-level rise in coastal aquifers, i.e.: (1) flux-controlled systems, in which ground water discharge to the sea is



persistent despite changes in sea level, and (2) head-controlled systems, whereby groundwater abstractions or surface features maintain the head condition in the aquifer despite sea-level changes (Figure 4.3.6). Other authors [25] suggest a third approach by relating the groundwater discharge to the head at the inland boundary of domain. In this work, as suggested by Carretero et al. [26], due to high rock hydraulic conductivity (ranging from 60 to 700 m/d), low coast elevation, general inability of the water table to migrate vertically, and low LSLR with respect to the aquifer thickness, it is likely that the conceptual model approaches a *head-controlled system*. This means that there is a distance, generally higher than 1 km from the Salento seacoast, at which the piezometric head ϕ_0 [L] and depth of seawater/freshwater interface edge B [L] will remain unchanged even when the sea-level rises of 2 m. Moreover, under the *head-controlled system* in this work, we assume that the LSLR will induce a reduction in the seaward groundwater flux, because the cross-section of outflow per unit of coast length (i.e. H(x) × 1) will be reduced (see Figure 4.3.6).

At Salento, the fractured aguifer was idealized in a layered (i.e. confined) model [27; p. 272] made by several horizontal fractures bounded by impermeable rocks (see Figure 4.3.6). This idealization was confirmed by tracer (Rhodamine-Wt and lodine) tests carried out in the same aquifer, under pumping and natural pressure gradient [7]. Each fracture is characterized by variable apertures which can be derived from the aquifer transmissivity values estimated in wells of the study area, by mean of stochastic methods [28]. In each fracture, we can define the stationary interface position by considering the hydrostatic equilibrium of freshwater/saltwater pressures, based on the Ghyben-Herzberg equation (see Figure 4.3.6). In addition, using the Dupuit assumption, we assume that inside the fractures freshwater flows in a horizontal direction [29; p. 196-206]; [30; p. 395]. In the proposed conceptual scheme all fractures were assumed to have hydraulic connections between them and to have the same mean aperture 2bi [L], whereas the sharp interface approximates the 50% salt concentration contour line in the water. The analytical solution of the stationary (i.e. steady flow) interface position can be derived from integration of the Laplace (i.e., the continuity) equation in the vertical plane, where the total freshwater out flows into the sea. The groundwater discharge per unit of seacoast length Q_0 [L³/t/L] was derived from the flow solution of the Navier-Stokes' equations in a single fracture bounded by two parallel plates

$$Q(x) = -\frac{b_i^2}{3} \frac{\gamma_f}{\mu_f} nH(x) \frac{\partial \phi(x)}{\partial x} = const = Q_0$$
(6)

where *x* [L] is coordinate along the fracture length towards the sea direction; γ_t/μ_t (=10⁷ m⁻¹s⁻¹ at 20 °C) is freshwater density/viscosity ratio; $\phi(x)$ [L] is the piezometric head of freshwater in *x* direction; H(x) [L] is the depth of the sharp interface below the sea (i.e., freshwater thickness); and *n* [-] is effective aquifer porosity.



Based on the analogy of Equation (1) with the Darcy's formula we can state the hydraulic conductivity K [L/t] of the aquifer

$$K = \frac{b_i^2}{3} \frac{\gamma_f}{\mu_f} n \tag{7}$$

As known, *n* defines the uniform ratio of the void-space per unit volume of aquifer and at the section where is x=0 it will be

$$n = \frac{\sum_{i=1}^{N_f} 2b_i}{B} \tag{8}$$

where Σb_i (m) is the sum of all the horizontal apertures in the vertical aquifer column with unitary horizontal area (1x1 m²) and thickness *B* [L], while *N_f* is the total number of the fractures of the parallel set. In addition, as all fractures have been assumed to have the same mean aperture $2b_m$ [L], it follows that, on average:

$$Q_{0} = N_{f}Q_{i} = \frac{\sum_{i=1}^{N_{f}}b_{i}}{b_{m}}Q_{i}$$
(9)

where Q_i [L³/t/L] is the flowrate of the single fracture of the parallel set per unit of coast length. Following the Ghyben-Herzberg formula, in every cross-section at distance *x*, for $0 \le x \le L$, where *L* is the distance of coastline from the Ghyben-Herzberg interface toe position (see Figure 4.3.6), we can write the freshwater piezometric head *H* as:

$$H(x) = \phi \frac{\gamma_f}{\gamma_s - \gamma_f} = \delta_{\gamma} \phi$$
(10)

where $\delta_{\gamma} = \gamma_f / (\gamma_s - \gamma_f)$ [-] (=33-35, in Mediterranean sea) and, Equation (6) can be rewritten as

$$Q_0 \times \partial x = -K \frac{H(x)}{\delta_{\gamma}} \partial H(x)$$
(11)

Equation (11) is a first order differential equation in *x* and *H*, which can easily be integrated between the sections: i) x=0 at H=B, and ii) the generic vertical cross-section *x* at H=H(x)

$$Q_0 \times x = K \frac{(B^2 - H(x)^2)}{2\delta_{\gamma}}$$
(12)

(as it is $\partial H < 0$, for $\partial x > 0$). At the outflow section, i.e., at *x*=*L*, we may set *H*(*L*)=*H*_s and

$$Q_{0} \times L = K \frac{B^{2} - H_{s}^{2}}{2\delta_{\gamma}} = n \frac{b_{i}^{2}}{3} \frac{\gamma_{f}}{\mu_{f}} \frac{(\delta_{\gamma}\phi_{0})^{2} - H_{s}^{2}}{2\delta_{\gamma}}$$
(13)

where L [L] is minimum extent from coastline required to avoid seawater intrusion and H_s [L] is the depth (below the sea surface) of the sharp interface at the outflow section.



The reader should note that the origin (*x*=0) of *L* measurement is defined at the position where is $\phi = \phi_0$ (or H(x) = B) and not at coastline.

In the present work the distance from origin of the estimated position where the freshwater outflow should take place, L_d [L], is defined by groundwater flow model by means of position of ϕ_0 from the coastline. The depth H_s may be usually set equal to zero leading to the well-known equation [30; p. 395] of stationary interface toe position in confined aquifers. Really the Ghyben-Herzberg interface is an approximate theory which considers that at outflow section is H(L)=0. This is of course not possible and in the real situation (see Bear and Verruijt [29; p. 204]) the interface always terminates at depth H_s on the sea bottom at some distance from the coastline. Then, $\phi(L) = 0$, defines the position with respect to the coastline where the groundwater outflow takes place: i.e., 1) inland, for L_d < L (i.e., there is seawater intrusion); 2) at coastline, L_d =L (no intrusion), or 3) offshore, L_d >L, below the sea surface (i.e., there is a submarine spring). Equation (13) allows the sharp seawater/freshwater interface to be drawn in a three-dimensional domain of a fractured aquifer.

Under this conceptual framework we may assume that the extent of seawater advancement caused by LSLR can be similar to the effect caused by an over-pumping. This means that due to LSLR the distance from the new coastline of the aquifer vertical cross-section where is $\phi = \phi_0$, that is L_d (see Figure 4.3.6), is less than minimum distance L required by Equation (13) to avoid seawater intrusion. This causes the seawater intrusion extent of L-L_d due to LSLR. Moreover, by inverting Equation (13), we may also evaluate the groundwater discharge reduction per unit of coast length, ΔQ [L³/t/L], which is due to the sea advancement of L-L_d.



3.3. Measures to improve the groundwater quality and quantity

The measure to improve the groundwater quality by contrasting seawater intrusion in coastal aquifers is the Management of Aquifer Recharge (MAR).

The principal benefits of the concept of MAR are twofold:

- It allows storage of large quantities of surface water (including surface runoff, storm water, reclaimed water, and also freshwater from desalination) at those periods of the hydrological year when availability exceeds demand and to restore them when demand exceeds availability.
- The underground passage (unsaturated and saturated zone) can constitute a complementary treatment step, due to physical, chemical and biological processes that will affect water quality.

The major challenge to meet is thus a potential conflict of the MAR system with other uses, mainly in terms of water quality (risk of degradation of chemical or biological background quality for one or more parameters due to infiltration or infiltration-induced chemical processes in the storage medium). In order to address those benefits and risks, the designer or operator of any MAR system will need to address the following key questions:

(1) How efficient is my system in terms of recovery of the recharged water?

(2) How long will the water and solutes reside in the system and be in contact with reactive minerals and biofilms?

(3) In which way will the recharge-recovery cycles affect the quality of the recovered water and the background water, on short term and long term?

These questions will be asked from the very beginning of the planning phase and over the whole lifetime of the MAR project and groundwater models provide the unique possibility to preview the feasibility of the MAR system in the regional context, to optimize the choice of the site, the configuration of an appropriate recharge-recovery system, to optimize operating conditions in a way to meet fixed quantity and quality targets. Those targets are most frequently quantified through the key parameters recovery efficiency, residence time, and recovered water quality compared to target quality. Recovery efficiency [31] as a measure of success of a MAR system, is defined either by the percentage of injected water that can be recovered or by the percentage of usable water (meeting a defined target quality, e.g. drinking or irrigation water standards) compared to the injected volume per cycle of injection.

Residence time or transfer time (in the case of Aquifer Storage, Transfer and Recovery, ASTR) will be the average duration of water and solutes in the reservoir determining the time available for water-rock interactions and bio-geochemical reactions. Residence time will largely influence the potential for degradation of pollutants and thus the



efficiency of Soil Aquifer Treatment (SAT) systems and to estimate this parameter may therefore be legally compulsory. A typical example is the Californian draft regulations applying to new recharge projects [32].

They define the minimum retention time to allow identification of treatment failures and implement remediation actions and to guarantee the overall treatment efficiency. Target quality for the groundwater quality is generally defined by law and water reuse guidelines. Potential use of recovered water is also defined in these guidelines. The quality of the recovered water has to be constantly compared to this target quality and is determined by the quality of recharged water, the attenuation potential of the unsaturated and saturated aquifer and the background water, frequently but not necessarily of lower quality than the recharged water (e.g. freshwater injection into saline aquifers). The underlying processes controlling water quality are (1) mixing by advection and hydrodynamic dispersion (2) density dependent stratification (3) ambient groundwater displacement and (4) reactions within the aqueous phase induced by mixing and reactions with aquifer material and subsurface microbial communities.

Those key parameters are determined by intrinsic, physical factors (aquifer properties like permeability, effective porosity, dispersivity, preferential flow zones and the natural hydraulic gradients, aquifer mineralogy and background water quality) and by operational variables (e.g. storage period, volumes recharged, and recharge/recovery rates). The intrinsic properties are generally constant but may evolve over the lifetime of a MAR system (e.g. through clogging [33]; [34]). Intrinsic factors will depend on the selection and design of the system, operational variables on the strategy for MAR operation. Groundwater models can help for both purposes.

Currently available groundwater models allow quantifying recovery efficiency, residence time and quality of recovered water. However, a complete response to the questions listed above may need the use of state of the art models (reactive transport models) or go beyond the current capacities of the state of the art (bio-geochemical reaction modelling). Even simple models (analytical models) can provide sufficient information at least for preliminary design or evaluation of MAR systems but, most frequently, numerical models will be used. Standard numerical models will nowadays be able to simulate up to full 3D advective (e.g. through particle tracking) and dispersive flow and transport of water and solutes. Supplementary features may be needed as, in the order of increasing complexity:

• Density driven flow (in the context of highly saline waters, like in coastal aquifers)

• Sorption and (bio-) degradation of solutes (e.g. through sorption isotherms, degradation factors)

• Variable saturation flow (in the case of a significant thickness of the unsaturated zone, in particular if the latter plays an important role for water quality improvements in SAT systems)

· Geochemical reactions through the combined use of flow-transport models and



thermodynamic equilibrium models or thermo-kinetic models taking into account the reaction kinetics

• Biologically mediated geochemical reactions (specific models available)

• Aquifer ecosystem simulation accounting for changing microbial communities and their assimilation of nutrients, competencies for metabolism of organic contaminants, enzymatic attack on pathogens and their influences directly and through microbial products (such as polysaccharides) on aquifer porosity and hydraulic conductivity.

The IRSA outlines the use of groundwater models suitable for MAR focusing on the strategic phases of a MAR system (site selection, MAR design, MAR operation), on the data needs to build and run such models.

Applications of models within the OSTUNI pilot area of DRINK ADRIA will be carried out in the Work Package 6.



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Water quality analysis and trends on test area in northwestern Slovenia

Faculty of Natural Sciences and Engineering University of Ljubljana (FB5)

Ljubljana, 2014

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Lead Author/s	Petra Žvab Rožič, Boštjan Rožič, Timotej Verbovšek, Barbara Čenčur Curk	
Lead Authors Coordinator	Petra Žvab Rožič	
Contributor/s	Mihael Brenčič, Tomislav Popit, Andrej Šmuc, Petra Vrhovnik, Nina Zupančič	
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1 Introduction

In this report water quality data analysis and trends are presented for the test areas of Slovenian project partner (FB5) within the DRINKADRIA project. Slovenia test areas cover three potential aquifers; Kobariški Stol, Mia and Matajur aquifer, which are located in NW Slovenia. The source for water quality data is the national monitoring of surface and groundwater quality.

2 Description of test areas

The test areas of Slovenian project partners are Kobariški stol, Mia and Matajur aquifers, which are located in NW Slovenia. The area belongs to Northern Primorska region and present border area between Slovenia and Italy (Figure 1a). It covers the mountain ranges called Kobariški stol in the north and Mija - Matajur in the south that are extending from the city of Kobarid and village Livek towards the west to Italy to the villages of Pradielis and Musi.

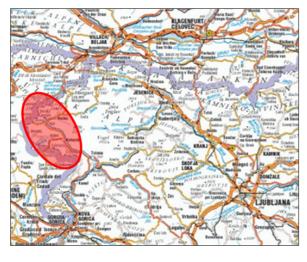


Figure 1a) Geographical location of Kobariški Stol aquifer (Atlas okolja, 2014)

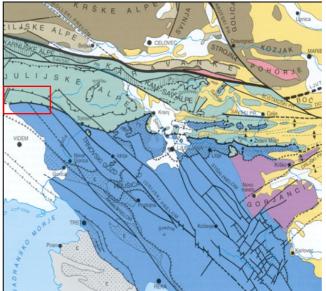


Figure 1b) General structural division of the Slovenian territory (test area marked with red squere) (Placer 1998)

The investigated area structurally belongs to the contact area between External Dinarides and Southern Alps, more exactly to the Trnovo Nappe and Tolmin Nappe (Buser, 1986, Placer, 2008) (Figure 1b). Paleogeographically, the area in the Late Triassic to Lower Jurassic belonged to a transitional area between Dinaric Carbonate Platform to the south, Slovenian Basin to the east and Julian Carbonate Platform to the north (Miklavič & Rožič, 2008; Šmuc, 2012). The later drowned in the Middle Jurassic and turned into pelagic plateau known as Julian High. In the Cretaceous, the progressive deepening of the



sedimentary environment is observed, which resulted in basinal, i.e. flysch sedimentation across the entire area at the end of Cretaceous.

The aquifers consist predominantly of Late Triassic Dachstein Limestone and Lower Jurassic lagoon limestone (Figure 2) that in the upper part contain Lithiotis-type bivalves (Buser, 1986). In the northern slope of Kobariški stol narrow, fault bounded belt of Late Triassic Main Dolomite occurs. In the Middle Jurassic the succession is characterized by nodular micritic limestone intercalated with even-bedded calacarenites. Both lithotypes contain chert nodules.

The Upper Jurassic differs between the aquifers. In the northern Kobariški stol aquifer it is represented with only several-methers thick succession of ammonitico rosso-type limestone (Šmuc, 2012), in the Mija aquifer the nodular limestone pass upward in Upper Jurassic and late Lower Cretaceous reef limestone (Buser, 1986), whereas on the Matajur, these beds are not preserved (Miklavič and Rožič, 2008).

The Upper Cretaceous begins with thin-bedded micritic and calcarenitic limestone with chert nodules known as Volče Limestone. This formation laterally wedges out. With erosional contact the latest Cretaceous flysch deposited over the entire area. Due to highly irregular lower boundary it lies practically on all previously described formations. It begins with limestone breccia which is laterally discontinuous and shows highly variable thickness (Miklavič and Rožič, 2008). It is overlain by flysch which represents hydrogeological barrier. Within lower part of the flysch limestone breccia interbeds are still present. They are up to 10 meters thick and form isolated, small-scale aquifers.

Carbonates are forming fissured and karst aquifers (Figure 3). In the valley of Nadiža and Soča river there are small, low productive porous aquifers



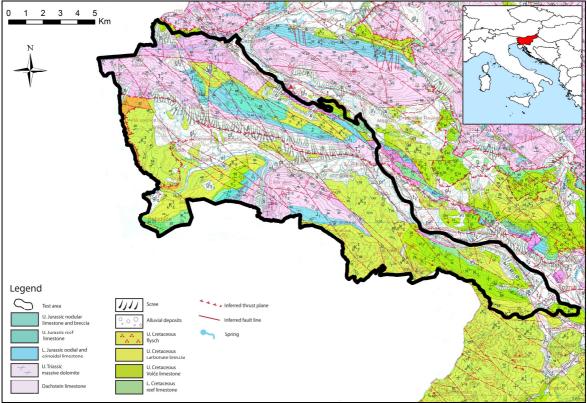
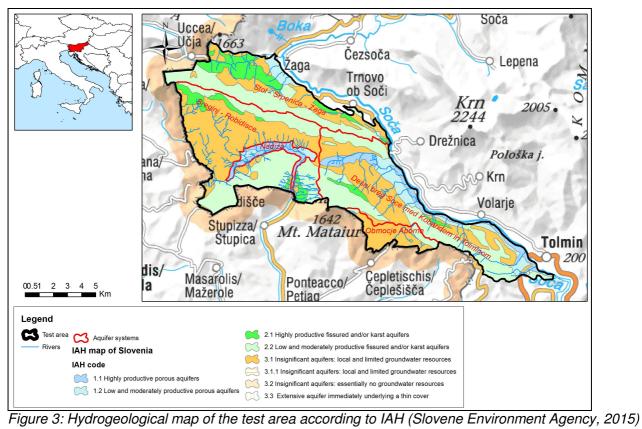


Figure 2: Geological map of the test area (Buser, 1987)





3 Water quality monitoring network

There are four national monitoring stations for water quality within the investigated area: two for surface water and two for groundwater. The national monitoring is performed by the Environmental Agency of the Republic of Slovenia. Coordinates of the national groundwater quality monitoring stations and monitoring periods of available data are presented in Table 1.The basic information and the locations of measuring locations are presented in Table 1 and Figure 4.

Monitoring frequency for surface water is 12 times per year and for groundwater twice a year. The number of measurements for statistical analysis in the case of surface water is representative, while the groundwater results due to the small number of measurements were not statistically analysed.

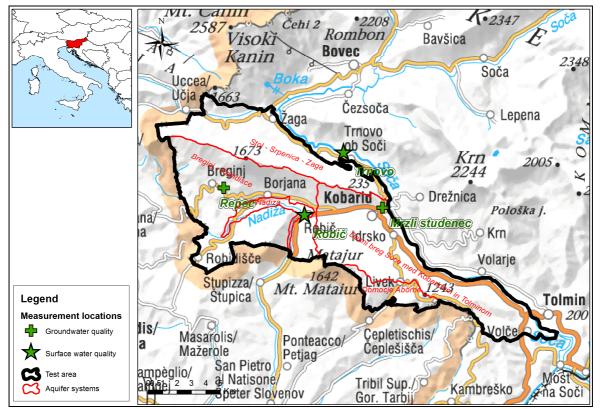


Figure 4: Locations of water quality measuring points within test area



Table 1: Basic information about the monitoring stations for surface and groundwater quality at investigated area.

Name of location	Code	GKY	GKX	Level (m.a.s.l.)	Measurements	Water body (WFD)	Monitoring period and frequency
Robič	8730	385527	123315	264.5	surface water quality	WB Nadiža (SI66VT102)	2005-2006, 2008- 2013 / monthly
Trnovo	8070	388239	127680	312.1	surface water quality	WB Soča (SI6VT157)	2005-2013 / monthly
Repec nad Breginjem	l16040	379904	125167	598.6	groundwater quality	Julian Alps in the Soča river basin	2007, 2008, 2012 / 2 times per year
Mrzli studenec, Kobarid	I25010	390951	123778	276	groundwater quality	Julian Alps in the Soča river basin	2007, 2008 / 2 times per year

For surface water the following water quality parameters were measured: organoleptic properties of water (colour, smell, turbidity); physical and chemical properties (temperature, pH, electrical conductivity, suspended solids after drying); oxygen regime (dissolved oxygen and oxygen saturation); nutrients (nitrogen compounds and phosphorus compounds); organic matter (mineral oils, phenols); heavy metals (copper, zinc). For groundwater the following water guality parameters were measured: organoleptic properties of water (colour, smell, taste); physical and chemical properties (temperature, pH, redox potential, electrical conductivity, total hardness, carbonate hardness, alkalinity, hydrogen carbonate); ions (fluoride, chloride, sulphate, calcium, magnesium, sodium, potassium, boron); oxygen regime (dissolved oxygen and oxygen saturation); nutrients (nitrogen compounds and phosphorus compounds); organic compounds (COD (KMnO₄), total organic carbon (TOC), anionic detergents (MBAS index), mineral oils, organochlorine pesticides, pesticides-herbicides and organophosphorus, alachlor and pentachlorophenol, PCBs); heavy metals (iron, manganese, aluminium, antimony, arsenic, copper, barium, beryllium, zinc, cadmium, cobalt, tin, chromium, molybdenum, nickel, selenium, silver, strontium, lead, vanadium, mercury, titanium); bacteriological indicators (total Coliforms, faecal Coliforms, faecal Streptococci (Enterococci).



4 Water quality and trends

4.1 Surface water quality

Measurements of national monitoring of surface water are carried out at two locations within the investigated area (Table 1 and Figure 4). At the location Trnovo the water from Soča river is sampled and at location Robič the Nadiža river is collected. The period of measurements from two locations included in our analysis is from 2005 to 2013. There are no available data for Trnovo station from 2007.

4.1.1 Physical and chemical composition

4.1.1.1 Water temperature

Variations in water temperature at both sampling sites show an annual cyclicity (Figure 5 and 6). The lowest temperatures were observed in mid-January (Trnovo 2,2 °C in 16.01.2006 and Robič 1,1 °C in 17.01.2012) and the highest water temperature at the beginning of August (Trnovo 16,5 °C in 02.08.2005 and Robič 24,4 °C in 01.08.2005). There were two colder winter period observed at both sampling locations, the first was in 2006 and the second in 2012, and additionally also in 2005 at Robič site. There are slight trend of water temperature observed at both sampling locations. Increase at Trnovo site is most probably the result of warmer winter in 2013. At Trnovo sampling location (Soča River) the annual average temperature increase (from 2005 to 2013) as well as winter and summer temperature increase was observed (Figure 7). Slightly summer increase (no significant trend) was also determined at Robič sampling location (Nadiža River), while for annual and winter no trend of water temperature was observed (Figure 8).

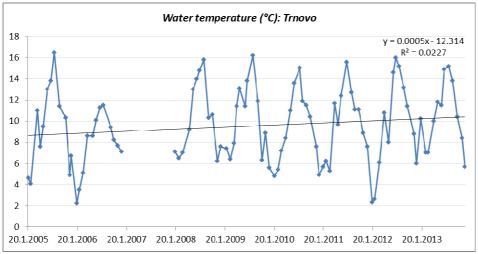


Figure 5: Surface water monthly temperature (\mathcal{C}) at sampling location Trnovo with trendline



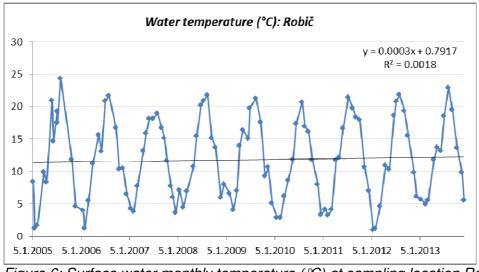


Figure 6: Surface water monthly temperature (∞) at sampling location Robič with trendline

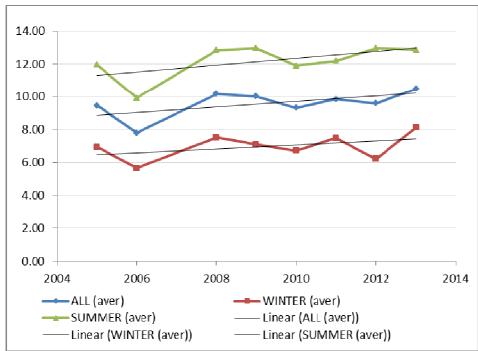


Figure 7: Average annual, summer and winter water temperature ($^{\circ}$ C) at sampling location Trnovo with trendlines



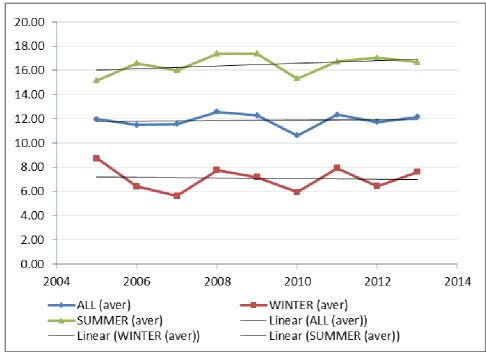


Figure 8: Average annual, summer and winter water temperature (\mathcal{C}) at sampling location Robič with trendlines

4.1.1.2 pH

Average pH values are similar at both sampling locations and vary from 7.75 to 9.0. At sampling site Trnovo, pH is between 7.75 (13.12.2006) and 8.8 (05.09.2012), at Robič site between 7.6 (31.07.2006) and 9.0 (08.03.2012 and 17.04.2012).

4.1.1.3 Electrical conductivity (EC)

EC values recorded in surface water at two sampling locations are presented in Figure 9 and 10. At Trnovo monitoring station EC values are ranging between 132 – 329 μ Scm⁻¹ (on average 224 μ Scm⁻¹), while at Robič monitoring station EC values are on average slightly higher and are ranging between 241 – 345 μ Scm⁻¹ (on average 302 μ Scm⁻¹). Generally, values were at both locations higher in late autumn and winter, and lower in spring and summer. While at Trnovo sampling site slightly decreasing and not significant EC trend occur, at Robič location practically no trend is observed.



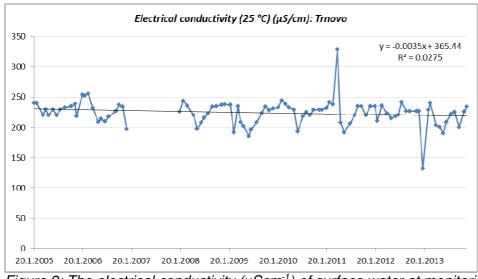


Figure 9: The electrical conductivity (µScm⁻¹) of surface water at monitoring station Trnovo

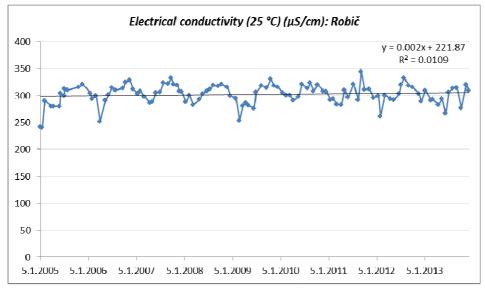


Figure 10: The electrical conductivity (μ Scm⁻¹) of surface water at monitoring station Robič.



4.1.1.4 Suspended solids

The suspended solids in surface water varied from <1.2 to 43 mgl⁻¹ (on average 5.1) at Trnovo monitoring station (Soča river; Fig. 11) and from <1.2 to 33 mgl⁻¹ (on average 2.5) at Robič monitoring station (Nadiža River; Fig. 12). The amount of suspended solids is generally low and shows normal annual fluctuations. Higher values are most probably the result of individual rain events or interventions in the river bed. Therefore, an increase trend of suspended solids is observed at Robič location, while at Trnovo no trend is observed.

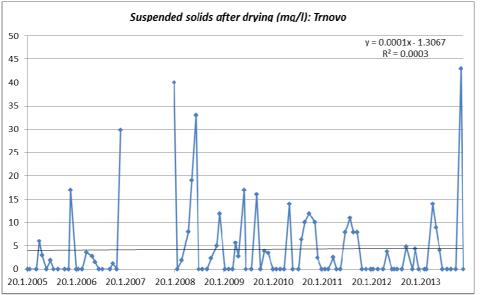
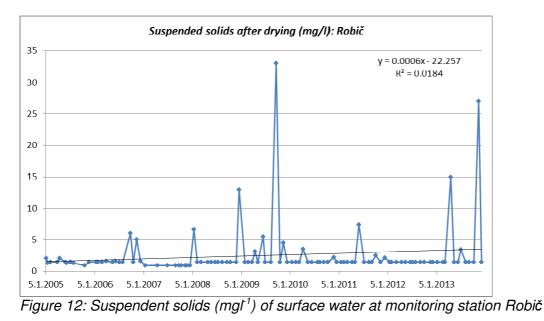


Figure 11: Suspendent solids (mgl¹) of surface water at monitoring station Trnovo





4.1.2 Oxygen regime

4.1.2.1 Dissolved oxygen (DO)

Levels of dissolved oxygen (DO) for surface waters are presented in Figures 13 and 14. DO levels at Trnovo monitoring station ranged from 7.3 mgl⁻¹ to 13.6 mgl⁻¹ (on average 10.3 mgl⁻¹) with the saturation range of 73 to 111 % (on average 92.9 %), respectively. Similarly, DO levels at Robič monitoring station vary from a minimum 6.2 mgl⁻¹ to a maximum 14.1 mgl⁻¹ (on average 9.9) with the saturation range between 72 and 116 % (on average 92.4 %), respectively. The trend of decreasing of DO values is observed at both sampling locations. Generally, higher DO values are during the winter and lower in the warmer months.

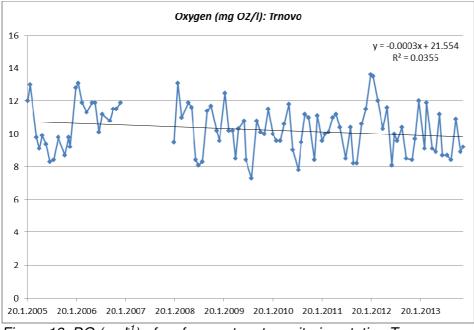
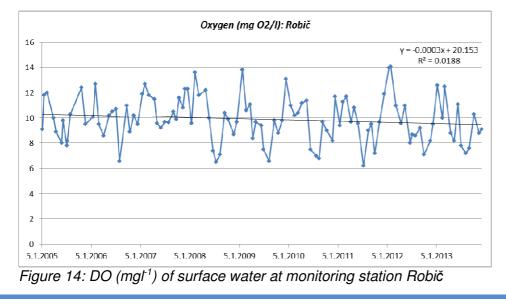


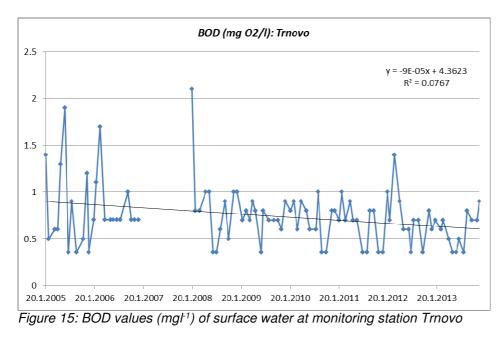
Figure 13: DO (mgl⁻¹) of surface water at monitoring station Trnovo





4.1.2.2 Biochemical oxygen demand (BOD)

The BOD in surface water is presented in Figures 15 and 16. At both monitoring station the BOD range is the same: between <0.5 and 2.1 mgl⁻¹; only average values slightly differ (0.7 mgl⁻¹ at Trnovo and 0.8 mgl⁻¹ at Robič location). General trend of slight BOD decrease was observed for both sampling sites.



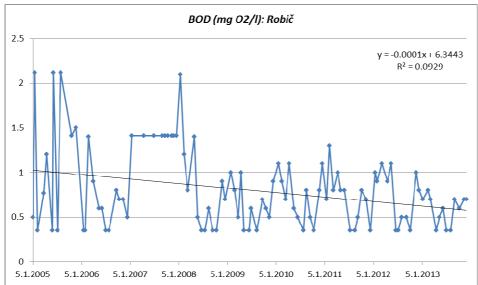


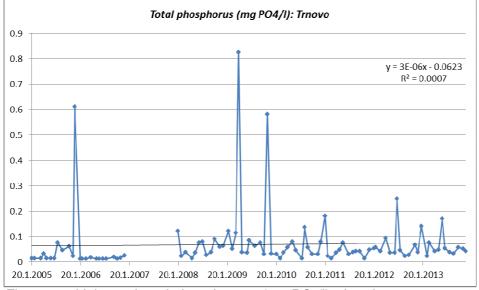
Figure 16: BOD values (mgl¹) of surface water at monitoring station Robič



4.1.3 Nutrients

Concentrations of all measured nitrogen compounds (NO_2^-, NO_4^+) were bellow detection limit, therefore only the values of total phosphorus (PO_4^{3-}) from both sampling locations are presented in Figure 17 and 18.

Generally, PO_4^{3-} concentrations in surface water from both locations are below 0.07 mgl⁻¹. Rather higher phosphorus content was observed three times at Trnovo site: 0.6 mgl⁻¹ (05.12.2005 and 16.11.2009), 0.8 mgl⁻¹ (15.04.2009), and two times at Robič site: 0.4 mgl⁻¹ (05.01.2005 and 16.11.2009).





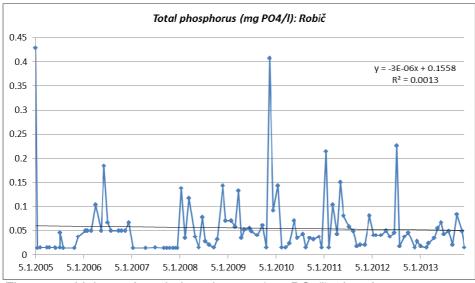


Figure 18: Values of total phosphorous (mg PO₄/I) of surface water at monitoring station Robič



4.2 Groundwater quality

National monitoring of groundwater quality is performed at two locations within the investigated area (Table 1, Figure 4). The location Repec nad Breginjem is located near Nadiža river, and the location Mrzli studenec near Soča river. At the location Repec two measurements per year were done for groundwater quality monitoring in 2007, 2008 and 2012. At location Mrzli studenec two measurements were carried out in 2007 and one in 2008. Due to small number of the results, general trends of presented parameters are not meaningful.

4.2.1 Physical and chemical composition

4.2.1.1 Water temperature

The groundwater temperature at both sampling locations is constant (Figure 19). At Trnovo sampling site the average temperature of groundwater is 9.9 °C and at Mrzli studenec 8.7 °C. There are no significant seasonal fluctuations observed for both monitoring stations also probably due to small number of available data.

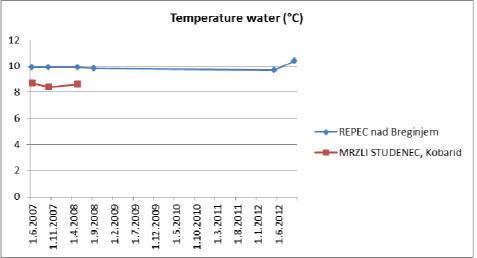


Figure 19: Groundwater temperature ($^{\circ}$ C) at monitoring station Repec nad Breginjem and Mrzli studenec

4.2.1.2 pH and Electrical conductivity (EC)

The pH values are at both monitoring stations are rather constant; at Repec site from 6.9 and 8.0 (on average 7.6) and at Mrzli studenec location from 7.8 to 8.3. The pH values are within the common range of pH for natural waters that is between 5 and 8.5 (Hem, 1985). Similar, also the EC in groundwater is relatively constant; on average 242 μ Scm⁻¹ at Repec site and 219 μ Scm⁻¹ at Mrzli studenec monitoring station (Figure 20). The measured EC values indicate good water quality, which is between 50 and 750 μ S/cm (Saulnier et al., 2011). Both of these parameters indicate natural groundwater conditions (Chapman and Kimstach 1998).



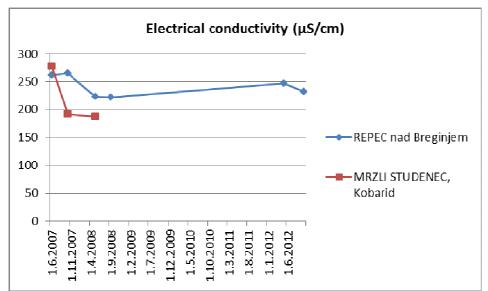


Figure 20: The electrical conductivity (μ Scm⁻¹) of groundwater monitoring stations Repec nad Breginjem and Mrzli studenec

4.2.2 Oxygen regime

4.2.2.1 Disolved oxygen (DO)

The DO levels in sampled groundwater were from 7.6 to 12.0 (on average 10.1 mgl⁻¹) with the saturation range of 62 to 110 % (on average 92.3 %) at Repec nad Breginjem monitoring station. At Mrzli studenec monitoring station measured oxygen was from 11.5 to 12.9 (on average 12.2 mgl⁻¹) with the saturation range of 101 to 111 % (on average 107 %).

4.2.2.3 Redox potential

The values of redox potential are similar and relatively constant at both monitoring stations (Figure 21): on average 424 mV at Repec and 439mV at Mrzli studenec site.



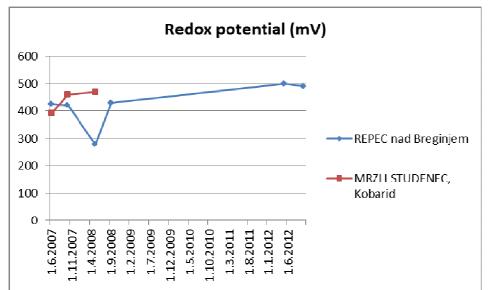


Figure 21: The redox potential (mV) of groundwater monitoring stations Repec nad Breginjem and Mrzli studenec

4.2.3 Total organic carbon (TOC)

The values of TOC are low and on average comparable (0.37 mgl^{-1}) at both monitoring stations (Figure 22): from 0.26 and 0.54 mgl⁻¹ at Repec nad Breginjem site and from 0.28 and 0.45 mgl⁻¹ at Mrzli studenec.

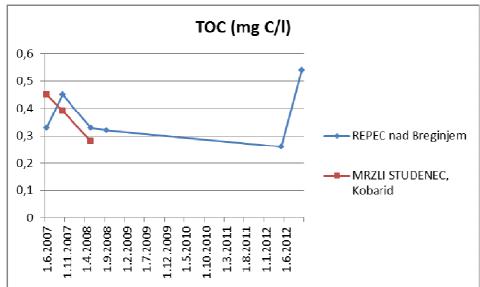


Figure 22: The TOC (mgl¹) of groundwater monitoring stations Repec nad Breginjem and Mrzli studenec



4.2.4 Nutrients

Concentrations of phosphorus compounds in groundwater were bellow detection limit, therefore only the values of nitrate (NO₃⁻) from both sampling locations are presented in Figure 23. The NO₃⁻ values from both locations were low and varied between 3.0 and 4.5 mgl⁻¹ (on average 3.6 mgl⁻¹) at Repec nad Breginjem site, and from 3.1 to 3.4 mgl⁻¹ (on average 3.2 mgl⁻¹) at Mrzli studenec location. All measured nitrate values are significantly below the water quality standard level according Decree of groundwater status (2009b) and drinking water proposals according Rules of drinking water (2004).

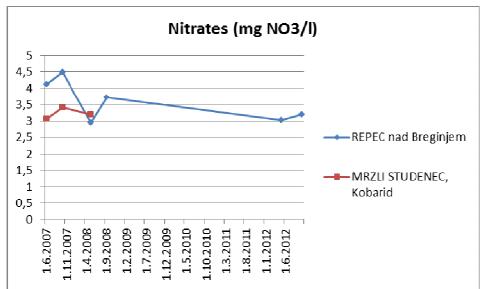


Figure 23: The nitrates concentartion (mgl¹) of monitoring stations from Repec nad Breginjem and Mrzli studenec locations.

4.2.4 Cations and anions

Concentrations of major cations and anions in groundwater are presented in Table 2. Dominated ions are HCO_3^- and Ca^{2+} ions and therefore groundwater belongs to $Ca - HCO_3$ hydrogeochemical type. This type of water reflects the dissolution of carbonate minerals within the aquifer of limestone composition. Besides, the Mg^{2+}/Ca^{2+} molar ratio (3.6-5.1) indicates that calcite weathering is the major source of solutes within the aquifer, which coincides with water type results typical of limestone. All other ions are presented in relatively low concentrations. The geochemical composition of the groundwater from two monitoring stations is presented in the Piper diagram (Figure 24).



Samlping location	Date	Hydrogen carbonates	Sulphates	Chlorides	Calcium	Magnesium	Sodium	Potassium	Calcium	Magnesium	Mg/Ca
		mg HCO3/I	mg/l	g/l mg/l		mg/l	mg/l	mg/l	mg/l	mg/l	
REPEC nad Breginjem	8.6.2007	182	4.09	0.86	49.2	8.2	1.90	0.20	49.2	8.2	3.6
REPEC nad Breginjem	23.10.2007	185	3.43	0.78	49.6	8.3	2.20	0.24	49.6	8.3	3.6
REPEC nad Breginjem	22.5.2008	158	3.10	0.74	44.0	5.6	0.97	0.10	44.0	5.6	4.8
REPEC nad Breginjem	18.9.2008	184	2.85	0.66	49.0	7.4	1.70	0.20	49.0	7.4	4.0
REPEC nad Breginjem	24.5.2012	182	2.91	0.62	50.0	7.8	1.60	0.21	50.0	7.8	3.9
REPEC nad Breginjem	18.10.2012	166	2.72	0.68	46.0	5.5	0.84	0.13	46.0	5.5	5.1
MRZLI STUDENEC, Kobarid	8.6.2007	127	2.10	0.70	36.7	5.5	0.46	0.14	36.7	5.5	4.0
MRZLI STUDENEC, Kobarid	30.10.2007	129	2.21	0.62	35.1	6.0	0.47	0.15	35.1	6	3.5
MRZLI STUDENEC, Kobarid	26.5.2008	126	2.41	0.66	35.0	4.3	0.45	0.11	35.0	4.3	4.9

Table 2: Concentrations of major ions in groundwater at two monitoring stations

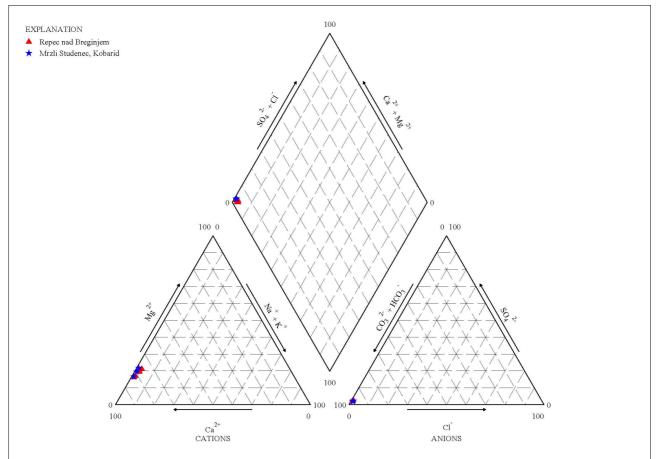


Figure 24: The Piper diagram of groundwater samples from Repec nad Breginjem and Mrzli studenec monitoring stations.

4.4 Microbiological parameters

Microbiological conditions of presented groundwater samples were on the whole good. The results of total *Coliforms*, faecal *Coliforms* and faecal *Streptococci* were entirely below the detection limit (none present).



4.5 Metals

In Figure 25 selected metals in groundwater are given that show the values above the detection limit. The concentrations of the remaining metals were below the detection limit. The values of all presented metals are significantly below the proposed concentrations for drinking water according Rules of drinking water (2004) suggesting good quality status of groundwater within test area.

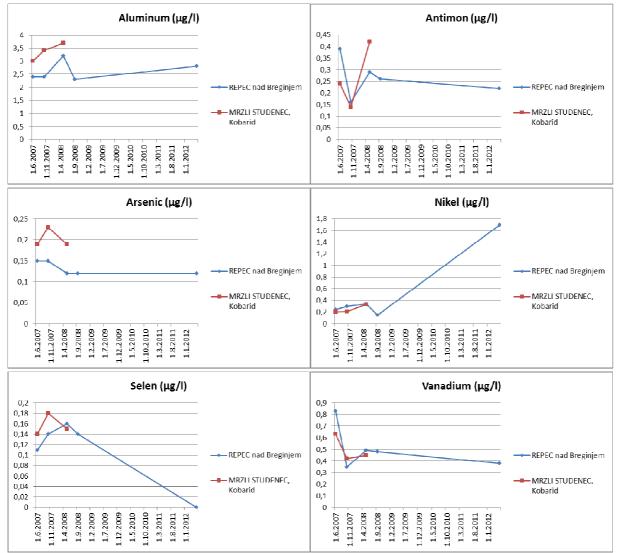


Figure 25: Concentrations of selected metals in groundwater samples from Repec nad Breginjem and Mrzli studenec monitoring stations.



4.6 Organic compounds

The values of all measured organic compounds were below the detection limit of the method used suggesting the absence of potential organic pollutants within the observed groundwater body.

5 Water quality assessments

Water quality assessments for surface and groundwater in test areas was evaluated according valid national regulations that determine the maximum permissible levels of certain substances in water; Decree on groundwater status (2009a), Decree on surface water status (2009b) and Rule on drinking water (2004).

All above described quality parameters show values much below the permissible levels suggesting good quality status of described surface waters and graoundwaters. The water quality state of particular area is very connected to the land use and human activities in the area (industry, agriculture, etc.) as well as to natural characteristics of the environment (geological properties, climate etc.). Therefore, changes in the physical-chemical characteristics of surface and groundwater are influenced by both, natural and anthropogenic factors.

Investigated area represents less populated foothill area mostly covered with grassland and forests (Figure 26). Human activities occur only in settlements and do not affect the quality of the aquifer. On lowland and highland pastures grazing is present. These unnatural impacts in combination with favourable natural characteristics (carbonate lithology, steep topography and relatively large amount of rainfall) influence positively on surface and groundwater quality status of this area.



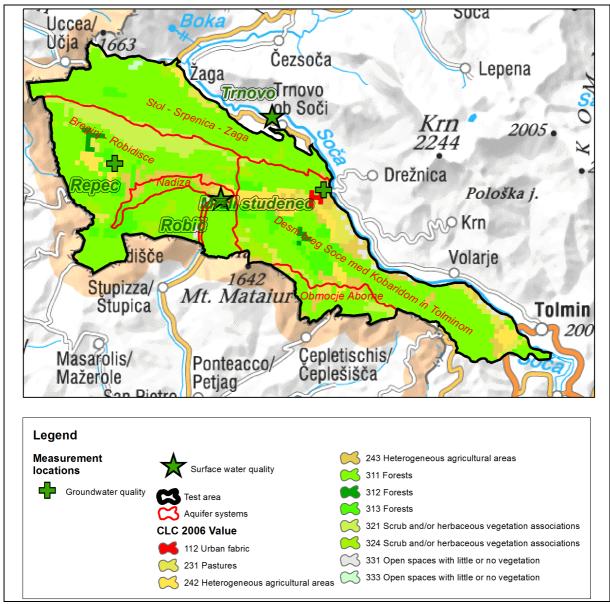


Figure 26: The CLC (2006) categories within of test area



6 Conclusions

The physical and chemical parameters of surface and groundwater show the characteristics of natural conditions and also possible locally human impacts of the area that are practically absent within test area. All measured parameters (pH, EC, oxygen regime, TOC, nutrients, microbiology, and metals) indicate that surface water and groundwater in test areas are not polluted and have a good chemical status. Groundwater belongs to Ca - HCO₃ hydrogeochemical type.

National surface and groundwater quality monitoring in test areas in NW Slovenia (Kobariški stol and Mia - Matajur aquifers) shows good quality status. Therefore these trans-boundary aquifers present a potential for drinking water supply.



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Water quality analysis and trends on test area in northwestern Slovenia - Ljubljana, December 2014





The project is co-funded by the European Union, Instrument for Pre-Accession Assistance Water quality analysis and trends on test area Northern Istria springs Gradole, Sv. Ivan and Bulaž (Croatia)

> Faculty of Civil Engineering University of Rijeka (FB8)

Lead Author/s	Barbara Karleuša, Goran Volf
Lead Authors Coordinator	
Contributor/s	Ivana Radman
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1. Introduction

In this report water quality data analyses and trends are presented for Croatian test area in northern Istria that includes karstic springs: Sv. Ivan, Bulaž and Gradole, within DRINKADRIA project.

Water quality analyses are based on Public Health Institute of Istrian Region reports [1-11] and on data obtained from Croatian Waters for the period 2003 -2013. The Water quality monitoring programe refers to all natural resources of water which are used in water supply systems of Istrian Region and to all natural resources which can be included in supply systems if necessary.

For public water supply, in Croatia, drinking water quality standards are regulated since 2013 by:

- Act on water intended for human consumption (Official gazette 056/2013; orig. Zakon o vodi za ljudsku potrošnju) [12] and
- Regulation on compliance parameters and analysis methods for water intended for human consumption (Official gazette 125/2013, 141/2013, orig. *Pravilnik o parametrima sukladnosti i metodama analize vode za ljudsku potrošnju*) [13].

Before these regulations the old *Regulation on the health safety of drinking water* (Official gazette 182/2004 and 047/2008; *orig. Pravilnik o zdravstvenoj ispravnosti vode za piće*) [14] was in use.

Quality standards for water resources used for drinking were regulated, until 01/01/2011, with:

- Decree on water classification (Official gazette 077/1998, 137/08; orig. Uredba o klasifikaciji voda) [15] and
- Decree on hazardous substances in water (Official gazette 078/1998, 137/08; orig. Uredba o opasnim tvarima u vodama) [16].

These regulations were put out of force by *Decree on water quality standards* (Official gazette 89/2010, last version from Official gazette 73/13, orig: *Uredba o standardu kakvoće voda*) [17].

Regulation on the health safety of drinking water had standards in the form of Maximum Allowable Concentrations (MAC).



On the basis of *Decree on water classification* [15] water resources quality was assessed and water resources were classificated in 5 categories depending on conditions for water use for specific purposes. The clasification was done in regard to limit values of individual groups of indicators, which characterize the sources and causes of water pollution.

2. Test areas and water quality parameters

Istrian Region has three water supply systems: Istrian water supply system Buzet, Labin water supply system and Pula water supply system. Test areas in Istria (Croatia) within DRINKADRIA project are Istrian water supply system Buzet springs: Sv. Ivan, Bulaž and Gradole (see *Figures 1, 2, 3 and 4*).

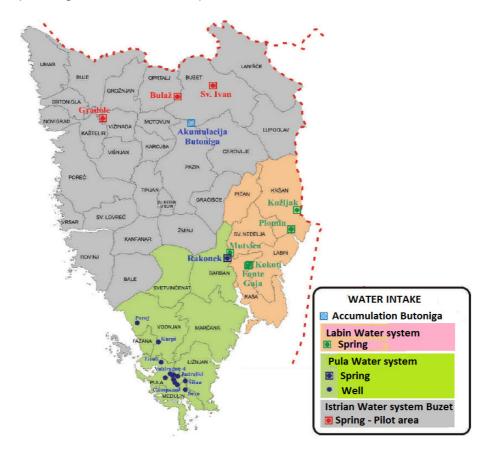


Figure 1: Monitoring stations for water resources used for water supply in Istrian Region [11]



On test areas the following water quality parameters were monitored [1-11]:

- Organoleptic properties of water (color, odour and flavour);
- Physical and chemical properties: temperature, pH, alkalinity, total hardness, electrical conductivity, total solids dried at 105°C, suspended solids;
- lons: fluoride, chloride, sulfate, sodium, potassium, calcium, magnesium, dissolved silica, total cyanides;
- Oxygen: dissolved oxygen and oxygen saturation, COD-permanganate index, BOD₅;
- Nutrients: nitrogen compounds (ammonia, nitrites, nitrates, organic N, Kjeldahl N and total N) and phosphorus compounds (orthophosphate and total phosphorus);
- Organic matter: anionic detergents (MBAS index), non-anionic detergents, total phenols expressed as an index, mineral oils, total organic carbon (TOC), volatile organic hydrocarbons, organochlorine pesticides, pesticides-herbicides and organophosphorus (only in the program of Croatian Waters), alachlor and pentachlorophenol (only in the program of Croatian Waters), polycyclic aromatic hydrocarbons (PAH);
- Heavy metals (cadmium, copper, zinc, iron, manganese, total chromium, lead, mercury, nickel, arsenic and aluminum);
- Bacteriological indicators (total coliforms, fecal coliforms and/or *Escherichia coli*, fecal streptococci (enterococci), the number of bacteria at 37°C and *Clostridium perfringens* and *Pseudomonas aeruginosa* (only in the program of Istrian Region).



Figure 2: Spring Sv. Ivan





Figure 3: Spring Bulaž



Figure 4: Spring Gradole

The monitoring frequency (number of samples per year) depends on tested water quality parameter, usually from 2 to 13 times per year. But for most of the parameters is 12 times per year according to the program of Croatian Waters.

Relevant values were calculated from annual data measurements and compared with the permitted values of indicators. Calculation of relevant values depended on the number of data. For a number of data of 12 or more, the relevant value is calculated as the value of 90% of percentiles (except for biological indicators, dissolved oxygen and oxygen saturation). When the number of data is less than 12, the relevant value was calculated as



the median value (including biological basis), while the dissolved oxygen and oxygen saturation were taken as the relevant value of 10% of percentile, regardless to the number of data.

In case of karst springs like Sv. Ivan, Bulaž and Gradole, it has to be taken in consideration one limitation of the monitoring program that can bring different (usually better) picture on ground water quality. The karst springs are very sensitive to sudden changes in the hydrological regime. In case of intensive rainfall in the catchment area of each spring high water turbidity, large amounts of suspended solids and a very strong microbiological contamination occurs. Such events occur at intervals from few times a month to several times a year and their impact on water quality is significant though short-lived (a few hours to several days). These phenomena are not detected during regular monitoring (as in the days of such occurrence there is no sampling), but can be detected by frequent analyses that can be done by the Water Utility laboratory.

7



3. Water quality analysis results and trends

3.1. Physical and chemical composition

Basic physical-chemical and geo-chemical properties of spring waters do not show significant deviations except in normal annual fluctuations when depending on hydrological conditions in the catchment. Changes that are not caused by hydrological conditions may indicate flows of water with different mineral origin [10].

The impact of rainwater or surface flood waters during periods of intensive rainfall on springs is generally measurable, which can be manifested as a decrease in the value of electrical conductivity.

On *figures 5* and *6* monthly measured values for total suspended solids and turbidity on test area in period 2006-2013 are shown.

On *figure 7* mean annual values for total suspended solids (TSS) on test area in period 2003-2013 are shown.

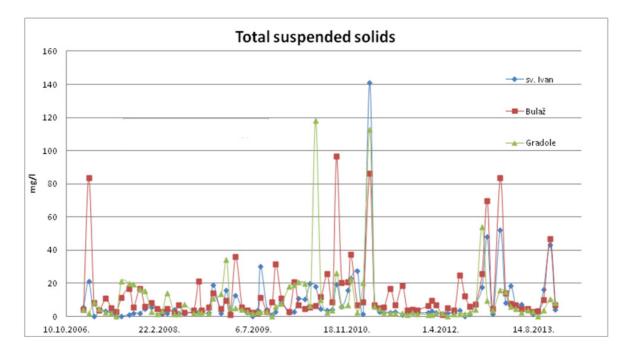


Figure 5: Total suspended solids (TSS) on test areas measured once a month (Limit value is 10 mg/l)



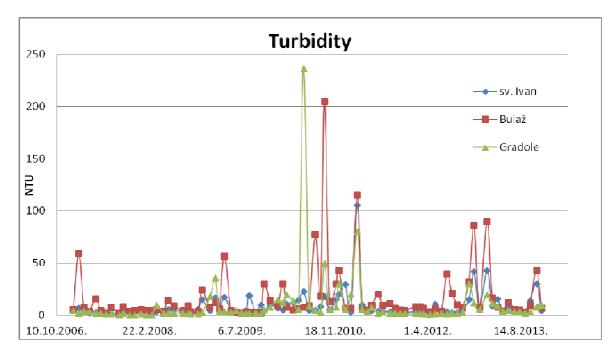


Figure 6: Turbidity on test areas measured once a month (Limit value is 4 NTU)

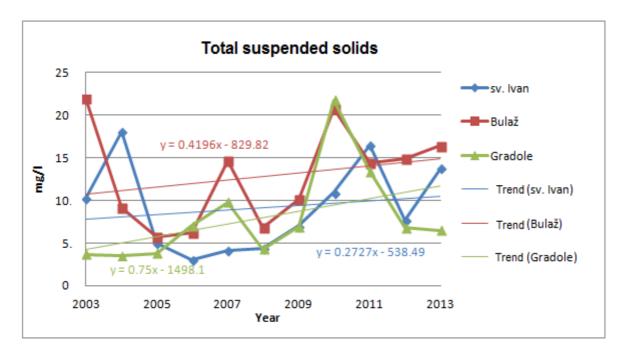


Figure 7: Mean annual values for total suspended solids (TSS) on test areas



3.2. Oxygen regime

All springs are well saturated with oxygen, owing to the well-developed underground relief.

On *figures 8* and *9* mean annual values for Biological oxygen demand-BOD₅ and Chemical oxygen demand-COD on test area in period 2003-2013 are shown.

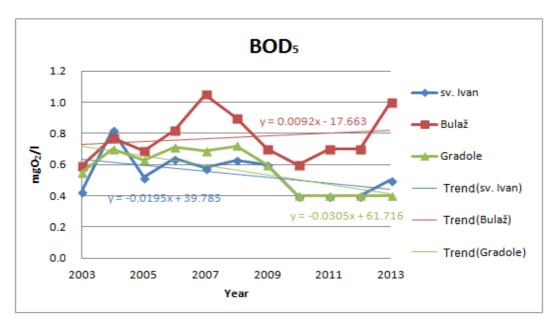


Figure 8: Mean annual values for BOD5 on test areas

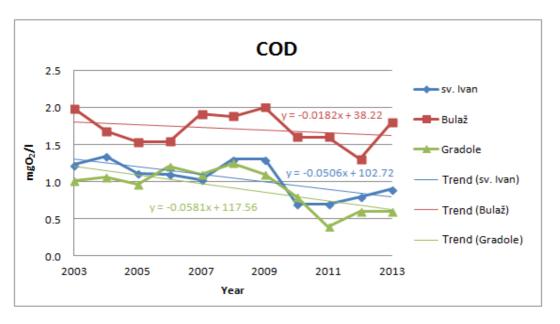


Figure 9: Mean annual values for COD on test areas



3.3. Nutrients

Nutrients are compounds of nitrogen and phosphorus. For all springs phosphates and total phosphorus are very low. On *figure 10* mean annual values for total phosphorus are shown; it can be seen that the trend is decreasing on all springs.

The largest contribution to the total nitrogen is from inorganic content of nitrogen due to the nitrate content. Generally the content of the inorganic nitrogen is almost all composed of the nitrates, which means that the content of ammonium and nitrite, as indicators of present fresh contamination is very low and very rarely appears in detectable low concentrations. Nitrate content on springs that drain water from Ćićarija Mountain and the northern part of Istria (Sv. Ivan and Bulaž) is low. Due to the more developed agricultural activities in the catchment of spring Gradole which drains water from the inlands of Istria the content of nitrate is higher (*Figure 11*). But on all springs during last years there is a decreasing trend, although up to year 2007 there was an increasing trend for total N and nitrates (*Figures 12, 13 and 14*) [5].

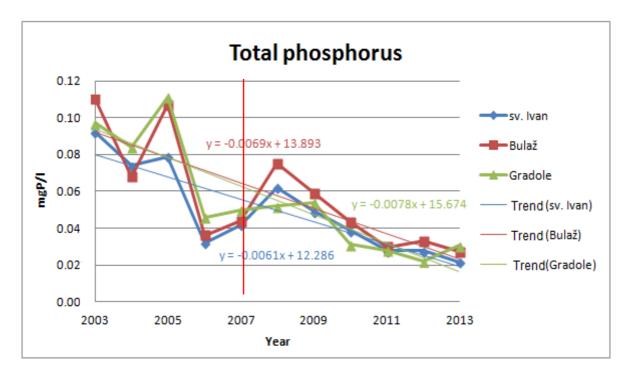


Figure 10: Mean annual values for total phosphorus on test areas from 2003-2013



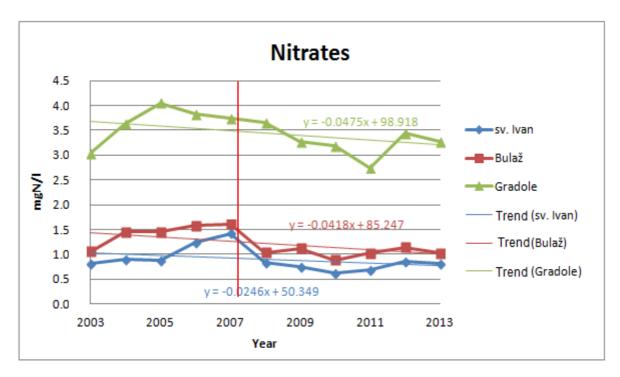


Figure 11: Mean annual values for nitrates on test areas from 2003-2013

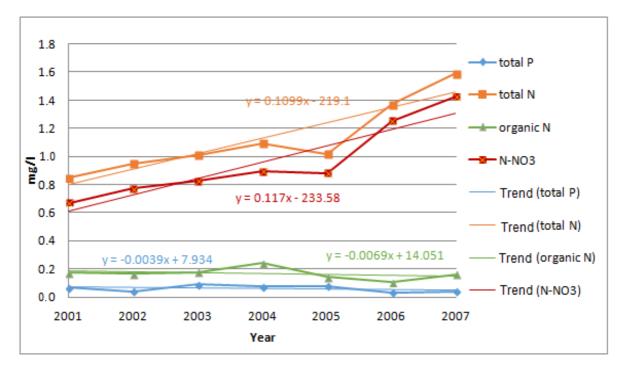


Figure 12: Mean annual values of total nitrogen, organic nitrogen, nitrates and total phosphorus for 2001-2007 for spring Sv. Ivan [5]



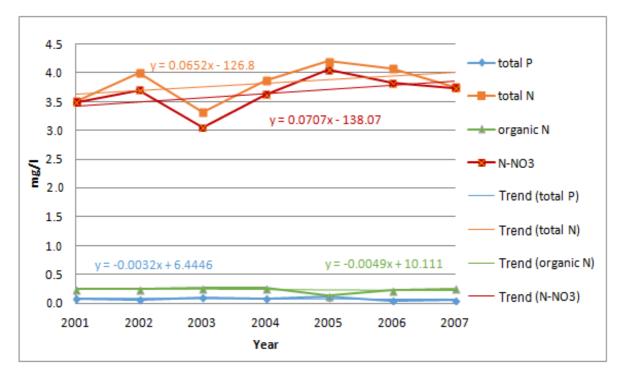


Figure 13: Mean annual values of total nitrogen, organic nitrogen, nitrates and total phosphorus for 2001-2007 for spring Gradole [5]

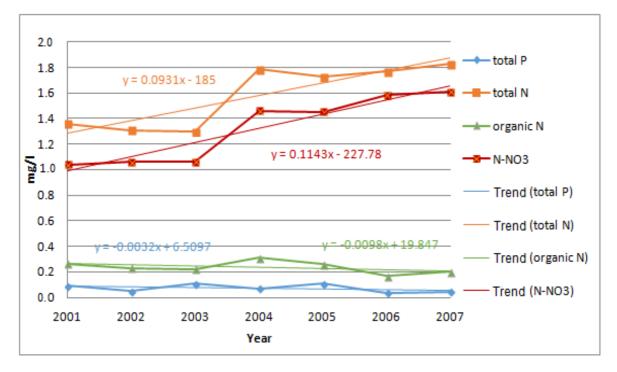


Figure 14: Mean annual values of total nitrogen, organic nitrogen, nitrates and total phosphorus for 2001-2007 for spring Bulaž [5]

3.4. Microbiological parameters

Microbiological contamination is present at all springs and is associated to the hydrological conditions in the watersheds. High values are associated with the occurrence of torrential waters and increased amounts of silt which is entering in the aquifers. Due to turbulent flow of water, move of the internal sediment occurs and then results with the appearance of turbidity.

Higher concentrations of total number of microorganisms and microorganisms of fecal origin were observed also at all springs, but occasionally and depending on different hydrological conditions. The source of these organisms can be wild animals or livestock in the watershed areas of springs, but mostly the main sources are untreated urban waste waters from settlements in the observed watersheds.

3.5. Metals

Due to occurrence of extreme turbidity (above 180 mgSiO₂/l or more) increased concentrations of iron and manganese occur in natural waters which are above the Maximum Allowable Concentration (MAC) for drinking water. This refers to the springs of Sv. Ivan, Bulaž, Gradole. On *figure 15* changes in metal concentrations due to turbidity on spring sv. Ivan for 2004 are shown [2].

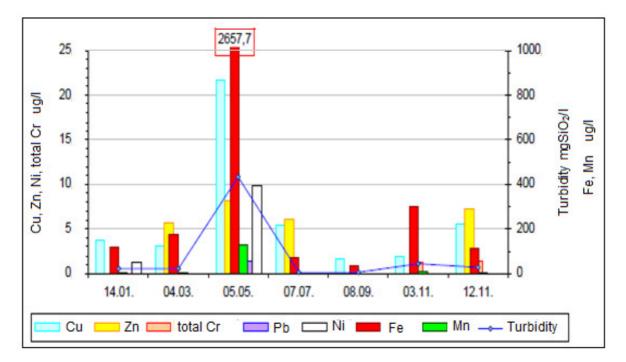
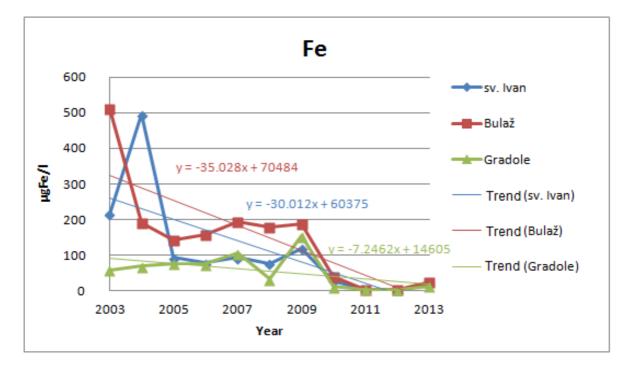


Figure 15: Changes in metal concentrations due to turbidity on spring Sv. Ivan for year 2004 [2]



On *figures 16 and 17* mean annual values for Iron - Fe and Manganese - Mn on test area springs in period 2003-2013 are given.

Figure 16: Mean annual values for Iron - Fe on test areas

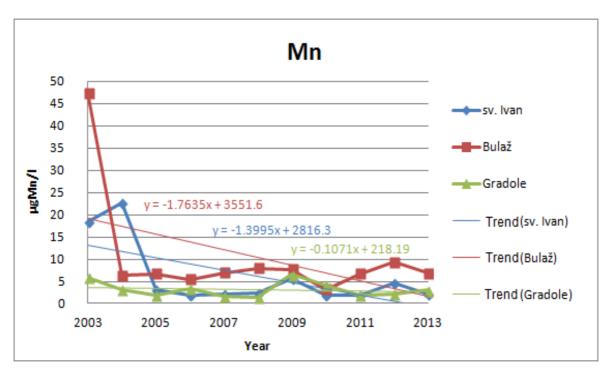


Figure 17: Mean annual values for Manganese - Mn on test areas



Note on purification technology:

At springs Sv. Ivan and Gradole procedures of sedimentation, filtration and disinfection are used. With use of sedimentation procedure and water filtration suspended solids are removed, and also with these procedures the concentrations of metals are reduced (in particular iron and manganese which exceed MAC) and lipophilic substances, including mineral oils (hydrocarbons) to the values that satisfy drinking water standards [9].

3.6. Organic compounds

In spring waters concentrations of organic compounds (generally hydrocarbons of mineral origin, volatile hydrocarbons, polyaromatic hydrocarbons, organochlorine pesticides, some organophosphorus pesticides) and other tested chemicals as phenols, cyanides, anionic and non-anionic surfactants are not detected measurable.

4. Water quality assesment

Water quality assessment in Public Health Institute of Istrian Region reports was conducted according to the *Regulations on the health safety of drinking water* [14] for each year so the assessment of water resources quality according to the regulations for drinking water refers to all measured values compared to the Maximum Allowable Concentration (MAC) for drinking water, which is at the same time indicator for the substances which should be removed from the water, or with proper technological process of purification their values should be reduced to the values that are below the prescribed Maximum Allowable Concentration of certain substances.

In tables 1, 2 and 3 all parameters that describe a certain substance or group of substances that have exceeded the MAC at each sampling station - spring are given.

Analysis of the quality of springs Sv. Ivan, Bulaž and Gradole by the individual indicators was done for all measured values during the year and MAC defined in regulations.

Table 1. Parameter evaluation of water resources according to the health criteria of drinking water - parameters with measured values above the MAC in period 2003 - 2013 on spring Sv. Ivan

Year	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013
Parameter	2003	2004	2005	2000	2007	2000	2009	2010	2011	2012	2013
Turbidity	X	X	X	X	X	X	X	X	X	X	X
Iron	X	X									
Manganese	X	X									
Microbiological	X	X	X	X	X	X	X	X	X	X	X

X – Parameters with value above MAC

Table 2. Parameter evaluation of water resources according to the health criteria of drinking water - parameters with measured values above the MAC in period 2003 - 2013 on spring Bulaž

Year Parameter	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013
Turbidity	X	X	X	X	Х	X	X	X	X	X	Х
Iron	X	X	X	X	X	X	X				
Manganese	X										
Microbiological	X	X	X	X	X	X	X	X	X	X	X

X – Parameters with value above MAC

Table 3: Parameter evaluation of water resources according to the health criteria of drinking water - parameters with measured values above the MAC in period 2003 - 2013 on spring Gradole

Year	2002	2004	2005	2006	2007	2002	2009	2010	2011	2012	0010
Parameter	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013
Turbidity	X	X	X	X	X	X	X	X	X	X	X
Iron			X	X	X		X				
Microbiological	X	X	X	X	X	X	X	X	X	X	X

X – Parameters with value above MAC

Waters according to the limit values of indicators under the old regulations *Decree on water classification* [15] (that was replaced on 1 January 2011 with *Decree on water quality standards* [17]) were classified in the categories from 1 (the best) to 5 (the worst) depending on conditions for water use for specific purposes:

Category 1 - Groundwater and surface water which ih it's natural state or after desinfection can be used for drinking or in food industry, and surface waters that can be used for high quality fish farming (trouts).

Category 2 – Water resources which in it's natural state can be used for bathing and recreation, water sports and other fish farming (cyprinidae) or that can be used for drinking or other purposes in industry after the appropriate treatment.

Category 3 - Water which can be used in industries which do not have specific requirements for water quality and in agriculture. These waters need to be treated to be used for certain purposes.

Category 4 - Water that can be used only after treatment in areas with severe shortage of water.

Category 5 – Water which can hardly be used for any purpose, because it does not meet the criteria under this Regulation.

All the groundwater used for water supply should be of the first (1) category. Classification was done for springs Sv. Ivan, Gradole and Bulaž on the basis of comparing the calculated relevant values and values in the range specified for each category of water for each indicator (Table 4).

Table 4: Evaluation of water resources according to Decree on water classification [15] forperiod 1997-2008

Indicator/Spring	Sv.Ivan	Gradole	Bulaž
A: physical and chemical parameters	1-2	2	1-2
B: oxygen regime indicators	1	1-2	1-3
C: nutrients	2	3	1-2
D: biological and microbiological indicators	2-3	2-3	2-3

The new *Decree on water quality standards* [17] which is in compliance with EU regulations separates the classification of surface and ground waters as well as coastal sea.

For the ground waters indicators that are monitored under the surveillance monitoring are: dissolved oxygen, pH, conductivity, nitrates, ammonium, active substances in pesticides and chosen additional parameters that indicate the impact of pollution, and that are important for protection measures. According to monitoring data an assessment on the state of groundwater body is provided, which has only two grades: **good** or **bad**. The assessment for springs Sv. Ivan, Gradole and Bulaž according to new Decree on water quality standards (based only on chemical parameters) after 2011 is good status.



5. Conclusions

All springs are well saturated with oxygen, owing to the well-developed underground relief. The content of the substance that can be oxidized and decomposed by microorganisms (expressed as a five-day biochemical oxygen demand-BOD₅) or by using a strong oxidant (expressed as a chemical oxygen demand-COD permanganante index), is very low.

For all springs phosphates and total phosphorus are very low.

The largest contribution to the total nitrogen is from inorganic content of nitrogen due to the nitrate content. Generally the content of the inorganic nitrogen is almost all composed of the nitrates, which means that the content of ammonium and nitrite, as indicators of present fresh contamination is very low and very rarely appears in detectable concentrations. Nitrate content on springs that drain water from Ćićarija Mountain and the northern part of Istrian peninsula (Sv. Ivan and Bulaž) is low. Due to the more developed agricultural activities in the catchment of spring Gradole which drains water from the interior of Istrian peninsula content of nitrate is higher. But on all springs in last years we have a decreasing trend, although up to year 2007 we have increasing trend for total N and nitrates. All values are bellow MAC for drinking water.

Nutrient content is shown through the content of nitrates and total phosphorus. For all springs maximum values of these indicators have decreasing trend. The values of total nitrogen are several times below the MAC (Maximum Allowable Concentration) for drinking water (for nitrate content is 50 mg/l and 11.3 mgN/l). Phosphorus content is generally below the MAC for drinking water for dissolved phosphates.

Microbiological contamination is present on all springs which is associated to the hydrological conditions in the watersheds. High values are associated with the occurrence of torrential waters and increased amounts of silt which is entering in the aquifers. Due to turbulent flow of water, move of the internal sediment occurs and then results with the appearance of turbidity.

Higher concentrations of total number of microorganisms and microorganisms of fecal origin were observed also on all springs (at least occasionally). The source of these organisms can be wild animals or livestock which moves in the watershed areas of springs, but mostly the main sources are untreated urban waste waters from settlements in the observed watersheds.

Due to occurrence of extreme turbidity increased concentrations, above the MAC for drinking water, of iron and manganese occur.



From observed mean annual values of BOD₅, COD, total suspended solids, nitrates, total phosphorus, iron and manganese it can be concluded that: on spring Sv. Ivan all tested parameters have declining trend only TSS have slightly increasing trend, on the spring Bulaž there are slightly increasing values of BOD₅ and TSS, and at spring Gradole increasing trend is only for TSS. However, the content of TSS depends primarily on hydrological conditions in the basin, on the amount and intensity of rainfall, so this should not be considered as an indicator of pollution.

From the analysis of the water quality for springs Sv. Ivan, Bulaž and Gradole can be concluded that the values of nearly all indicators are decreasing, respectively as the quality of the water on springs improves.

6. References

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- [2] The quality of the natural resources of water involved in water supply in the County of Istria in 2004 (orig: Kakvoća prirodnih resursa voda uključenih u vodoopskrbu u Istarskoj županiji u 2004. godini), 2005, Zavod za javno zdravstvo Istarske županije.
- [3] The quality of the natural resources of water involved in water supply in the County of Istria in 2005 (orig: Kakvoća prirodnih resursa voda uključenih u vodoopskrbu u Istarskoj županiji u 2005. godini), 2006, Zavod za javno zdravstvo Istarske županije.
- [4] The quality of the natural resources of water involved in water supply in the County of Istria in 2006 (orig: Kakvoća prirodnih resursa voda uključenih u vodoopskrbu u Istarskoj županiji u 2006. godini), 2007, Zavod za javno zdravstvo Istarske županije.
- [5] The quality of the natural resources of water involved in water supply in the County of Istria in 2007 (orig: Kakvoća prirodnih resursa voda uključenih u vodoopskrbu u Istarskoj županiji u 2007. godini), 2008, Zavod za javno zdravstvo Istarske županije.
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- [15] Decree on water classification (Official gazette 077/1998, 137/08; orig. Uredba o klasifikaciji voda)
- [16] Decree on hazardous substances in water (Official gazette 078/1998, 137/08; orig. Uredba o opasnim tvarima u vodama)
- [17] Decree on water quality standards (Official gazette 137/13, orig: Uredba o standardu kakvoće voda).







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Water quality analysis and trends on pilot areas in Southern Dalmatia – Croatia

Croatian Geological Survey (FB9)

Lead Author/s	Jasmina Lukač Reberski	
Lead Authors Coordinator	Josip Terzić	
Contributor/s	Tihomir Frangen, Josip Terzić	
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1. INTRODUCTION

This report presents results of hydrochemical analysis and trends of the most important parameters related on water quality on the two pilot areas in southern Dalmatia. The main focus in hydrogeochemical investigations and monitoring was on test area of spring Prud because its catchment is significantly larger and much more important for water supply than Blatsko polje. The majority of water quality data at Blatsko polje test area were collected during earlier research conducted as a part of the CC-WaterS project in Croatia. For the purpose of better defining hydrogeological characteristics of spring Prud catchment area, stable isotopic composition of hydrogen and oxygen ($\delta^{18}O$ and $\delta^{2}H$) were monitored monthly at observed springs. Analyzes of stable isotopes were made on the high precision isotope water analyzer Picarro L-2130i purchased within the DRINKADRIA project.

Investigated areas are located in the karst terrain which is known for its unpredictability. Groundwater in karst terrains can dramatically and rapidly fluctuate in response to surface events, even from very distant areas. Very fast infiltration and water transport mechanisms typical for karst water systems makes karst groundwater particularly sensitive to contamination.

One of the world's biggest problem is pollution of groundwater and aquifers. This may be linked to a lack of proper management of urban and industrial wastewater or agricultural runoff water-potentially giving rise to long term exposure to pollutants, which can have a range of serious health implications. Or it may be linked to naturally occurring constituents, which cause deterioration of health. There are many negative examples related on water pollution all around the world. Once groundwater and aquifer become contaminated, satisfying remediation can be extremely difficult and expensive, especially for drinking water supply. It is therefore of great importance to react in time to prevent negative trends of water quality and to keep safe levels of chemical contaminants in drinking water.

Several law regulations related to the safe use of drinking water are currently in use in Croatia. These are: Act on water intended for human consumption (Official gazette 056/2013) and the Regulation on parameters compliance and analysis methods for water intended for human consumption (Official gazette 125/2013, 141/2013). More detailed explanation of the regulations is given in the report for the pilot area of northern Istria.



2. PILOT AREAS AND TESTED WATER QUALITY PARAMETERS

There are two pilot areas in southern Dalmatia (Fig.1):

- 1. Prud spring catchment area and neighboring catchments (continental part)
- 2. Blatsko polje on the Korčula island (island part)

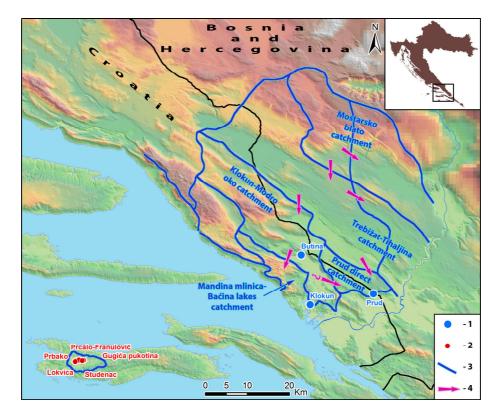


Figure 1 Locations of the pilot areas with positions of sampled springs and wells. Legend: 1 Spring, 2 Well, 3 Groundwater divide, 4 Groundwater flow direction.

The Prud spring catchment is located in continental part of southern Croatian, while the second pilot area is located on the island in the Adriatc sea (pilot areas represent catchments marked with blue line on Fig 1). Island area is significantly influenced by the sea water.

Prud spring is a few km from the sea and is located at low altitude (groundwater level in the sinkhole from which water is discharged at the spring is 1,6 m a.s.l. (Štambuk Giljanović, 2003).



Prud is the largest spring in that area (according to available data about 3 m³/s) which is exstracted for the regional Neretva-Peljesac-Korčula water supply system (Slišković et al., 1998). Prud spring catchment is a part of large hydrogeological system that consists of several subcatchments. Surface area of whole chatchmant is about 1500 km², while direct Prud spring catchment area is about 100 km². In addition to Prud, springs in neighboring catchments have been observed and sampled. In this report results of water quality for the springs Prud, Klokun and Butina will be presented. Among all observed springs, these are selected for presentation in this report because they are extracted for water supply.

Test area Blatsko polje is located in the most western part of the island Korčula, about 1,3 km away from the sea. The Blatsko polje covers about 3 km², and the area of hydrogeological catchment is 28,4 km² (Rubinić et al. 2011). Blatsko polje is the lowest polje on island. Catchment altitude ranges from 5,2 m a.s.l.(Blatsko polje) to 388 m a.s.l. It collects water from few smaller poljes and surrounding area. There are four public extraction sites (wells) used for this part of the island Korčula. Most important well today is Studenac, situated in eastern part of polje close to estavelle Mali Studenac. It extracts above 50 L/s even during dry season. Other wells (Gugić, Franulković and Prbako) participate in public water supply with up to 15 L/s.

3.LAND USE OF STUDIED CATCHMENT AREAS

Land use maps shows the human use of land, such as settlements and seminatural habitats such as arable fields, pastures, and managed woods. It also has been defined as the arrangements, activities and inputs people undertake in a certain land cover type to produce, change or maintain it (Watson et al., 2001). Land use and land management practices have a major impact on natural resources including water. Land use information can be used to recognize possible impacts on groundwater quality and to develop solutions for natural resource management issues such as salinity and water quality. Land use maps have been made based on Corine Land Cover 2006 showing land use on the pilot areas.

Water quality analysis and trends on pilot areas in Southern Dalmatia



3.1 CONTINENTAL PILOT AREA

Land use map shows that the continental pilot area is almost equally covered by forest and agricultural areas (Fig. 2, Tab. 1). Agricultural activities are intensive in catchment area of Prud and neighboring catchments, especially in Vrgoračko polje and Neretva valley, known for its production of strawberries and mandarins. The whole area is sparsely populated, with small dispersed settlements.

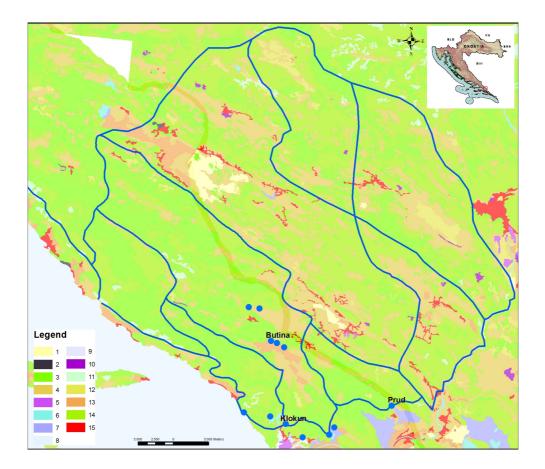


Figure 2 Prud catchment area land use map based on Corine Land Cover 2006. Legend: 1 Arable land 2 Artificial non-agricultural vegetated areas 3 Forests 4 Heterogenus agricultural areas 5 Industrial, commercial and transport units, 6 Inland waters 7 Inland wetlands, 8 Marine waters 9 Maritime wetlands 10 Mine, dump and construction sites 11 Open spaces with little or no vegetation 12 Pastures 13 Permanent crops 14 Scrub and/or herbaceous vegetation assotions 15 Urban fabric



Landuse	Area (km ²)	%
Arable land	44	0,9
Artificial, non-agricultural vegetated areas	2	0,0
Forests	1200	23,5
Heterogeneous agricultural areas	903	17,7
Industrial, commercial and transport units	8	0,2
Inland waters	31	0,6
Inland wetlands	41	0,8
Maritime wetlands	714	14,0
Mine, dump and construction sites	7	0,1
Open spaces with little or no vegetation	89	1,7
Pastures	88	1,7
Permanent crops	102	2,0
Scrub and/or herbaceous vegetation		
associations	1810	35,4
Urban fabric	73	1,4

Table 1. Landuse data calculated from Corine Land Cover year 2006 maps.

3.2 ISLAND PILOT AREA

As seen in the map (Fig.3, Tab.2), the island test area is substantially covered by arable land (61,7%), mostly vineyards and olive groves, designated as permanent crop according to Corine classification. Permanent crop describes such "cultivable land" that is not being used for annually-harvested crops such as staple grains. In such usage, permanent cropland is a form of "agricultural land" that includes grasslands and shrublands used to grow grape vines or coffee; orchards used to grow fruit or olives; and forested plantations used to grow nuts or rubber. Forest covers only 29,7 % of the test area, and mostly comprises of evergreen forest and macchia.The town Blato is the only settlement in the test area. Number of inhabitants of the town is constantly decreasing for the last 80 years.

Water quality analysis and trends on pilot areas in Southern Dalmatia



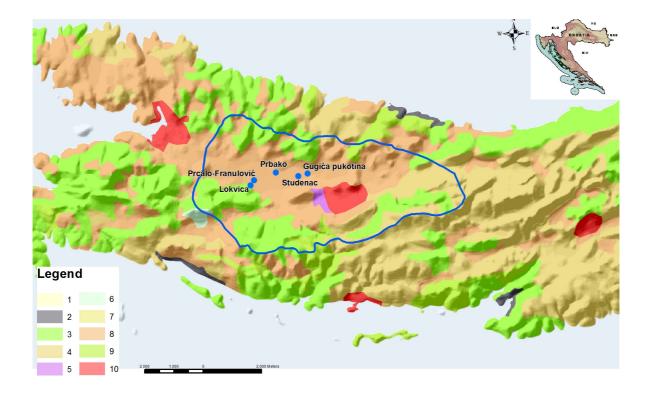


Figure 3. Blatsko polje land use map based on Corine 2006. Legend: 1 Arable land 2 Artificial non-agricultural vegetated areas 3 Forests 4 Heterogeneous agricultural areas 5 Industrial, commercial and transport units 6 Open spaces with little or no vegetation 7 Pasteures 8 Permanent crops 9 Scrub and/or herbaceous vegetation associations 10 Urban fabric

Landuse	Area (km ²)	%
Forests	8,43	29,7
Heterogeneous agricultural areas	4,15	14,6
Industrial, commercial and transport units	0,30	1,1
Open spaces with little or no vegetation	0,05	0,2
Permanent crops	13,36	47,1
Scrub and/or herbaceous vegetation	0,96	3,4
associations		
Urban fabric	1,15	4,1

Table 2. Landuse data calculated fro	om Corine Land Cover year 2006 maps.



4.TEST RESULTS AND TRENDS

At the Prud catchment test area, hydrochemical data were collected and analysed at monthly intervals from December 2013 until today (the sampling procedure is still in progress). In addition to this data, data for spring Prud were given from the Neretva-Peljesac-Korčula water supply company. For the Blatsko polje test area water quality data of monitored wells were given from the Vodovod Blato d.o.o. (Blato Water Supply) for the period from 1997 until 2010. Groundwater samples were taken from wells Studenac, Gugić, Prbako and Franulović and spring Lokvica at the pumping site Blatsko polje (Fig. 3). This data were collected for the purpose of CC-WaterS project and will be used for the purposes of this report (Hasan et all., 2011). The amount of data previously collected is sufficient and there was no need to collect more data. The water samples from Blatsko polje were collected every three months period.

Prior to sampling, the following parameters were measured on-site by probes of the WTW company: electrolytic conductivity (EC), temperature (T), pH and dissolved oxygen concentration. Alkalinity was also measured on field, by the titration method with 1.6 M H₂SO₄. Water samples for laboratory analysis were filtered on-site (0.45 μm, single use Schleicher&Schuell cellulose filters) and collected in cleaned polyethylene bottles. Samples for cation analysis were acidified with suprapur HNO₃. Samples were stored at 4°C until they were analysed. At the Hydrochemical Laboratory of the Department of Hydrogeology and Engineering Geology at the Croatian Geological Survey major anion concentrations (SO42-, NO3-and Cl-) were measured by Ion Chromatography (LabAlliance Ltd.) and major cations (Na⁺, K⁺, Ca²⁺ and Mg²⁺) were measured by Atomic Absorption Spectrophotometer (AAS) (Perkin Elmer Analyst 700), whereas the concentrations of orthophosphates and ammonium were measured by spectrophotometer DL/2010 (by the HACH Co.).



4.1 HYDROCHEMICAL FACIES

4.1.1 CONTINENTAL PILOT AREA

Piper diagram presents results of several hydrocehemical analyses at all extraction sites (Fig.4). According to the chemical composition, the water from all three springs range from Ca-HCO3 towards Ca-SO4 hydrochemical type. The sulphate in some springs of Tihaljina river is the principal anion, and since these waters contribute to the waters in the Prud spring catchment they also affect its water chemistry. The origin of the sulphate is attributed to the presence of gypsum and anhydrite deposits in the deeper parts of the karstic aquifer.(Slišković et al., 2014). Sometime water from Prud has slightly higher Cl concentration because mixing with seawater.

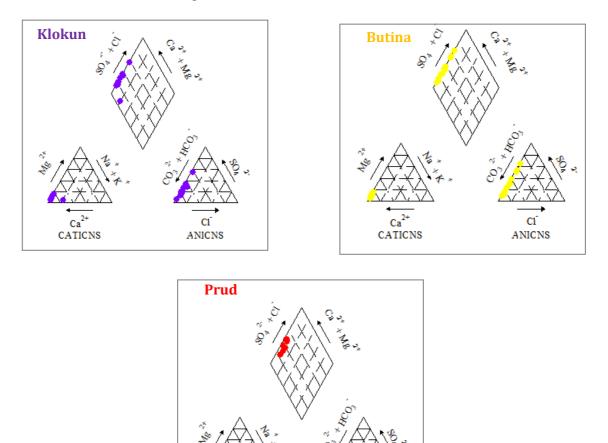


Figure 4. Piper diagrams of sampled waters for continental test area

CÍ

ANICNS



Ca²⁺ CATIONS

4.1.2 ISLAND PILOT AREA

The groundwater of the Blatsko polje aquifer belongs to Ca–HCO₃ and Ca–HCO₃Cl hydrochemical type, which is principally derived from dissolution of carbonate minerals in the limestone aquifer. The latter depends on the influence of seawater on the aquifer. The highest influence of seawater on water type is observed on spring Lokvica, where on June 2010, water belongs to Na-Cl type.

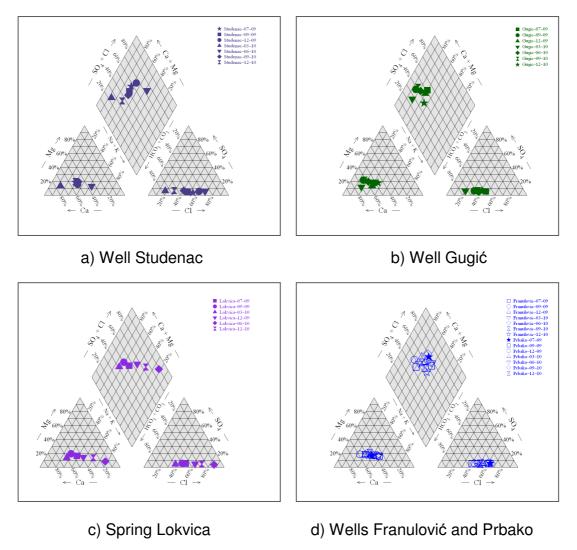


Figure 5. Piper diagrams of sampled waters for the island test area



4.2 PHYSICO-CHEMICAL PROPERTIES

Physicochemical properties of water provide us with first insight into water quality. It is typically measured in the field because they are very sensitive to changes in environmental conditions.

The water temperature of springs and wells indicates the mean annual temperature of the recharge area of the wells. Temperature values at all observed locations are changing during the year according to change of seasons and changes in air temperature. Such changes are common, but the differences between the minimum and maximum values, and the speed of their changes indicate hydrogeological characteristics of their aquifer.

Electroconductivity (EC) values at wells and spring in coastal area depend largely of sea water intrusions which are connected with hydrologic conditions in the aquifer. Lowering of the groundwater level allow entry of sea water into the aquifer and thus salinized water causing degradation in the quality of the water. This is one of the most common and biggest problems in coastal aquifers. As the electroconductivity of sea water is much higher than fresh water, it is a very good indicator of salinization of spring and well waters (in the coastal area). In the case of continental springs that aren't under the influence of sea water intrusions, electroconductivity values may reflect the hydrodynamic properties.

Figure 6. and 7. shows values temperature, electroconductivity and pH values at observed wells and springs on both test area, continental and island.



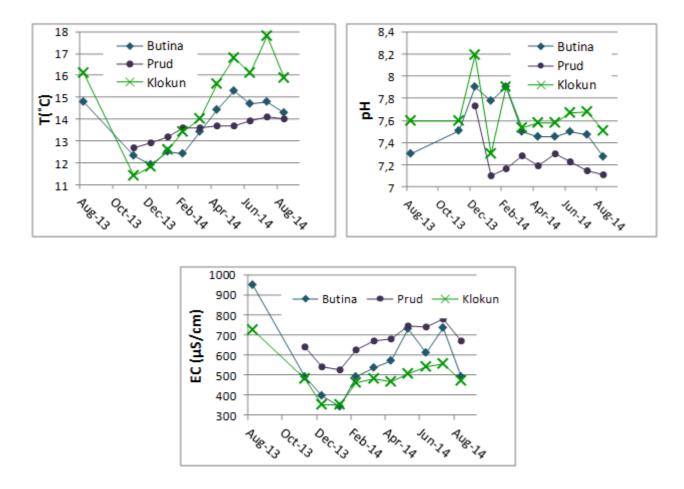


Figure 6. Values of physicochemical indicators at springs in continental test area



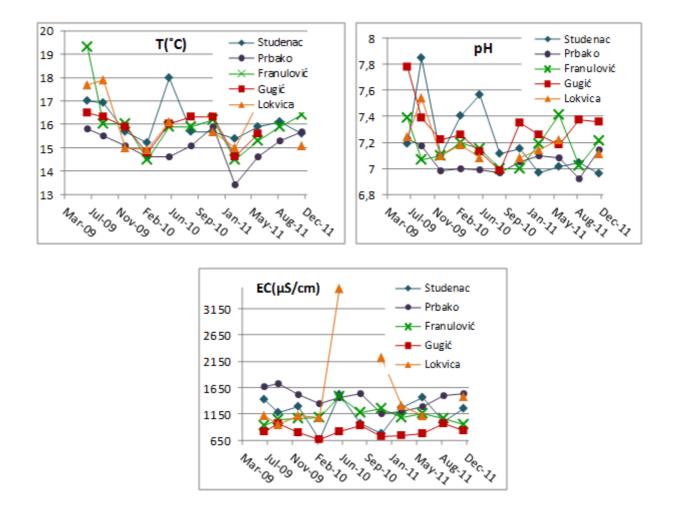


Figure 7. Values of physicochemical indicators on island pilot areas wells



4.3 METALS

In sampled waters following elements, mainly from the group of metals which have negative effects on health, have been analyzed: iron (Fe), manganese (Mn), copper (Cu), fluorine (F), zinc (Zn), chromium (Cr) bromine (Br), cobalt (Co), lead (Pb) and cadmium (Cd). The concentrations of all parameters are less than the maximum allowable concentration (MAC) in drinking water (OG. 125/13). Since all the observed waters are neutral to slightly alkaline, and mobility of the analyzed parameters is very small in alkaline environments, most of these indicators is even below the detection limit. Somewhat higher concentrations, but still far below maximum allowable concentration in drinking water, have only metals Fe, Mn and Cu (Figure 8). One of the causes of elevated copper concentration certainly is associated with the spraying of vineyards and orchards in Vrgorački field which has extensive agricultural activity.

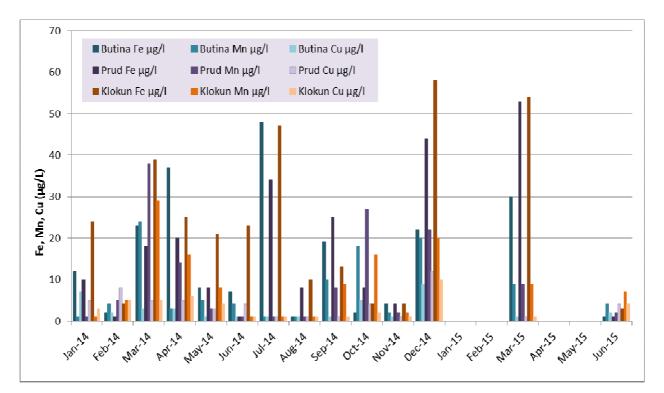


Figure 8. Concentration of Fe, Mn and Cu in spring waters at Prud test area



4.4 MICROBIOLOGICAL INDICATORS

At sampled waters following microbiological parameters were measured: total coliforms, aerobic bacteria on 22 °C and 37 °C, Escherichia coli and enterococci (Tab. 3). The highest microbiological contamination is present during high water in January. This is most likely due to leaching from the surface due to melting snow. Elevated levels of microbiological parameters are common in karst springs (Štambuk-Giljanović, 2011). Groundwater that moves through the karst aquifers has much less possibility for self-purification than groundwater in sediments with intergranular porosity. Therefore karst groundwater are significantly more vulnerable to pollution and mostly have to be treated before use for human consumption.

		Total coliforms	Aerobic bacteria 37 °C	Aerobic bacteria 22 °C	Escherichia coli	Enterococci
		n/100 ml	cfu/1 ml	cfu/1 ml	n/100 ml	cfu/100 ml
	Jan-13	> 201	63	180	5	6
Butina	Apr-14	0	12	17	0	0
But	Jul-14	8	5	7	3	0
	Nov-14	41	11	38	4	0
	Jan-13	145	62	132	8	5
Prud	Apr-14	0	8	12	0	0
P	Jul-14	6	2	3	2	0
	Nov-14	>200	63	98	15	14
_	Jan-13	> 201	57	152	0	0
Klokun	Apr-14	0	11	16	0	0
Klo	Jul-14	74	7	12	4	5
	Nov-14	0	13	34	0	0
	MAC	0	20	100	0	0

Table 3. Microbiological indicators in sampled sprig waters

Water quality analysis and trends on pilot areas in Southern Dalmatia



4.5 STABLE ISOTOPES IN SPRING WATERS

Stable isotope of hydrogen and oxygen (δ^{18} O and δ^{2} H) were monitored monthly at observed springs. Analyzes of stable isotopes were made on the high precision isotopic water analyzer Picarro L-2130i (Fig. 9).



Figure 9. High precision isotope water analyzer Picarro L-2130i, purchased within the DRINKADRIA project

The δ^{18} O and δ^{2} H values fit very good the Local Meteoric Water Line (LMWL) for Dubrovnik (Vreča at al. (2006), town located at the Adriatic coast, about 100 km SE of the Prud spring (Fig. 10).

Water quality analysis and trends on pilot areas in Southern Dalmatia



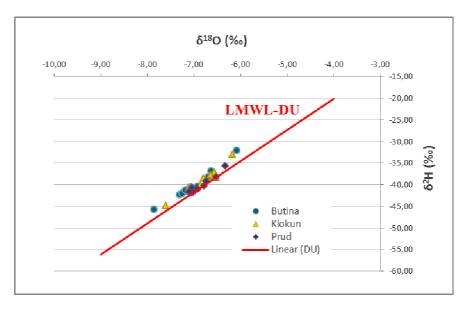


Figure 10. Relation between $\delta^{18}O$ and $\delta^{2}H$ values of spring waters with indications of Local meteoric water line (LMWL) for Dubrovnik as published by Vreča et al. (2006).

On sampled spring waters seasons effect can be noted. In general, rain in the summer is isotopically heavier (more positive δ values) than rain in the winter. The values of isotope ratios are most positive in December, when groundwater, in which the proportion of summer precipitation are more pronounced, are discharged. In February, the most negative values are measured as a result of snow melting, and greater influence of winter precipitation (Fig. 11). These results should be interpreted with caution, considering that 2014 was hydrologically uncommon year, with absence of usual summer minimum discharges.



Figure 11. The seasonal variations of $\delta^{18}O$ on sampled spring waters



Oxygen and hydrogen heavy isotope contents in rainwater decrease with increasing altitude (Gonfiantini et al., 2001). This altitude effect is useful in hydrogeological studies to calculate the mean elevation of the recharge area of aquifers (Longinelli and Selmo, 2003). To calculate mean elevation of the recharge area for springs Prud, Butina and Klokun vertical gradient for south Adriatic region (0,24 ‰ per 100 m), calculate by Vreča et al. (2006), was used. Only autumn and spring precipitations were taken into account as recommended by Fritz and Clark, 1997. It was impossible to calculate absolute elevation of the recharge areas were obteined: Prud - 2860 m a.s.l., Klokun 3029 m a.s.l. and Butina – 3072 m a.s.l. It's obvious that calculated altitudes are too large because the highest elevation in the catchment is much lower than those values and the surrounding areas are also significantly lower than the values obtained. However, from those relative elevations we could conclude that the spring Prud has lower catchment area than springs Klokun and Butina.

4.6 WATER QUALITY TRENDS

4.6.1 CONTINENTAL TEST AREA

Previous studies were classified Prud spring water into the second category of water based on quality of water (Štambuk Giljanović, 2003). The second category includes water used in its natural state for swimming and recreation, sports or for other species of fish and the treated water used for drinking and other industrial purposes. Both, the value of chloride and nitrate, are quite dispersed, but long-term trend for both parameters showing decreasing trend, which has a positive impact on water quality (Fig.12).

Water quality analysis and trends on pilot areas in Southern Dalmatia



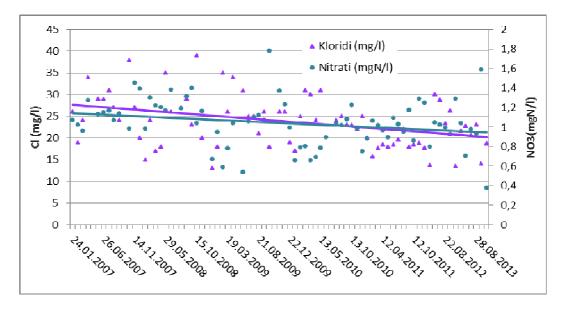


Figure 12. The chloride and nitrate concentrations distribution and trends at Prud spring

4.6.2 ISLAND TEST AREA

Chloride concentration (Fig. 13) varies in all the wells, from 103 to 4100 mg/l. Such wide variations with extremely high values in summer 2002 are the consequence of lack of precipitation and higher pumping rates of wells. The year 2002 was a very dry year with lack of precipitation.

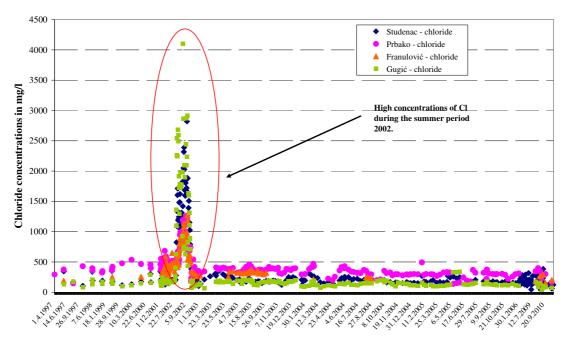


Figure 13. The chloride concentrations distribution in monitored wells

Water quality analysis and trends on pilot areas in Southern Dalmatia



The analysis of chloride concentrations trend showed decreasing trend in waters of all wells (Fig. 14). Higher decreasing trend was observed in waters of wells Franulović and Prbako and lower decrease in water of well Gugić. The lowest decrease is in the main well Studenac.

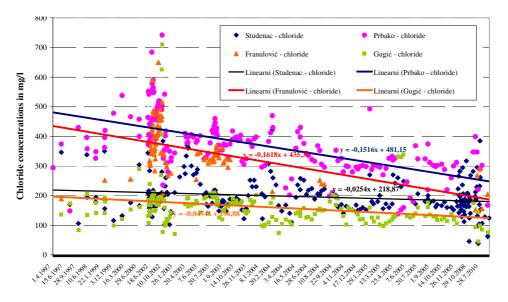


Figure 14. Chloride concentrations trends in monitored wells at Blatsko polje pumping site

Nitrate concentrations in groundwater are low during the dry season (from 5 to 20 mg/l), but in the wet season the contribution of unused NO_3^- from the soil zone (unsaturated zone) increases the concentration of NO_3^- in groundwater (from 35 to 43 mg/l near the maximal permitted concentration, which is 50 mg/l in Croatia) (Fig. 15).

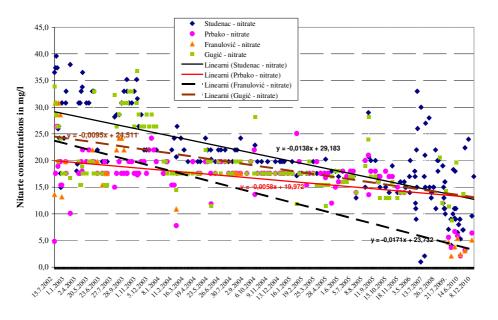


Figure 15. Nitrates trends in monitored wells



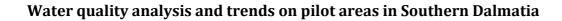
5. CONCLUSIONS

In order to evaluate groundwater quality in pilot areas in southern Dalmatia physicochemical parameters, hydrochemical facies, metal content and microbiological indicators was determined.

Results indicate that the hydrochemical facies of the two pilot areas in southern Dalmatia are significantly different. Sampled waters from island pilot area range from calcium-hydrogencarbonate to sodium-chloride hydrochemical facies which indicates strong influence of the sea water intrusions. Waters from continental pilot area range from calcium-hydrogencarbonate to calcium-sulfate hydrochemical facies, suggesting recharge from deposits rich in sulphate minerals.

Trends of indicators of water quality in both pilot areas are negative, meaning that concentration of water quality indicators falling over time. Concentrations of metals are far below the maximum allowable concentration in drinking water according to Croatian regulations. Microbiological indicators are periodically increased, but it should not be considered as a problem because it is common for karst springs.

All conducted research indicate that the quality of groundwater in the spring Prud catchment is very good. In the catchemnt of Blatsko polje, which is much smaller then Prud's catchment, chloride and nitrate are occasionally elevated, but analysis showed that their trends are decreasing.





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Water quality analysis and trends on pilot areas in Southern Dalmatia



Water quality analysis and trends on pilot areas in Southern Dalmatia (Croatia)





The project is co-funded by the European Union, Instrument for Pre-Accession Assistance

Water Quality of the Veliki Rzav River And Its Tributaries

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Lead Author/s	Vladimir Jelenković
Lead Authors Coordinator	Dejan Dimkić
Contributor/s	Ana Djačić
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Water Quality of the Veliki Rzav River And Its Tributaries

Introduction

The Veliki Rzav River flows through ravines and gorges of the southeastern slopes of Zlatibor mountain. Along the way towards the Sevelj profile, it receives water from several tributaries – the rivers Ljubisnica, Katusnica and Pristevica – as well as from the Mali Rzav, its most important tributary and the closest one to the water intake site. These are mountain, torrential streams, with rocky river-beds, water-rich during springtime, whereas in summer and during dry periods, some of the tributaries dry up or end up on the verge of biological minimum.

Thanks to the enthusiasm of experts from the "Rzav" Water System and to their good cooperation with the of the town of Uzice's Regional Institute for Health Protection, the water system has an extensive archive of data on physical, chemical and microbiological characteristics of water in the Veliki Rzav and its tributaries. The overview of the tributaries' water quality has been made by using the reports the Uzice Institute had submitted to the Rzav water system. The earliest analyses date back to 1997, and have been followed by a series of results collected by mid-2014. Samples have been abstracted at the spots where each tributary meets the Veliki Rzav, whereas the samples of the Veliki Rzav water have been collected at the water intake site.

Water quality of a watercourse is assessed in accordance with the "Regulations on the Parameters of Ecological and Chemical Status of Surface Water and Chemical Parameters and Quantitative Statuses of Groundwater", Gazette of RS, 74/2011). Moreover, water quality is also assessed in accordance with the "Regulation on Limit Values of Pollutants in Surface and Ground Waters and Sediments, and Deadlines for Achieving Them", Gazette of RS No. 50/2012. Since water is used for water supply, special attention was paid to the parameters defined in the Regulations on the hygienic quality of drinking water, Gazette of FRY No. 42/98.

Classic Water Quality Parameters

Water Temperature

Watercourses in the Veliki Rzav catchment area are, as already noted, small and as such follow external temperatures. However, in summer, the water temperature rarely exceeds 30°C, since these streams flow through woodlands, often with steep banks sloping towards the river.



pH Values

The measured pH values vary within a narrow range from 7.8 to 8.8, with the mean value of 8-8.4. An analysis of water abstracted from the Katusnica river, shows a significant deviation, but, since all other parameters are within the normal range, it is assumed that incorrect data has been entered. Figure 1 shows the changes in pH values in the water from Veliki Rzav and its tributaries.



Figure 1 Changes in pH values in water courses over the time period from 1997 to 2014

Suspended Solids

Our regulations (Decree No. 50/2012) cover only class I and class II up to 25 mg/l of suspended solids in surface water, whereas this parameter is not regulated for other classes.

The suspended solid values in all the streams may vary from 0 to 120 mg/l, but their mean values are typically between 14 and 20 mg/l. Occasional significant deviations only confirm torrential character of the watercourses and their veliki sensitivity to the weather conditions (Figure 2).





Figure 2 Changes in the content of suspended solids in streams

Total Mineralisation

The total mineralisation ranges between 200 and 250 mg/l. The lowest values have been registered in the Katusnica river - 204 and in the Mali Rzav - 209, while the Ljubisnica – 240 and the Pristevica - 250 mg/l are somewhat more mineralised. The Veliki Rzav, as the sum of all its tributaries, has medium mineralisation of 215 mg/l. An overview is shown in Figure 3.

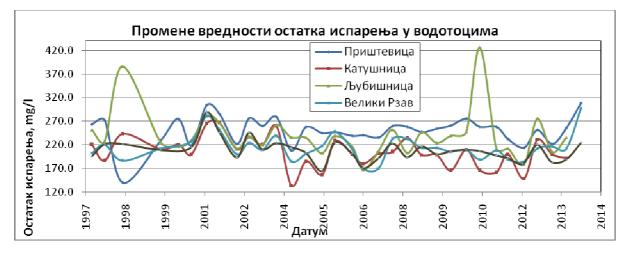


Figure 3 Changes in the mineralisation of water courses over the 1997-2014 time period

Dissolved Oxygen

The content of dissolved oxygen is essential for plant and animal life in a water course. Its concentration can vary widely over 24 hours and over the year, mainly depending on the



flow rate, the level of organic load, as well as on the productivity and content of algae in the water.

In the past, the content of dissolved oxygen in water courses has been varying within a wide range, from 4.2 to over 12 mg/l (Figure 4). The mean values have been around 10 mg/l approximately.



Figure 4 Changes in the dissolved oxygen content over the 1997-2014 time period

BOD₅ values

Biochemical oxygen demand after five days (**BOD**₅) is a biochemical indicator of the level of easily bio-oxydative organic matter present in the water. In addition to organic substances of natural origin, ammonium ion, nitrites, etc. oxidise as well.

In the Veliki Rzav river catchment area, the mean values of BOD₅ range from 1.6 to 2 mg/l (Figure 5).



Figure 5 Changes in the BOD₅ values over the 1997-2014 time period



Nitrogen Compounds

Nitrogen compounds, the "nitric triad", ammonium ion, nitrites and nitrates, are all important indicators of pollution of watercourses. Ammonium ion and nitrites indicate fresh organic pollution, mainly from sanitary wastewater, whereas the nitrates are attributed to the old pollution, after the time necessary for the oxidation of lower valence forms of nitrogen. Thanks to the rapid flow rate, the richness of oxygen and relatively low intensity of pollution in the streams, the analytic methods have not been applied to ammonium ion and nitrite. Any potential present ammonium ion ends up oxidised into nitrates via nitrites.

Nitrates, NO₃ – N

Nitrate concentrations in the Veliki Rzavu and its tributaries have not exceeded 3.7 N mg/l, which, according to the Regulation Book on the Hygienic Quality of Drinking Water, does not indicate a risky parameter, as the allowed N content in drinking water is 10 mg/l.

However, nitrates are an important parameter whose changes, no matter how small, can indicate the trend of pollution of watercourses. By observing the mean nitrate concentration in all streams, it can be seen that the highest levels are found in the Mali Rzav - 1.7 and the Pristevica stream - 1.6 mg/l. This can be explained by the stronger presence of households in the areas of these streams. Bearing in mind the presence of a large number of trout ponds in the Mali Rzav, it can be assumed that the slight increase of nitrate content is the direct result of fish farming in coastal areas of the watercourse (Figure 6).



Figure 6 Changes in the nitrate content over the 1997-2014 time period



Chlorides

All of the samples have had the mean chloride concentrations ranging between 6,4 and 7,4 mg/l, with, as in the case of the nitrates, slightly higher concentrations found in the Mali Rzav.

Watercourses, especially the small ones, are exposed to the direct impact of external factors. Even limited amounts of contaminated water can dramatically change the quality of watercourses in a shorter or longer term. Thus, on October 20th 2010, the Ljubisnica water analysis showed a chloride content of over 100 mg/l, at the same time when the the value of the electrical conductivity was extremely increased. The exact cause of these changes has never been established. The presence of chlorides in a watercourse, or even in drinking water, does not pose a threat (according to the Regulations, the allowed concentration in drinking water is up to 150 mg/l). However, given that the "Sevelj" water intake is located in the open watercourse, as well as the possibility of the pollution, moving from the spot where it has entered the watercourse (the Veliki Rzav or any of its tributaries), can reach the water intake within a few hours, at most a day or two, emphasises the importance of preserving the catchment area and a regular water quality control. The chloride content is shown in Figure 7.

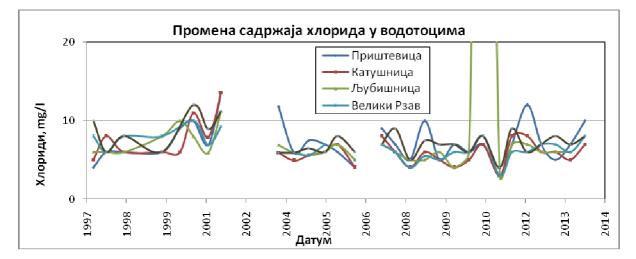


Figure 7 Changes in the chloride content in the watercourses over the 1997-2014 time period

Other parameters provided in the Regulations, and covered by the "B Scope of Analysis", such as the contents of iron, manganese, surfactants - detergents and phenolic compounds, have not shown any deviation, which is why they are not included in the overview. Only dissolved iron has occasionally appeared in concentrations of several tens of micrograms, which in its own way suggests that the catchment area lacks the presence of minerals rich in iron.



A table with the maximum and mean values of the most important classic quality parameters is shown below. Statistical data have been analysed for the time period from 1997 to 2014, with approximately one or two analyses per year. The number of samples for each river and each parameter, has ranged between 22 and 32, but that information has not been included in order to save space, and make the Table clearer.

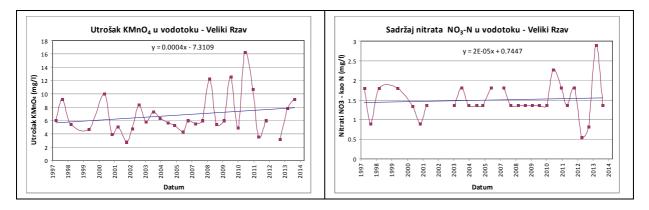
Watercourse →	Veliki Rzav		Mali Rzav		Ljubisnica		Katusnica		Pristevica	
Parameter↓	Max.	Mean	Max.	Mean	Max.	Mean	Max.	Mean	Max.	Mean
Water Temperature °C	12	10	12.1	9.0	12	9.04	17	10.3	16.5	11.5
Turbidity °NTU	25	3	41	13	9.5	2.3	4.8	2	20	2.4
Colour, Unit Pf-Co-Scale	37	2	5	0.2	51	3.2	5	0.3	34	1.8
pH Value	8.6	8	8.7	8.3	8.7	8.4	8.8	8.5	8.6	8.3
Electrical Conductivity µS/cm	419	331	432	317.6	636	362.9	397	311.9	453	387.5
Nitrates NO₃-as N, mg/l	2.89	1	2.72	1.7	2.27	1.4	2.27	1.4	3.75	1.6
Chlorides CI-mg/l	10	7	12	7.4	107	9.9	13.5	6.4	13.5	7.4
Consumption of KMnO ₄ , mg/l	16.3	7	11.6	6.1	13.8	6.9	25.2	11.7	37.8	8.3
BOD mg/l	5.5	2	4	1.7	4.9	2.0	5.8	1.6	5	1.9
O ₂ mg/l	11.9	10	12.3	10.4	11.5	10.3	11.2	9.9	11.2	9.8
Other Vapours	298	215	289	209.1	426	240.2	266	204.4	309	249.8
Suspended Solids	88.2	14	49.6	14.3	154	19.5	116	17.7	48.8	15.1

Table 1 Overview of the classic parameters' extreme values for the 1997-2014 time period

Change Trends in River Water Quality

The graphs with linear trends of several interesting - characteristic parameters (NO3 Nitrates - as N, mg/l, consumption of KMnO4 mg/l, BOD mg/l, the rest of unfiltered water vapours) are shown below (Figure 8 - 12).

Veliki Rzav River





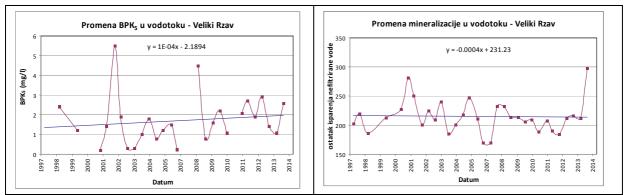


Figure 8 Change trends in the Veliki Rzav river water quality over the 1997-2014 time period

Mali Rzav River

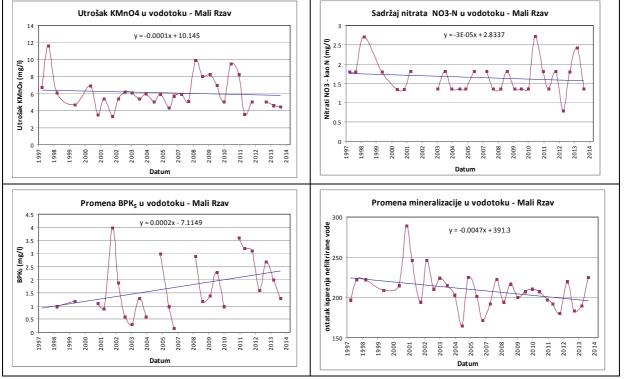


Figure 9 Change trends in the Mali Rzav river water quality over the 1997-2014 time period



Ljubisnica River

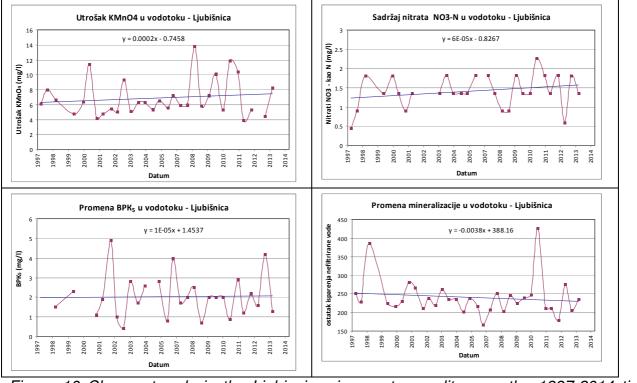
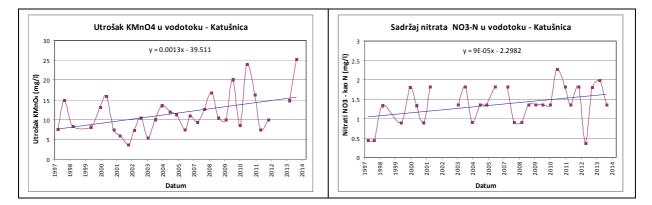


Figure 10 Change trends in the Ljubisnica river water quality over the 1997-2014 time period

Katusnica River





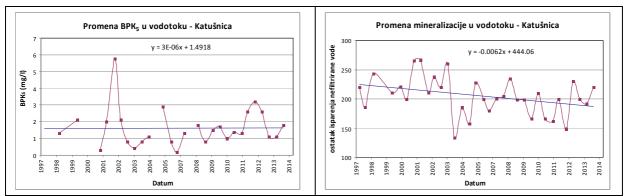


Figure 11 Change trends in the Katusnica river water quality over the 1997-2014 time period

Pristevica River

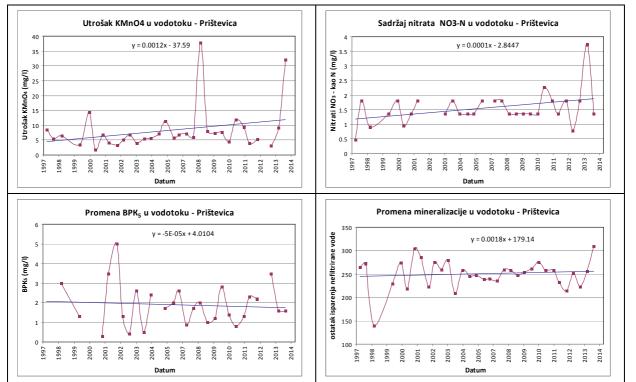


Figure 12 Change trends in the Pristevica river water quality over the 1997-2014 time period

From the graphs of the Veliki Rzav and its tributaries, we see an increasing trend in consumption of potassium permanganate (KMnO4) and nitrates (except in the case of Mali Rzav), a trend close to zero in most of the rivers with regard to five-day biological oxygen demand (BOD5), while the mineralisation mainly shows a declining trend.



Water Quality in the Rzav River at Water Intake Site During Inclement Weather

The Veliki Rzav is very vulnerable to the impacts of weather, with the mountainous terrain configuration and steep slopes in its catchment area. Additionally, there are areas exposed to erosion, as well as arable land, making it clear why the conditions of heavy rainfall or rapid snowmelt bring on drastic deterioration in water quality.

Thus, 2014 was a typical year, as extremely humid, with abundant rainfall during certain periods and with the risk of flooding.

Table 2 Selected dates showing the deterioration of the Veliki Rzav water quality at the water intake site caused by bad weather

Date	Turbidity, NTU	Colour, Pt-Co Scale	pH Value	Electrical Conductivity. µS/cm	Dry Residue. mg/l	Consumption of KMnO _{4,} mg/l	NO₃- N, mg/l	Cl, mg/l
07.03. ′14	18	20	7.8	274	183	24.4	1.36	5
22.04. ′14	65.5	20	7.92	250	194	10.7	1.92	5
15.05. ´14	167	20	7.9	262	175	27.6	1.36	6
18.06. ´14	27.9	10	8.0	280	187	16.7	1.82	6
16.07. ´14	30.1	10	8.0	231	155	27.6	1.82	5
01.08. ′14	87.6	20	8.1	305	204	16.7	1.82	6

Table 2 clearly shows significant changes in turbidity, colour and consumption of KMnO4, in comparison to the average values of the same parameters previously described.

Population's Impact on Watercourses

In the Veliki Rzav catchment area, there are almost 10,000 permanent residents making up some 3,595 households. Since all the major industrial production has virtually died out, the population is primarily engaged in keeping livestock, or where the terrain configuration allows, in agriculture. These are usually small farms, where in addition to grain, people grow vegetable crops - mostly potatoes, tomatoes and carrots - and fruit, such as raspberries, blackberries, plums, apples, pears, etc. Due to the natural predispositions, the number of kept animals is not huge, and it is estimated that in the whole catchment area, there are approximately 6,000 cows and some 15,000 sheep.





Figure 13 Households in the vicinity of the Veliki Rzav

The road network exists, and the roads of regional importance are paved and relatively regularly maintained. However, the local roads are in poor condition, and in the wintertime, they are very difficult to travel.

Water supply is solved locally by one or more family drawing drinking water from the nearest spring, while only a handful of places have organised supply of drinking water from the central water supply system.

Collection, drainage and treatment of wastewater are all still in their infancy. Households, as a rule, have their own septic tanks. Sometimes, pit latrines or drainage pipes leading from the bathrooms, are situated on the very river bank. The situation is similar with the collection and storage of manure from the stables and corrals. Space for storing manure is not regulated and it is often found in the form of an uncovered heap of solid manure situated on a plateau near the stables from which the liquid manure slides down the nearest slits. Usually during springtime, as a part of preparing the soil for sowing, manure is taken to the fields, where it is spread over the surface and plowed.

In terms of risk from the impact of urban wastewater on the watercourses, it can be said that it is quite convenient that a sewer network has never been built, resulting in the largest part of waste matter being retained in the local septic tanks, while the overflow water is being partially purified on its way towards the watercourse. The dispersed settlements with scattered households over the hills and valleys, do not overload the watercourses with pollutants - parameters characteristic of sanitary wastewater.

Sources of water pollution can be roughly classified into two categories: scattered and concentrated ones. Concentrated pollution is characterised by the point of discharge of



wastewater into the recipient, whereas the scattered sources of pollution are generated spatially. The population connected to sewerage are the most significant point source of pollution. The scattered sources of pollution include all surface and groundwater pollutants which, directly or indirectly, enter the watercourses, and originate from: the population not connected to the sewerage, tillage, leaching from forest and soil surfaces, livestock, unregulated municipal landfills and other human activities.



Figure 14 Arable land and fruit crops in the valley of the Veliki Rzav river





Water Quality of the Veliki Rzav River And Its Tributaries -Belgrade, August 2015

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Water Supply and Sewerage Association of Albania (SHUKALB) (FB11)

Tirana, May 2015

Stavri Peci
Arlinda Ibrahimllari, Anisa Aliaj
Alban Kuriqi
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Final report









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1. INTRODUCTION

Pollution from diffuse (e.g. agriculture) or point sources (e.g. industrial and urban wastewaters etc.) is a matter of concern throughout the "extended" Drin River basin. It results to impacts to the ecosystems of the Drin as well as of the Adriatic Sea and poses a risk to human health. A considerable amount of nutrients ends up in the Drin hydrologic system and possibly to the Adriatic Sea; 95% of the nutrient load is attributed to anthropogenic sources (Borgvang S. et al., 2008). Whereas agriculture is the main source of nitrogen and phosphorus in the river system as a whole, the contribution of each source varies from site to site. While in the lower parts of the drainage system, in the Buna/Bojana River, most of the phosphorus load derives from agriculture, sewage is more important in the upper parts of the Black Drin. Unsustainable management of domestic liquid and solid waste exerts pressure in the water quality in other parts of the basin as well (Shkoder/Skadar and Buna/Bojana) [1].

The riparian countries are slowly taking measures to address urban wastewater pollution. For instance, in Albania waste water treatment plants have/are being constructed for major towns. Inadequate wastewater collection and lack of treatment is an issue in the Albanian part of Micro Prespa; wastewater is discharged in surface waters or underground. The level of diffuse pollution cannot be estimated. Macroscopic observations (according to reports from local population in Albania, water transparency has decreased to only a few centimeters) and scientific evidence (e.g. the composition of the phytoplanktonic community) suggests that the Lake is currently heading towards eutrophication; however, there is not enough information available to the authors with regard to the causes. As an outcome there is major pressure exerted on fish population and there are impacts on the balance of the ecosystem which hosts many species including endangered ones. According to current data the Macro Prespa Lake can be characterized as mesotrophic; although a final conclusion about its trophic state, as well as the related trends, cannot be reached due to lack of adequate systematic monitoring for neither the lake nor its tributaries, there are indications suggesting that it is in the process towards eutrophication. The composition of the diatom population community indicates the state of the lake today to be mesotrophic to eutrophic.

Nutrients input –mainly from the FYR Macedonian side that hosts the biggest share of the population and economic activities in the watershed – is considered to be the main cause.



This input comes as a result of insufficient wastewater management and unsustainable agricultural activities e.g. improper use of fertilizers and irrigation techniques; in addition, erosion may also contribute to nutrient inputs due to the poor land management (agriculture). Organic pollution leads to depleted dissolved oxygen concentrations –particularly in summer months- contributing to degradation of water quality with a potential impact on aquatic life. The main source of organic pollution is believed to be the town of Resen and the industry in the same region. Furthermore, excessive apple production usually ends up in the streams entering the lake increasing their organic carbon loads. Insufficient wastewater management leads to bacterial pollution too in certain areas of the lake and its tributaries. Diffuse pollution from agriculture in the Albanian part is minimal and where present it should be of local character.

The nutrient and organic loads entering the lake due to insufficient wastewater management is a factor of pollution that may have –data are not available- an impact of local character; it should be of less importance if compared to trans boundary pollution. In contrast, the impact of wastewater discharge is major in the Albanian part in terms of bacteriological pollution; the situation becomes critical at certain locations during particular periods of the year. The health risks are high for people who use untreated water abstracted from the lake for drinking purposes or when using the lake for recreation. There is virtually no information available regarding the concentrations of hazardous and toxic substances in the local aquatic system (water column, sediment or biota). Nevertheless, the use of herbicides and pesticides at the FYR Macedonian side of the basin is substantial, mainly within the Golema River sub-watershed, affecting both the river and the northern end of the Lake.

Use of inappropriate types of pesticides in FYR Macedonia –e.g. agrochemicals banned, by the law, are obtained and used in both Prespa and Ohrid sub-basinsmay pose a threat to the ecosystem. Water quality deterioration is most intense at the littoral zone of Ohrid Lake especially:

- FYR Macedonia in the: sections adjacent to the urban areas of Struga and Ohrid; shoreline to the south of Saint Naum; areas that the larger tributaries discharge into the lake, especially the Sateska, Daljan, Grasnica and Koselska Rivers;
- Albania in the: sections adjacent to the urban areas of Pogradec and; in the shoreline where recreational activities take place i.e. Drilon, Pojska, and Lin. Ohrid is an oligotrophic lake, however, there are indications of progressing eutrophication.



Nutrient loading from both littoral countries exert pressure to the system causing acceleration of the "aging" process of the lake. Concentrations of phosphorus and nitrogen have been increasing over time. Considering the very large volume of water in the lake this increase represents a very significant change. Both the phytoplankton and zooplankton communities are shifting to a species composition more characteristic of a mesotrophic condition and so do the macrophytes and benthic fauna in the shallow-water zone. Lake Ohrid is being "fertilized" from the FYR Macedonian side by sewage due to inefficient and in some cases insufficient infrastructure for wastewater collection and treatment and diffuse pollution due to uncontrolled and excessive use of fertilizers. There are plans for the expansion of the sewerage network as well as the treating capacity of the wastewater treatment plant serving the sub-watershed [2]. Urban wastewater discharge has been the main input of nutrients from the Albanian side leading also to organic and bacterial pollution of local importance- at the littoral zone.

Treatment of urban wastewaters of the Pogradec area, since 2009, has had a positive effect with regard to the organic matter and phosphorous concentration trends as well as to the bacterial contamination of water. According to observations some improvement in the water quality in the adjacent part of the lake is evident. According to some information phosphorous is transported via the karstic underground connection from the Prespa watershed. Inappropriate disposal of solid wastes and non-compliance of the existing landfills to modern standards in both sides of the basin is another threat for surface and ground water. There is some preliminary evidence in Ohrid Lake with regard to hazardous substance pollution.

In FYR Macedonia pesticides used by farmers in the watershed may threaten fish in the lake; traces have been found in the tissues of some fish collected. In addition, there have been inflows of toxic wastes from industrial facilities in the area of Ohrid. Economic reasons have forced the closure of many industrial plants in the past two decades thus sources of pollution have been "de facto" greatly reduced. However, a recent study indicated an elevated level of PCB in edible fish. Mining activities at the Albanian shoreline have been sources of heavy metals pollution (e.g., chromium, copper, cobalt, nickel as well as iron, etc.). The impacts to the ecosystem had been considerable. According to publications, flora and fauna (especially some fish species) of the lake had been seriously affected in the adjacent to Guri i Kuq lake area. Sediments in the littoral zone in adjacent to the mines areas are substantially polluted, presenting a potential toxic risk for the aquatic life and through the food chain also to humans.



The closing down of mines and the removal and disposal of the site tailings in Guri i Kuq addressed to a certain extent these important pollution sources. Depositions of residual material left in open pits in abandoned mines constitute still a pollution source; the initiation of operation of some illegal mines may be an issue in this regard. A potentially significant risk to living organisms is still present. The main sources of pollution in the Black Drin River in FYR Macedonia are considered to be: domestic sewage and solid waste; agriculture; mining activities throughout the watershed. There is no adequate information available to the authors with regard to water quality; according to some data, nutrient levels appear to be low if compared to the other sub-basins of the extended Drin River basin. According to the Spatial Plan of FYR Macedonia (2004) Black Drin is among the watercourses of the country that shows "permanent deterioration of its quality". There is also no adequate information with regard to water quality in the part of the Drin River watershed extending to the Albanian side. The following are among the potential sources of pollution:

- Inappropriate disposal of solid waste throughout the watershed; deposits, including of hospital waste, are present on the river banks and lake shores in residential areas;
- Domestic sewage that is discharged untreated along the course of the river as well as in the artificial lakes;
- Waste from mining and industrial activities throughout the watershed and in particular in the Kukes region where mining industries are placed.

According to some publications concentrations of nitrates and DIN are rather high compared to the values observed in the Prespa and Ohrid Lakes. According to the Albanian Ministry of Environment, Forests and Water Administration the overall water quality in the Drin River is good. Despite the fact that the Shkoder/Skadar Lake receives pollutant loads, the quality of water appears to be reasonably good, due to high renewal rate of 2-2.5 times per year. Inappropriate wastewater management results in pollutants entering the Shkoder/Skadar Lake Buna/Bojana River system. Improvement of related infrastructure in Podgorica and construction of infrastructure in Shkodra is underway. In the Montenegrin side, untreated or poorly treated municipal wastewater and diffuse pollution from the Zeta Plain pollute surface water and groundwater. Pollution reaches the lake through tributaries and springs [3].

Increased concentrations of nutrients (phosphates and nitrates) are monitored in the lake near the river mouths, in particular of Crnojenica and Moraca Rivers; concentration peaks are observed during summer season.



In the Albanian part the pollution contributed is due to absence of wastewater treatment, insufficient solid waste management and agricultural runoff results in the pollution of the Lake. Sewage from the Skhodra city is collected into a pool and then pumped into the Drin River at a short distance before its confluence with Buna/Bojana. Occasional failures of the sewerage system lead to spills posing a threat to the quality of the Lake. The discharged wastewater affects the Buna/Bojana River all the way down to its delta and in periods of high waters in Drin and floods, the Lake. Bacterial pollution seems to be an issue of local importance during spring / summer in Moraca River downstream the Podgorica wastewater treatment plant; this is also true occasionally, during the summer period at the point that Moraca enters Shkoder/Skadar Lake. The Aluminum Plant in Podgorica (KAP: Kombinat Aluminijuma Podgorica); pollutants associated with the operation of the plant include fluoride, phenols, SO2, NOx (emitted in the atmosphere), PCBs that had been stored under poor conditions, phenolic compounds, PAHs and mercury-containing wastes.

Pollution by PCBs is currently regarded as of low concern due to the export in 2006 of accumulated waste reserves and the proper storage of newly generated PCBs since the privatization of the company in the end of 2005. The Steelworks Niksic that is located near one of the tributaries of the Zeta River, is responsible for a range of pollutants, such as waste oils, heavy metals and toxic substances that reach the Zeta and Moraca rivers. While hazardous substances (heavy metals, PAHs, PCBs, etc.) had been observed in the period prior to 2000 in the Shkoder/Skadar Lake, improvement of the water quality has been noticed in the last years. The pollutants that have reached the lake in the past seem to have been accumulated in the sediments. Moderate and, in few cases, high concentrations of heavy metals have been (monitored) identified at specific sites of the lake in the sediments. Concentrations of PAHs and PCBs in sediments were found to be higher at the entry points of the Moraca River than the pelagic zone, and exhibited a decreasing trend from 1993-1996 to 2005. Traces of pollution from the Steelwork factory in Shkoder/Skadar Lake are minor. Trace metals were found to be relatively higher in the Albanian side of the Lake.

According to some stakeholders (information is not confirmed) Drin contributes, to some extent, trace metal pollution to the Buna/Bojana River from mining activities upstream. Inadequate solid waste management is of particular importance and constitutes a serious pressure. While in the Albanian part there is an almost complete absence of waste management, the situation is slightly different in Montenegro where the core of the problem is that waste collection system covers mainly the urban population. Currently, only Podgorica, Cetinje and Danilovgrad are served by a sanitary landfill.



The rest of the wastes are dumped in a large number of uncontrolled disposal sites or even in the vicinity of watercourses that frequently wash the litter into larger streams and/ or the Buna/Bojana River and the sea, a situation exacerbated by floods. Efforts to improve the solid waste management system in both countries, including construction of sanitary landfills, are ongoing. There are insufficient data with regard to impacts due to pollution; nevertheless, the nature of pressures as well as their intensity in some cases, lead to the conclusion that water pollution is a threat to the ecosystem and potentially to the health of local population.

Compared to the Shkoder/Skadar Lake the nutrient levels in the Buna/Bojana River are elevated and reflect, most probably, the discharges of urban wastewater of the city of Shkodra as well as the nitrogen and phosphorus loads entering the system through agricultural runoff in Albania. Localized bacteriological contamination is also an issue. In periods of high waters in Drin and floods (see above "Water Balance") the lake is affected as well.

2. PILOT AREAS AND TESTED WATER QUALITY PARAMETERS

Drini River watershed comprises a considerable area of 14173 km2 (within Albania), continuing also beyond Albanian borders, covering very important aquatic ecosystems, not only from the economic point of view but also naturally. Beside the river course, its related tributaries and closely related artificial lakes of Drini cascade (Fierza, Komani and Vau-deja) in Drini watershed are situated the big transboundary lakes of Ohrid, Prespa and Shkodra, three groups of mountainous glacial lakes of Lura, Ballgjaj and Dhoksi. Close to Drini delta an important lagoon system is situated, with three main lagoons: Merxhani, Ceka and Kenalla. Increase in human population and development of tourism cause harmful changes in ecosystems. The consequences of that are changes in qualitative and quantitative compositions of biosensors. Because of that is possible to explore conditions in some ecosystems by using composition of organisms that live in it bio indicators. Being rather tolerant to different environmental conditions, many rotifer species are good indicators of water quality and can be used for the ecological monitoring of water bodies [4].

The aim of this study was to explore fauna of Rotifera from eastern littoral zone of Lake Ohrid and to determine the water quality on the basis of the noted bioindicative rotifers. In the present paper is also given a view of microscopic algae (diatoms – Bacillariophyta).



The reporting is considering all the diatom taxa found and already published by different authors, from Albania and from the neighboring or other European countries, together with the personal data taken during different expeditions (some of them not published). A checklist of species is given and discussed, both in floristic and ecological aspects. Some problems that endanger the biodiversity and water quality will be emphasized, with some recommendations to maintain or restore the water quality. According to determination, water resources can considered polluted, then, causing for human activities which discharge any materials in water, or when they can change temperature,physical, biological and chemistry characteristic in that level that we can't use for any reasonable aim. In other manner, if water can not be available for any reasonable aim, then water can be polluted.

Pollution can cause from presence of any materials which are foreigner for waters. These materials can be hazard, or can be biodegradation and cause high request for oxygen. The aim of this project was investigation water quality in Drini i Bardhë River. Drini i Bardhë spring in Radavc, Pejë. For a long time was mainly drinking water supplier for several regions when passes this River. This River goes through many urban places, and knows he is like collector of urban and industrial pollutant waters. In River basin of Drini i Bardhë run down some small Rivers, streams and water bearers from different agriculture soil drainage. Water protection from pollution and water management has strategic importance for Kosovo. Planning and creating of optimal network and investigation program of water resources quality from economic and functional aspects, and risk of accidental breaking, are like priority duty, considering new water status. Collection of materials has starting from spring of 2002 until autumn 2002. In this period has done closing of cycles for a year (chemical and biological cycles) even is very difficult to foreseen that when it will start and when will finish such cycle, is very difficult to say that when happening seasonal differences, which depended from climatic condition (Balvay, 1991). Place when we take sample has choose in that manner that are in a distance of 500 -1000 m from potential of pollutant (Figure 1).





Figure 1.Samples area, Drini Bardhe river tributary of Drini River [5]

Sample places were: A1 source in Radavc, A2 after discharging of municipality and industrial waters in Peja with suburbs, A3 after discharging of Klina and Ereniku river in Gjakova and other secondary bearers, A4 after discharging of water of Rahovec, in frame of which are involved these point, B1 for discharging of water pollution of Rahovec and suburb, B2 discharging of industrial and agriculture waters and B3 discharging of industrial, agriculture and urban waters in this region, A5 after discharging of river Lumbardhi i Prizrenit and other industrial and agriculture bearers. Samples for water analyses has be taken and conserved in manner which has been foreseen with Regulation for water standard [Dalmacija B, 2000]. Mainly parameter of water polluteted are: chemical oxygen demand (COD), biological oxygen demand (BOD), dissolved oxygen (DO) some chemical parameters (ammonia, nitrate, nitrite, phenols, heavy metals etc.). In field from water samples has been measured pH amount and wasted oxygen amount After that with standard methods [American Public Health Association, 1992], It has been done measurement of these parameters for water quality: conductivity BOD5, heavy metals (Pb, Cd, Cu, Zn and Ni.), Phenols, ammonia, nitrate and nitrite.



3. RESULTS

3.1. Physical and chemical composition

In European countries, results of river quality estimation are reported based on classification system where water quality is considered satisfactory from first category until third category. Applied classification system, numbers of measured and compared parameters, manner of calculation are based on physical, chemical, biological characteristics of water are different for different places. In this project we present water quality of Drini i Bardhë river in 8 different places. The places for water example are: Radavc (A1), Pejë (A2), Rogovë (A3), Lukinaj A4, Vërmnicë A5 and in branch of river Drini i Bardhë, river of Rahovec; Bërnjak (B1), Fortesë (B2) and Xërxë (B3), has been monitored water quality every year with the water quality indicators. Estimation has been done based on selected water quality indicators determined in the (Table 1) for Classification from Economic Commission of United Nation for Europe, UNECE [6]. Physical and chemical parameters for water quality of river Drini i Bardhë and his branch, Rahovec River has been monitored for one year. But, because of simplicity, we will introduce only results of estimated parameters for a period (April 2002). Results are presented in the Table 1 and in graphic manner in figure 2-4. From (Table 1), the results of measured parameters are showing a difference of determinates parameters for water quality of river Drini i Bardhë.

Parameters	Unit	A1	A2	A3	A4	A5	B1	B2	B3
рН	-	8.02	8.22	7.82	7.89	7.71	7.51	7.32	8.16
Conductivit	μS/c	408	412	424	516	644	645	644	636
DO	mg/L	10.8	8.02	7.15	6.2	6.2	5.15	5.05	5.37
Turbidity	mg/L	2.45	3.23	12.6	13.4	13.9	5.43	6.06	6.93
TDS	mg/L	207	218	221	233	238	326	308	326
COD	mg/L	3.82	4.25	4.85	11.46	11.66	11.47	15.5	20.15
BOD5	mg/L	2.85	3.85	3.96	10.5	10.82	7.78	10.82	15.9
Nitrate	mg/L	5.5	45.5	51.5	52.3	53	58	60	45.5
Nitrite	mg/L	0.005	0.16	0.03	0.04	0.16	0.18	0.1	0.15
Ammonia	mg/L	0.06	2.8	2.6	2.018	2.28	4.57	5.2	5.36
Phenols	mg/L	-	0.061	0.045	0.04	0.038	0.31	0.28	0.26
Pb	mg/L	0.0013	0.0015	0.0126	0.0148	0.0015	0.003	0.022	0.022
Ni	mg/L	0.0065	0.08	0.064	0.0812	0.088	0.098	0.108	0.118
Zn	mg/L	0.0045	0.07	0.0324	0.0768	0.082	0.07	0.117	0.059
Cu	mg/L	0.001	0.0009	0.0007	0.0006	0.0009	0.001	0.001	0.000
Cd	mg/L	0.0008	0.004	0.0032	0.0048	0.0051	0.005	0.004	0.003



Dissolved oxygen is consummated in reaction and during that time are produced new microbial cells from organic substance which are present in water. After a time, old cells die and organic materials which are joint with them will be consummated in the following reaction. This synthesis and dissolution of cells will go on, until number of live cells will be minimized and in the water remain only organic materials, which are relative resistant, which are like humus. Concentration interval for this important indicator of water guality in our samples, are about 6.20 - 10.8 mg/L (Drini i Bardhë) and Rahovec River discharged in Drini i Bardhë River has value 5.05 - 5.37 mg/L.Biochemical oxygen demand (BOD5) is a value of presence of organic materials in water which can support increasing of microbe organisms. BOD5 is well known test to control water pollution. It is clearly that BOD5 measure only one piece of this general process. BOD5 can be measured with dissolved oxygen amount, during aerobic oxidation of microbes of one water sample, during due period and due temperature. Usually, time is five day and temperature is 20°C and the results is recognized as five day biochemical consumption for oxygen and usually noted as BOD5.

Concentration of organic substances, presented with BOD5 in our samples was 2.85 - 10.82 mg/L for Drini i Bardhë and 7.78 - 15.9 mgO2/L for Rahovec river. From the gained results we can see that river Drini i Bardhë and his branches are charged with considerably organic materials (Table 1, Figure 2). Amount of materials that subservient oxidation in one water sample and which can be oxidised from chemical strong oxidation is known as chemical oxygen demand (COD) [7]. Usually, as oxidant is used dichromate potassium and acid sulfuric valorized solvent. Correlation between COD and BOD5 is not easy and depend very much from nature of organic materials in sample. Some organic components are biologically degraded, but, they do not dissolve from dichromate acid, for example acid acetous, whereas, opposite of that is reality for organic component like cellulose. COD has advantage because, the prove can be done faster than BOD5, in question are some hours compare with some days. From the results of our measurements we can see that contamination of COD it goes from 3.82-11.66 mgO2/L in Drini i Bardhe River, while 11.47-20.15 for river of Rahovec (Figure 2). Rahovec River where still we have higher result of organic substances as consequence of runoff of polluted waters from Rahovec industry (wheat factory, vine plant, plastic measures and maniacal sewage waters).



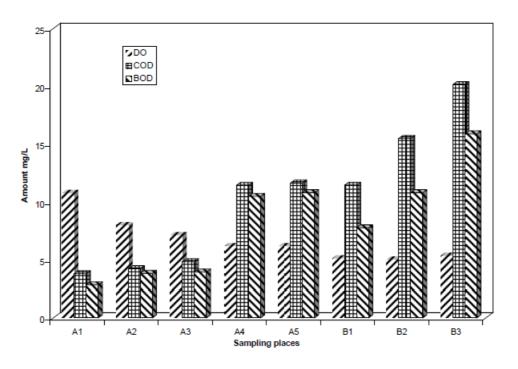


Figure 2. Amount of OD, COD and BOD

Waters in natural condition (unpolluted) have relative low contamination of nitrogen and phosphorus. In these cases view of water is clear, with small or without vegetation and the bottom of river water is clear. From nutrients loaded in natural waters in some relevant conditions, especially where in waters there are unloads with anthropogenic origin reach with nitrogen and phosphorus it can be observed a sensitive intensification of photosynthesis processes and big increase of alga quantity with waters and view of waters changes, it becomes green juice and turbulent. Concentration of nutrient salt of nitrogen in water as ammoniac, nitricand nitrates are causing process of eutrophication.

Ammonia is the product of disintegration of organic materials; it can be also toxic for fishes and other water organisms. Nitrates as last products in process of nitrification, in higher concentrations are toxic for organisms of new ages. Ammonia concentration in our measurements is from 0.06-2.80 mg/L in waters of Drini i Bardhë and 4.57- 5.36 mg/L for Rahovec River [8]. Concentration of nitrites is from 0.005-0.16 mg/L for Drini i Bardhe River and 0.10-0.18 mg/L for Rahovec River. Nitrates have these concentrations after measurements from 5.50-53.0 mg/L, for Drini i Bardhe River while for Rahovec River from 45.5 - 58 mg/L (Figure 3). In waters of Drini i Bardhë and his branches, observed in Rahovec River has an increased concentration of phenol which is from 0.038 - 0.061 mg/L for Drini i Bardhe River and 0.26-0.31 for Rahovec River.



Concentration of phenol is higher in Rahovec River than in Drini i Bardhë because of water slimming and this concentration is decreased apparently (figure 3). With unload of polluted water in these rivers it comes a considerable quantity of heavy metals (as lead, nickel, zinc, copper and cadmium), that takes part as micro-polluters. These concentrations exceed maximal quantities allowed to these polluters in natural water in some cases (Table 1, Figure 4).

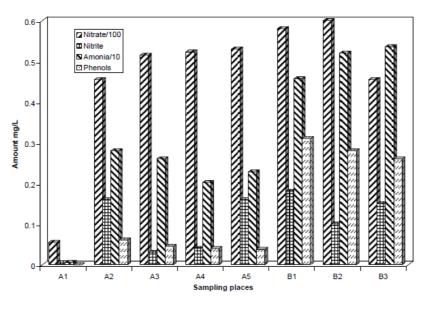
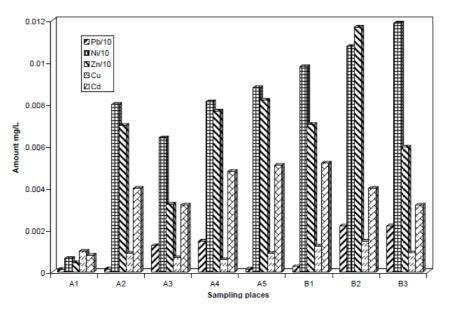
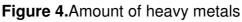


Figure 3. Amount of nitrate, nitrite, ammonia and phenols







From table 1 it seems that value of pH it doesn't make any apparent problem of water quality from river and this value it comes mainly in cadre of normal values for natural ecosystems (from 7.82-8.16), while concentration and turbulent shows that these waters are loaded with different pollutants. Based on the chemical statistics for the water quality Drini i Bardhë River, in comparison with Directives of European Union above classification of natural waters, waters of these rivers doesn't fulfill conditions even for waters of II category (in exception of river sources), even in some points these rivers are of III and IV category for superficial waters and this mean that the water in this current cannot be used for recreation and shower, for water sports, for cultivation of fishes etc. From the results of the analyzed samples within the starting period April 2002 until October 2002 can be said that level of quality of this water is getting worst. It is great concern for the water quality of the rivers Drini i Bardhë River of Rahovec because some of the indicators like are COD, BOD5, dissolved oxygen, phenol, nitrate, nitrate shows are having an increased tendency of all sample-points and in particular for the branch of river Drini i Bardh [9].

3.1.1. Water quality evaluation

Fresh water is essential in many spheres of human life and in general it is seen as an essential input to human production and an effective tool of economic development. It plays a significant role in social prosperity and the well-being of all people. Unfortunately, in many countries around the world, including Albania, some drinking water supplies have become contaminated and the deteriorated quality of surface waters is becoming a grave issue in many parts of the globe. Water pollution from diffuse sources and various types of pollution is not only a serious environmental issue but also an economic and human health problem . Changes in the physico-chemical characteristics of water quality are influenced not only by anthropogenic factors, but also by the combined interactive natural processes such as hydrological conditions, topography and lithology, climate precipitation inputs, catchment area, tectonic and edaphic factors, erosion, weathering of crustal materials and bedrock geology, in combination with environmental influence. Freshwater sources in Albania exist as natural springs, rivers, lakes, and groundwater aguifers. The water supply for drinking purposes comes mainly from natural springs and underground water sources. Albania has abundant water resources, but the lack of drinking water at the tap is a critical problem . The available average quantity of fresh water is an estimated 8,700 cubic meters per capita per year, which is one of the highest in Europe.



However, it is reported an average of 11.1 hours/day continuous water supply service for the year 2010 in Albania. The drinking water at the source is of good quality. However, there are many problems concerning drinking water supply in Albania. Albania has a distribution network problem, not a production problem. The situation of water supply infrastructure is critical. During the last years, the water supply service in Albania has achieved substantial and significant improvements; however, these improvements are performing slowly. There are some cities that operate with a new infrastructure (main and distribution networks) that provide a 24-hour-per-day water supply. The city of Pogradec (Figure has been one of them since 2007. Traditionally, including Albania, water quality has been assessed by comparing the values with the local norms.

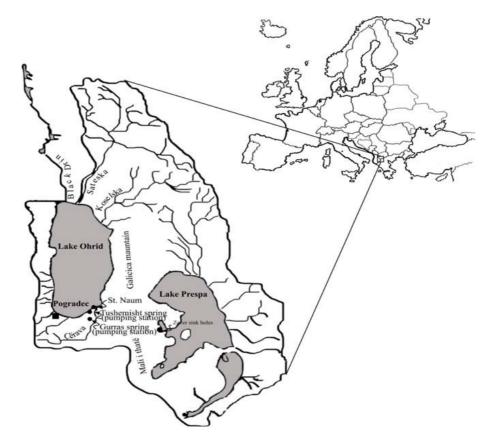


Figure 5. Locations of Pogradec city, Tushemisht, and Guras surface water springs of Lake Ohrid [10]



Rank	WQI value	Description
Excellent	95-100	Water quality is protected with a virtual absence of threat or impairment conditions very close to natural or pristine levels.
Very Good	89-94	Water quality is protected with a slight presence of threat or impairment conditions close to natural or pris- tine levels.
Good	80-88	Water quality is protected with only a minor degree of threat or impairment, conditions rarely depart from natural or desirable levels.
Fair	65-79	Water quality is usually protected but occasionally threatened or impaired conditions, sometimes depart from natural or desirable levels.
Marginal	45-64	Water quality is frequently threatened or impaired, conditions often depart from natural or desirable levels.
Poor	0-44	Water quality is almost always threatened or impaired, conditions usually depart from natural or desirable levels.

Table 2.Water quality index for city of Pogradec part of Drini basin

3.1.2. Data for WQI Calculation

The following physical, chemical, and bacteriological parameters were determined according to standard methods: taste (TDN – taste dilution number), odor (ODN – odor dilution number), temperature (oC), pH – value, conductivity (EC; μ S/cm), turbidity (NTU), nitrate (mg/L NO3⁻), nitrite (mg/L NO2⁻), ammonia (mg/L NH4⁺), chloride (mg/L Cl⁻), and microbial load (total bacteria count, N/100 ml). According to the Albanian standard [35], the unit of measure for taste and odor is taste/odor dilution number (T/O DN). For the original (undiluted) sample, where the taste/odor is deemed taste- and odor-free T/O DN = 0. The data (from laboratory of Water Supply and Sewerage Enterprise Pogradec) used in this study for all parameters are monthly averages collected from six fixed points in the city, every day during the year 2011. The data of these variables are used in the calculation of CCME WQI model using sets of Albanian standard (objectives) values of drinking water quality (Table 3).



	Parameters										
Months	Odor	Taste	Turb	Temp⁰	рΗ	EC	NO3 g/L	NO2 g/L	NH4 g/L	. CI mg/L	TC
	ODN	TDN	NTU	С		µS/cm					N/100
January	0	0	0.67	11.8	7.5	318	2.56	0.001	0.002	0.1-0.3	0
February	0	0	0.861	12.6	-	308	2.41	0.002	0.001	0.1-0.3	0
March	0	0	0.57	13.5	7.45	316	2.24	0.002	0.002	0.1-0.3	0
April	0	0	0.47	13.5	7.55	299	1.91	0.001	0.001	0.1-0.3	0
Мау	0	0	0.78	13.8	7.40	306	2.32	0.001	0.002	0.1-0.3	0
June	0	0	0.42	14.2	7.50	304	2.36	0.001	0.001	0.1-0.3	0
July	0	0	0.74	15.1	7.65	298	2.43	0.001	0.002	0.1-0.3	0
August	0	0	0.68	15.3	7.45	300	1.89	0.001	0.001	0.1-0.3	0
September	0	0	0.56	14.8	7.50	289	2.13	0.001	0.002	0.1-0.3	0
October	0	0	0.82	13.2	7.62	278	2.36	0.003	0.001	0.1-0.3	0
November	0	0	0.72	12.9	7.45	302	1.87	0.001	0.001	0.1-0.3	0
December	0	0	0.98	12.5	7.43	316	2.34	0.001	0.003	0.1-0.3	0
Objective	0.0	0.0	0.4	15-sie	6.5-8.5	400	25	0,05	0.05	0,3	0.0
	0.0	0.0	0.1	10 010	010 010		20	0,00	0.00	0,0	0.0

Table 3. Physico-chemical parameters in drinking water of Pogradec

The values in bold do not meet the objective. Objective values as per standards given by .

The data of physical, chemical, and bacteriological properties given in (Table 4) indicate that the average values of all parameters are below the maximum permissible limits indicated in the Albania Official Standard for drinking water. Study all the water samples were odorless and tasteless. The pH measurement reflects a change in the quality of the source. Very acidic or very alkaline water produce sour or alkaline tastes. Also, higher values of Ph reduce germicidal potential of chlorine . In this study, the average values for pH ranged from 7.43 to 7.65. They are within the objective range of 6.5-8.5 for drinking water. The EC value is an index that represents the concentration of soluble salts in water. A high concentration of dissolved solids greatly affects the taste of the drinking water. The EC values for the investigated period show that tap water samples have similar values (278-318 μ S/m) and are lower than the objective of 400 μ s/cm. Nitrate and nitrite in the water samples are found to be in a range of 1.87 to 2.56 mg/L and 0.001 to 0.003, respectively. All the data satisfy the objective values for drinking water. Ammonia is an indicator for elevated pollution from organic substances. The measured values for this parameter are within the recommended objectives of 0.05 mg/L. Chlorides occur in all natural waters in varying concentrations.



No.	Term of index	Value	Rating of water quality
1	Scope – F1	18.18	Rank: Good
2	Frequency – F2	10.69	Water quality is protected with only
3	nse	0.07	a minor degree of threat or
4	Amplitude – F3	0.86	impairment; conditions rarely
5	WQI	87.81	depart from natural or desirable

Table 4. Calculated values of WQI in Pogradec drinking water [11]

Centrations in this study are within the recommended objectives of 0.3 mg/l. Water may be contaminated with microorganisms at the source, but contamination may also occur during distribution or transportation. The microbiological analyses of thewater indicate that the microbial loads do not exist. The zero values of the microbial load in the water are indicators for an effective disinfection process during treatment. The temperature was found to be in the range of 11.8 to 15.3oC and exceeds the objective in July and August. The water temperatures vary seasonally in the normal range within the objective. The exceeded values probably are due to non adequate depth of water supply network pipes.

Turbidity is a measure of the relative clarity or cloudiness of water. The occurrence of turbidity may be permanent or seasonal. Turbidity may result from insufficient filtration during water treatment or mobilization of sediments, mineral precipitates, or biomass within the water supply network. Changes in turbidity following rainfall may indicate contamination with untreated water. Turbidity is the main problem in the supply system during all analyzed periods. The observed values of turbidity are between 0.42 in June to 0.98 in December. All the samples have turbidity values greater than the objective value of 0.4 NTU, but values are less than the maximum permissible limits for drinking water by 4 NTU, indicated in the standard. The turbidity comes from the source and probably is a consequence of inert clay and chalk particles or of insoluble precipitations that can be related with its karstic origin, human activity in this region, and amortized water supply network of Gurras spring.

The high turbidity values observed in this study are an indication of the absence of the filtration process of water spring. Improvement of turbidity can be achieved by adding the water filtration process (actually only the chlorination process is used) and rehabilitation of Gurras spring capture and pumping station, planned for the next phase of the project. According to the total values of parameters examined, Table 2 calculates overall water quality CCME WQI [12]. The total numbers of parameters examined are 11, and the total numbers of individual tests are 131.



The number of parameters not meeting objectives are 2 (turbidity, temperature), and the number of tests not meeting objectives are 14. The calculated values and ratings of WQI are presented in (Table 4). The WQI of 87.81 indicates that drinking water quality for Pogradec city tap water is ranked 'good.' The "good" quality can be attributed to the measured turbidity that exceeds the objective and to its large excursion. It reflects the intervention between natural effects and those of anthropogenic activities [13].

4. CONCLUSIONS

Discharging of industry polluted water and untreated municipality sewage water in river Drini i Bardhë has a huge consequence for the waters' fauna and for the supplement of the inhabitants with drinking water. A long and uncontrolled discharge of municipal sewage water, agriculture and industrial waste in Drini i Bardhë River, inflicted the change of waters' quality. Therefore, it is special importance to a treat the polluted water (sewage) prior to discharge in the bank of river Drini i Bardhë. With the polluted water in the bank of Drini i Bardhëë River also the organic and inorganic substances are being discharge. Regardless of the evident gaps, still it is possible to reduce or to stop this negative trend, first of all to discontinue the pollution of the river Drini i Bardhë, and to enhance and keep safe its natural goods. The CCME WQI is an effective tool to evaluate water guality for water supply systems. The WQI model used for rating of drinking water quality in Pogradec city indicates that the quality is "good" (CCMEWQI is 87.81) for the year 2011. Turbidity is the most important parameter that determinates the rating of water quality, exceeding the standards (objective) of drinking water. To modify this parameter and to increase water quality, during the treatment process water should be implemented, even the filtration process. The information provided by CCME-WQI is a useful tool for describing the state of the drinking water quality and can be of great value for water users, suppliers, and planners, etc. Tastes and odors in water may be derived from a variety of conditions and sources. They may originate as a result of water treatment (e.g., chlorination). In this



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Water quality analysis and trends on Prud pilot area in BiH

Lead Author/s	Ninjel Lukovac
Lead Authors Coordinator	Sabina Hadžiahmetović
Contributor/s	Melina Džajić-Valjevac
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1 Introduction

In this report are given water quality trends and data analysis of Trebižat River which drainage into Prud spring which is a pilot area within project DRINKADRIA. Water analyses are based on annually reports of Adriatic Sea Watershed Agency in Mostar and on data they obtained from regular monitoring stations on Trebižat River in period between 2009 and 2014.

Observation program of water quality of rivers located around entire Adriatic region is obtained by regulatory body mentioned above on monthly basis. In this region, under the authority of Adriatic Sea Watershed Agency is following monitoring stations (Figure 1):

- Neum Hotel Neum beach
- Accumulation of hydro power plant Grabovica Jablanica
- Bistrica Livno upstream
- Bistrica Livno downstream
- Lake Boračko
- Swimming pool Jablanica Ostrožac
- Swimming pool Neretva Carinski Bridge
- Swimming pool Dam of Lake Jablaničko
- Swimming pool Marinovac Buško Blato
- Neum Sea
- Neretva Bačevići
- Neretva Dračevo
- Neretva Konjic upstream
- Neretva Konjic downstream
- Neretva Raštani
- Neretva Žitomislići
- Neum Hotel "Sunce" beach
- Neum Hotel "Zenit" beach
- Trebižat intake.



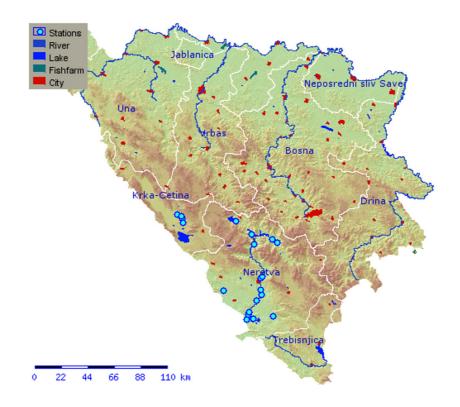


Figure 1. Regular monitoring stations of rivers located in Adriatic Region Area in Bosnia and Herzegovina

In this report are given water quality trends and data analysis of Trebizat River which drainage into Prud spring which is a pilot area within project DRINKADRIA.

Water analyses are based on annually reports of Adriatic Sea Watershed Agency in Mostar and on data they obtained from regular monitoring stations on Trebižat River in period between 2009 and 2014.

Starting point of a water supply system represents regulated and protected water source. Its quality largely determines the character of the entire water supply system, especially the quality of the water used for human consumption, operating and investment, maintenance and development of systems and protection measures. In addition, observation of quality on water sources enables locating problems in water quality, which can occur within the water supply system. The municipality public companies for water supply are responsible for regular monitoring at water sources which are used for public water supply at BiH Prud catchment area.

All features which water sources must satisfy of large number of conditions, such as sanitary and hygienic conditions, economic, social, cultural and technological conditions,



can be reduced to two basic indicators of water sources, such as quality and quantity of water.

Regulations on the health safety of drinking water have criteria in the form of maximum allowable concentrations (MAC) and evaluations "satisfy" or "not satisfy", in which lower values are desirable and recommended, but not necessary from the point of use, as long as the water quality was assessed as adequate. If the evaluation of the water was not up to standard for drinking water it was treated according to sanitary regulations, either through recommendation, limited or complete interruption of water supply, temporarily or permanently, depending on the assessment of threats and risks to health.

Regulation on water classification and Regulation on hazardous substances of natural waters are classified, evaluated and graded into types, where the limit values of indicators point to the sources and causes of changes in the water quality. A large proportion of numerical values of certain types of criteria (e.g. nitrates are classified into four types until they reach MAC for drinking water), is located in the area for "satisfy" of drinking water, because from the perspective of water protection, changes and trends, primarily in deterioration of water, must see and must have a certain space-time to take appropriate protection measures, and that water can still be used for a particular purpose. The transition in the area of evaluation "not satisfy" means that water for that purpose is either temporarily or permanently lost. In this case, the protection of water failed and all measures that following include solutions for resolving contamination or pollution which has already occurred.

According to decision from Water Law FBiH ("Official Gazette" 19/98) Regulation on Classification of Waters and Coastal Sea Waters within the Borders of Former Socialist Republic of Bosnia and Herzegovina (Official Journal of SR BiH no. 18/80) is still a valid document for classification of surface water, including sea and coastal water as well. For Republic of Srpska entity, according to Low on water (Official Gazette RS, no. 50/06), Regulation on classification and categorization of watercourses (Official Gazette RS, no. 42/01) is legislation which describe conditions of water classification on the territory of this entity and it take into account surface water only.

In the entity of Federation of BiH, Regulation on Dangerous and Harmful Substances in Water (Official Gazette of FBiH no. 43/07) has criteria for determination of physicalchemical quality of surface water. For determination of water body status there is still not a law regulation on the level of legislation, instead there is document Decision on Characterization of Surface and Ground Waters, Reference Requirements, and Parameters for the Assessment of Water Status and Water Monitoring (Official Gazette of FBiH no. 1/14) which is not yet in use for determination of water body status.



2 Pilot area and tested water quality parameters

Prud project pilot area is BiH – Croatia cross border catchment area. Prud water source is located in Croatia and it use for public water supply in Croatia. The largest part of the Prud catchment area is located in BiH, while small part is in Croatia.

As part of those surveys, it is also taken into account importance of Trebižat River quality, as a water body which drainage into ground water and maintaining the quantity of water resources of this significant cross – border spring. The position of existing water quality monitoring stations on Trebižat River are presented on the next Figure.



Figure 2. BiH-Croatia cross – border catchment area Prud and location of water quality monitoring stations on Trebižat River

The water quality monitoring at presented monitoring stations presented above includes following water quality parameters:

- Organoleptic properties of water (color, smell, taste);



- Physical and chemical properties: temperature, pH, alkalinity, total hardness (as mg CaCO₃/l), electrical conductivity, evaporation residue at 105°C, total suspended solids;
- lons: fluoride, chloride, sulfate, sodium, potassium, calcium, magnesium, silica dioxide, total cyanides;
- Oxygen: dissolved oxygen and oxygen saturation, COD-permanganate index, BOD₅;
- Nutrients: nitrogen compounds (ammonia, nitrites, nitrates, organic N, Kjeldahl N and total N) and phosphorus compounds (orthophosphate and total phosphorus);
- Organic matter: anionic detergents (MBAS index), non-ionic detergents, total phenols expressed as an index, mineral oils, total organic carbon (TOC), volatile organic hydrocarbons, organochlorine pesticides, triazine and organophosphorus pesticides, alachlor, aromatic polycyclic aromatic hydrocarbons (PAH);
- Heavy metals (cadmium, copper, zinc, iron, manganese, total chromium, lead, mercury, nickel, arsenic and aluminium);
- Bacteriological indicators (total coliforms, fecal coliforms and Escherichia Coli, fecal streptococci (enterococci), the total number of bacteria at 22°C and 37°C, Clostridium Species and Pseudomonas Aeruginosa.

Monitoring frequency on stations mentioned above is performing on monthly basis which means 12 times on year.

Reference values were calculated from annual data measurements and compared with the limit values of indicators for certain types of water. Calculation of reference values depended on the number of data. For a number of data of 12 or more, the relevant value is calculated as the value of 90% of percentiles (except for biological indicators, dissolved oxygen and oxygen saturation). When the number of data is less than 12, the relevant value was calculated as the median value (including biological basis), while the dissolved oxygen and oxygen saturation were taken as the relevant value of 10% of percentile, regardless to the number of data.

3 Analyses results and water quality trends

There are available only data for Trebižat – intake profile station for period 2010 – 2014. These data are elaborated as follows.

7



3.1 Physical and chemical quality

Basic physical-chemical properties of surface water on monitoring station Trebižat intake show quite deviations in evaluated water quality parameters values, but it is mostly in normal annual fluctuations when concentrations depends on hydrological conditions in the basin. Other changes of water quality potentially expected on Trebižat River basin could be mostly anthropogenic, due to possible influence of communal waste waters from places in the basin.

On the monitoring stations is generally measurable impact of rainwater or surface flood waters during periods of intensive rainfall, which can manifest as a decrease in the value of electrical conductivity.

On *figure 3 are* given monthly measured values for total suspended solids on Trebižat River on profile Monitoring station Trebižat – intake in period 2010 – 2014.

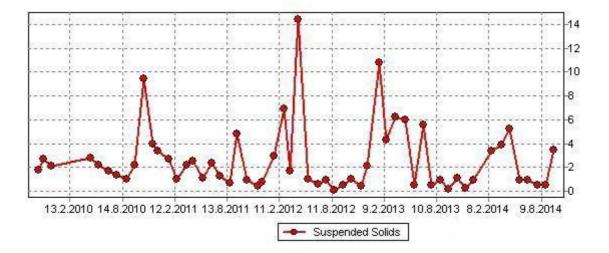


Figure 3. Total suspended solids in Trebižat River measured once on month (Limit value is 10 mg/l)

3.2 Oxygen regime and other parameters

On the Trebižat River, there was a period of time with significantly higher level of oxygen saturation, which could be indication of higher concentrations of nutrients due to increased activities of algae and oxygen could be mostly from photosynthesis process. According to legislations in both entities in BiH, concentrations higher of 105% decreases water class to II/III class, and concentration higher than 125% determines water in IV class.



On *figures 4 and 5* are given mean annual values for BOD_5 and COD on Trebižat River in period 2010 – 2014. According to *International Commission for Protection of Danube River – ICPDR*, bichromate COD is also measured, comparing surface water similar as waste water to determine possible influences of communal and industrial waste water if there are presented in the basin.

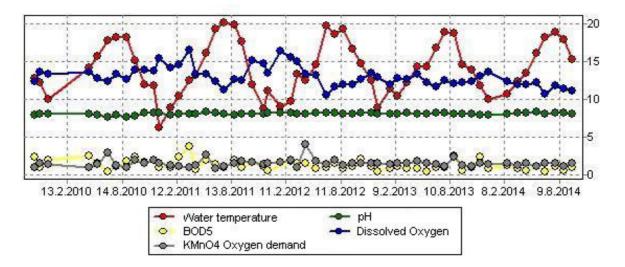


Figure 4. Mean annual values for COD (KMnO₄), BOD₅, dissolved oxygen and pH on Trebižat River

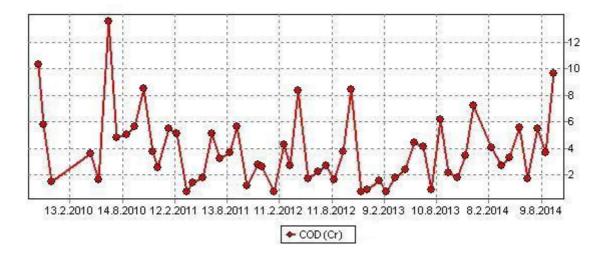


Figure 5. Mean annual values for COD (Cr) on Trebižat River (Bichromate oxygen demand is recommended by International Commission for Protection of Danube River – ICPDR)



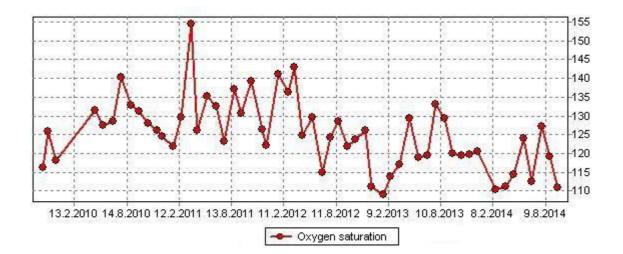


Figure 6. Mean annual values for oxygen saturation expressed in percentage on Trebižat River (Limited values are 90 – 105%)

3.3 Nutrients

Nutrients are compounds of nitrogen and phosphorus. For water sources as well as surface waters, expected concentrations of phosphates and total phosphorus are very low. On *figure 7* are given mean annual values for total phosphorus; it can be seen that it has decreasing trend over time on the Trebižat River – intake measuring profile.

The largest contribution to the total nitrogen is from inorganic compounds mostly due to the nitrate content. Generally the content of the inorganic nitrogen is mostly composed of the nitrates, which means that the content of ammonium and nitrite, as indicators of present fresh contamination is very low and rarely appear in detectable low concentrations. Nitrate content on the Trebižat River vary over time. Slightly higher concentration are measured in all period range from 2010 – 2014 mostly in small water periods, but still in range required for II class of water. Indicators of fresh contamination like ammonia and nitrites were in range of limited allowed concentration according to law regulation, so there is no indication of potentially constant anthropogenic impacts. Because this river is not deep, during the summer period it is expected to have quite higher conductivity, and according to that more nitrates as well.



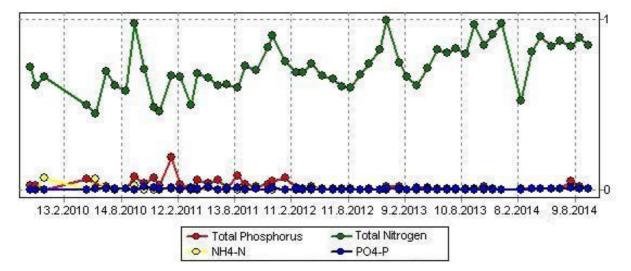


Figure 7. Annual values trends for total nitrogen and phosphorus, ammonia and ortho phosphates on Trebižat River from 2010-2014

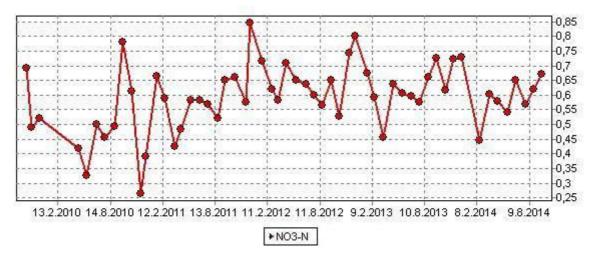


Figure 8. Mean annual values for nitrates on Trebižat River from 2010-2014



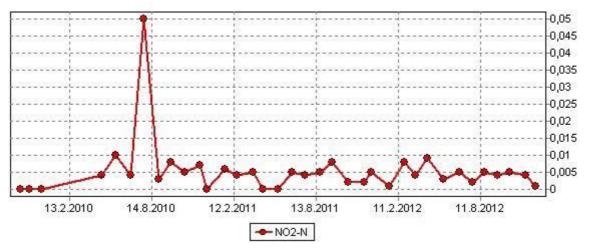


Figure 9. Mean annual values of nitrites on Trebižat River for 2010-2014

3.4 Microbiological parameters

Microbiological contamination is present in Trebižat River down the whole stream, and a large range is between minimum and maximum values which is associated to the hydrological conditions in the river basin. High values could be associated with the occurrence of torrential waters and increased amounts of silt which is common in this area during periods of high waters or occasional flooding of the river basing area. Due to turbulent flow of water, move of the internal sediment occurs and then result with the appearance of turbidity.

Higher concentrations of total number of microorganisms and microorganisms of fecal origin including Escherichia Coli were detected almost constantly on intake monitoring station. The main source of these organisms can be untreated urban waste waters from settlements in the observed river basin area.



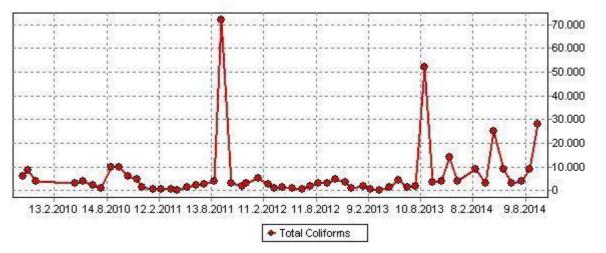


Figure 10. Trend in numbers of total coliforms in water on Trebižat River for 2010-2014

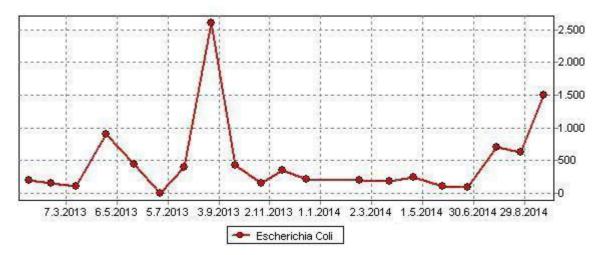


Figure 11. Trend in numbers of Escherichia Coli in water on Trebižat River for 2010-2014 (They should not be present in water in any number according to legislation)



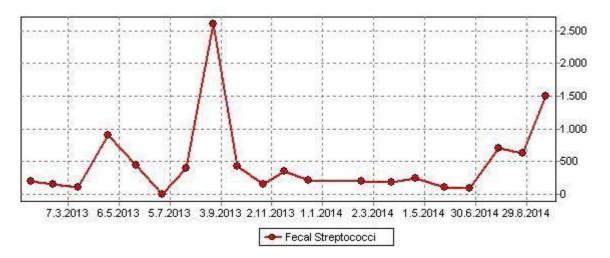


Figure 12. Trend in numbers of fecal Streptococci in water on Trebižat River for 2010-2014

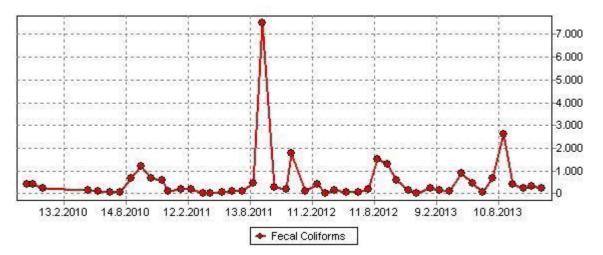


Figure 13. Trend in numbers of total Coliforms in water on Trebižat River for 2010-2014





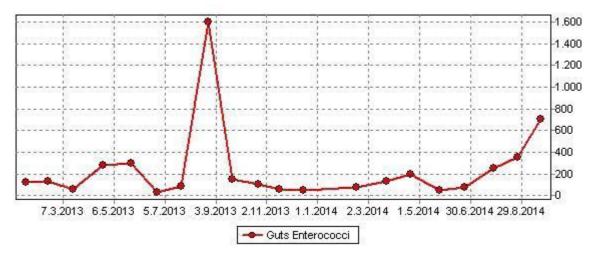


Figure 14. Trend in numbers of Enterococci in water on Trebižat River for 2010-2014

3.5 Heavy metals

In the period from 2010 – 2014 are measured increased concentrations of copper and total chromium which were above the Maximum Allowable Concentration (MAC) for surface water. Concentrations of lead were in the range of limit values except in 2010 when was measured a high amounts in summer period, due to lower water level in that hydrological conditions. However, for this parameter on observed period of time there is continuous decreasing trend with concentration constantly below MAC values.

On *figures 15 – 19* are given mean annual values Hg, Cd, Cr, Pb, Cu, Ni, Zn, Fe and As on Trebižat River in period 2010 – 2014.



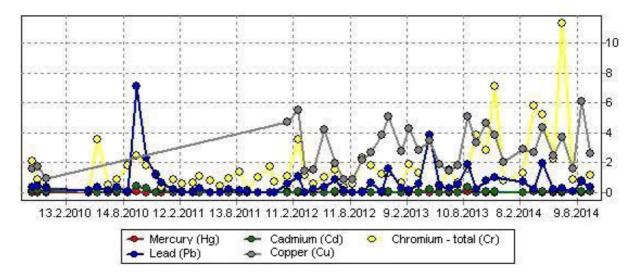


Figure 15. Changes in heavy metal concentrations on Trebižat River for 2010 – 2014

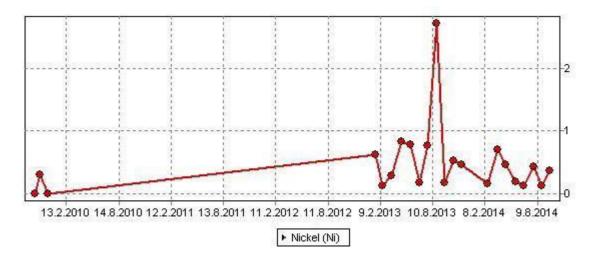


Figure 16. Changes in concentrations of nickel (Ni) on Trebižat River for 2010 – 2014



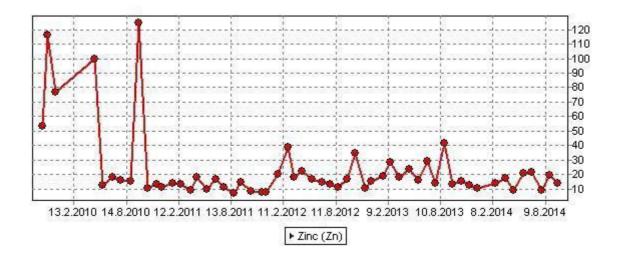


Figure 17. Changes in concentrations of nickel (Ni) on Trebižat River for 2010 – 2014

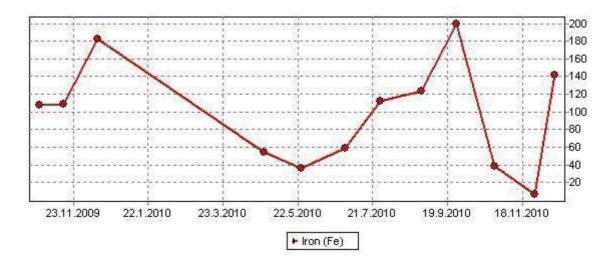


Figure 18. Changes in concentrations of iron (Fe) on Trebižat River for 2010 – 2014



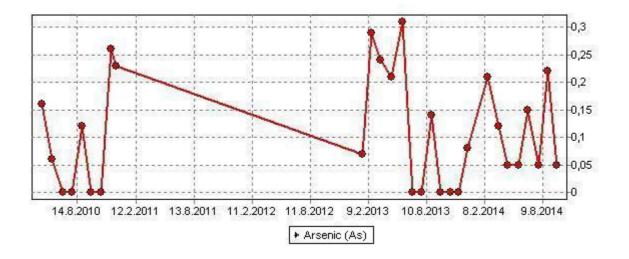


Figure 19. Changes in concentrations of arsenic (As) on Trebižat River for 2010 – 2014

At water source Prud are used procedures of settling, filtration and disinfection. With use of settling procedure and water filtration suspended solids are removed, and also with these procedures are reduced the concentration of metals and lipophilic substances, including mineral oils to the values that satisfy drinking water standards. Some of the heavy metals which could be found in ground water could be due drainage of Trebižat River which is important for maintaining a water quantity of source Prud.

3.6 Organic compounds

In the spring waters are not detected measurable concentrations of organic compounds, generally hydrocarbons (mostly C-10 – C-40), volatile hydrocarbons, polyaromatic hydrocarbons (PAH), organochlorine pesticides, some organophosphorus and triazine pesticides and other tested chemicals as phenols, cyanides, anionic and cationic surfactants.

4 Water quality evaluations

Water quality evaluation was conducted according to the valid regulations for each year. Evaluation of surface water according to the valid regulations refers to all measured values of required parameters compared to the Maximum Allowable Concentration (MAC) which is at the same time indicator for the substances (polluters) which should be removed from the water. For ground water which quantity, but also quality depends of drainage of Trebižat River also should pass through the proper technological process of purification,



so values of polluters mentioned above could be decreased to the values that are below the prescribed maximum allowable concentration of certain substances.

In Table 1 are given all parameters that describe a certain substance or group of substances that have exceeded the MAC at each sampling station.

Table 1. Evaluation of surface water resources according to the legislation - parameters with measured values above the MAC in period 2010 - 2014 on Trebižat River

Year Parameter	2010	2011	2012	2013	2014
Oxygen saturation	X	X	X	X	X
Nitrite					
Nitrate					
Ortophosphate					
Total Chromium	X	X	X	X	X
Lead	X				
Copper			X	X	X
Microbiological	X	X	X	X	X

X – Parameters with value above MAC

5 Conclusions

Water quality of Trebižat River shows highly saturation with oxygen, mostly due to fitobentos activities and occasionally content of the substances that can be oxidized and decomposed by microorganisms (expressed as a five-day biochemical oxygen demand - BOD₅) or by using a strong oxidant, expressed as a chemical oxygen demand - COD bichromate index.

Nutrients are compounds of nitrogen and phosphorus which could lead to eutrophication of water bodies due to increasing microorganism activities, mostly fitobentos which use those mineral compounds as part of essential nutrients. This could as a consequence have a high oxygen saturation, which is not pollution but according to legislations is strong indication of eutrophication and change in water living ecosystem and because of that change in water class as well (biological status is most important classification parameter). For the Trebižat River concentrations of phosphates and total phosphorus are very low.

The largest contribution to the total nitrogen of the inorganic part is nitrate content. Generally the content of the inorganic nitrogen is almost all composed of the nitrates, which means that the content of ammonium and nitrite, as indicators of present fresh



contamination is very low and rarely appear in detectable concentrations if water body is not exposed to direct fresh anthropogenic contamination. Nitrate concentration on Trebižat River is in the range which corresponds to II class of water. Water levels are dependent on water situations during year, and could contribute in nitrate concentrations which determine II class. It is not expected significant impact of eventually non adequate communal waste waters from urban area in river basin.

Microbiological contamination is present in Trebižat River down the whole stream, and a large range is between minimum and maximum values which is associated to the hydrological conditions in the river basin. High values could be associated with the occurrence of torrential waters and increased amounts of silt which is common in this area during periods of high waters or occasional flooding of the river basin area.

Higher concentrations of total number of microorganisms and microorganisms of faecal origin including Escherichia Coli were detected almost constantly on intake monitoring station. The main source of these organisms can be untreated urban waste waters from settlements in the observed river basin area.

In the period from 2010 – 2014 are measured increased concentrations of copper and total chromium which were above the Maximum Allowable Concentration (MAC) for surface water. Concentrations of lead were in the range of limit values except in 2010 when was measured a high amounts in summer period, due to lower water level in that hydrological conditions. However, for this parameter on observed period of time there is continuous decreasing trend with concentration constantly below MAC values.

From observed mean annual values of oxygen saturation, BOD₅, COD, total suspended solids, nitrates, total phosphorus and heavy metals, it can be concluded following: Trebižat River according to data collected from monitoring station Trebižat – intake all tested parameters have declining trend, only oxygen saturation have trend of continues maintaining of high values which could be indication of eutrophication of water body. Concentration of heavily oxidizing organic compounds (determined with dichromate index according to ICPDR legislation) is also constant, and could be considered as a potentially indicator of pollution.

Nutrient content is shown through the content of nitrates and total phosphorus. For Trebižat River maximum values of these indicators have trend of continuity in varying values but is should not expect concentration above MAC values. The values of nitrate content is 0,5 mg/l for I class and 0,5-1,5 mgN/l for II class. Phosphorus content is generally below the MAC for surface water.



From the analysis of the water quality for Trebižat River can be seen that there is absence of fresh pollution indicators in the basin, but this water body could be potentially eutrophicated which could have impact on biological status, which leads to the conclusion that the measures taken in terms of protection of drinking water sources should be increased.

Importance of cross border cooperation between BiH and Croatia is well shown on this pilot area because it is significant to take into account all potential impacts on entire area of Prud to diminish negative impacts and increase quality of both ground water and surface water of Trebižat River which drainage into Prud source watershed.



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Institut za hidrotehniku Građevinskog fakulteta u Sarajevu – Sarajevo, November 2014





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Water quality analysis and trends on pilot areas in Niksic

Public Utility "Vodovod i kanalizacija"- Niksic (FB14)

Lead Author/s	Papovic Mira
Lead Authors Coordinator	Papovic Mira
Contributor/s	
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1. INTRODUCTION

A water quality analysis regarding the pilot area of the city of Nikšić has been given in this Report within the DRINKADRIA project. The Report was prepared with reference to the springs Gornji Vidrovan, Donji Vidrovan and Poklonci, which are included in the water supply system of the city. The Report was prepared on the basis of a report on the quality of chlorinated and non-chlorinated water from the water supply system which was prepared by the Institute of Public Health in Podgorica for the purpose of Public Utility "Vodovod i kanalizacija"- Nikšić. The period of last 10 years has been analyzed.

The way of water use and management and requirements for performing water sector activities on the territory of Montenegro has been defined by the Law on Water (Official Gazette of RoM No. 27/2007 and Official Gazette of MNE No. 32/2011 and No. 47/2011.

The sources that are included in the water supply system in the pilot area of the town of Niksic have water management permits i.e. sanitary protection zones have been defined within the water supply system in accordance with the "Rulebook on the procedure for definition of sanitary protection of drinking water sources zones, maintenance and limitations in those *zones* (Official Gazette of MNE No. 66/2009 of 2.10.2009). Before entry into force of the said Rulebook, the "Rulebook on the procedure for definition of sanitary protection of drinking water sources *zones*, maintenance and limitations in those *zones* (Official Gazette of MNE No. 66/2009 of 2.10.2009). Before entry into force of the said Rulebook, the "Rulebook on the procedure for definition of sanitary protection of drinking water sources *zones*, maintenance and limitations in those *zones*"(Official Gazette of RoM, No. 8 / 97) had been applied.

The quality of water used for water supply has been defined by the "Regulation on hygienic drinking water quality" (Official Gazette of MNE No. 24/2012 of 04.05.2014.) Before entry into force of the said Regulation, the "Regulation on hygienic drinking water quality" (Official Gazette of FRY 42/98 and 44/99) had been applied.

The water sources Gornji vidrovan and Donji Vidrovan are capped karst springs very sensitive to changes in the hydrological regime. These two sources are connected to the water supply system throughout the whole year. In spring and autumn during high intensity rainfalls there is an increased turbidity and mild microbiological contamination.

The spring Poklonci is an underground water source that is connected to the water supply system by the system of well bores, and it is included in the water supply system only during the dry season. Certain physical-chemical parameters are monitored at a local lab on a daily basis, while the Institute of Public Health in Podgorica is engaged for complete water microbiological and physical-chemical analysis.



2. Pilot areas and tested water quality parameters

Regarding the pilot area in city of Niksic, the Institute of Public Health in Podgorica take samples for complete physical-chemical and microbiological analyses at five locations twice a month while physical-chemical analysis are carried out at a local laboratory on a daily basis and if there are any deviations from any values of Maximum Allowable Concentration then additional complete analysis of samples from all five locations are done.

The following table lists the results of physical-chemical quality parameters for the period from 2003 to 2013 – Public Utility Nikšić.

Year	Physical-chemical analysis						
	No of samples	correspond	not correspond	not correspond %			
2003	280	262	18	6.4			
2004	247	246	1	0.4			
2005	234	229	5	2.1			
2006	264	255	9	3.4			
2007	199	171	28	14.7			
2008	260	234	26	10			
2009	264	234	30	11.36			
2010	268	220	48	17.91			
2011	245	233	12	4.90			
2012	240	227	13	5.42			
2013	246	219	27	10.98			

Regarding physical and chemical analysis, turbidity is the only parameter whose value deviated from the Maximum Allowable Concentration within the previous period.

The increased turbidity occurs only in the rainy season because the sources Gornji Vidrovan and Donji Vidrovan are capped karst springs very sensitive to changes in the hydrological regime. The table shows an increased number of deviations in 2007, 2008, 2009, 2010 and 2013 and in those years there was a significant change in the hydrological regime i.e. there were frequent precipitations of greater intensity.

The following table lists the results of microbiological quality parameters for the period from 2003 to 2013 – Public Utility Nikšić.



Year	Microbiological analysis						
	No of samples	correspond	Not correspond	not correspond %			
2003	280	248	32	11.4			
2004	247	223	24	9.7			
2005	234	213	21	9			
2006	264	255	9	3.4			
2007	205	182	23	11.2			
2008	263	234	29	11.03			
2009	265	247	18	6.79			
2010	270	257	13	4.81			
2011	251	240	11	4.38			
2012	234	218	16	6.84			
2013	123	115	8	6.50			

In spring and autumn during high intensity rainfalls, there is a slight microbiological contamination. The bacteria such as Escherichia coli and total coliforms are present and their maximum registered value is 1/100 ml.

3. Test results

The water supply system includes three sources Gornji Vidrovan, Donji Vidrovan and Poklonci. The sources Gornji Vidrovan and Donji Vidrovan are capped karst springs while the water source Poklonci is of a type of a well and it is connected to the water supply system only during a dry season.

Regarding the pilot area in Nikšić, the following water quality parameters are monitored in a lab of Public utility "Vodovod i kanalizacija" on a daily basis:

- temperature
- colour
- pH
- alkalinity
- hardness
- chlorides
- electrolytic conductivity
- consumption of KMnO4
- ammonia
- nitrites
- nitrates



- iron
- manganese
- turbidity

The Institute of Public Health in Podgorica is engaged twice a year to do sampling and analysis of physical-chemical and microbiological parameters of water quality at five locations within the town.

These physical-chemical parameters are analyzed:

- temperature
- colour
- odour
- taste
- turbidity
- concentration of hydrogen ions
- consumption of KMnO4
- ammonia
- free chlorine in the field
- chlorides
- nitrites
- nitrates
- fluoride
- evaporated residue or total residue after evaporation
- electrical conductivity at 20 °
- iron
- manganese
- detergents-anionic
- phenols
- mineral oils



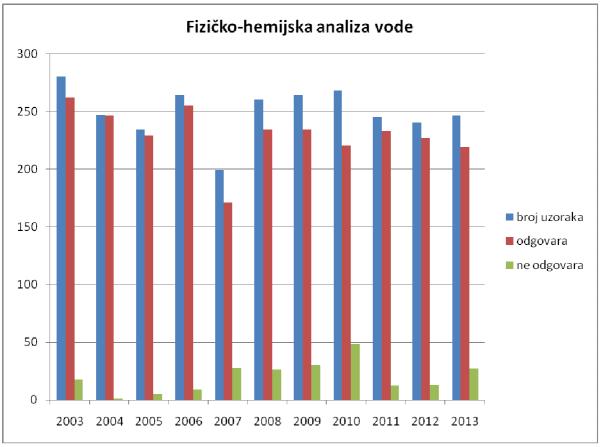


Chart No. 1: Graphic physical-chemical analysis of water in the pilot area in Nikšić for the period of 2003-2013 (No of samples, correspond not correspond).

The only listed parameter whose value deviated from Maximum Allowable Concentration within the previous period is turbidity. The increased turbidity occurs only in the rainy season because the sources Gornji Vidrovan and Donji Vidrovan are capped karst springs very sensitive to changes in the hydrological regime. The maximum value of turbidity measured in the previous period is 6 NTU and Maximum allowable concentration is 1 NTU.

Microbiological parameters to be analyzed are:

- Escherichia coli (MPN)
- Total coliforms (MPN)
- Enterococcus species
- Pseudomonas aeruginosa (MPN)
- Aerobic mesophilic bacteria at 37 °
- Aerobic mesophilic bacteria at 22°
- Parasites and protozoa



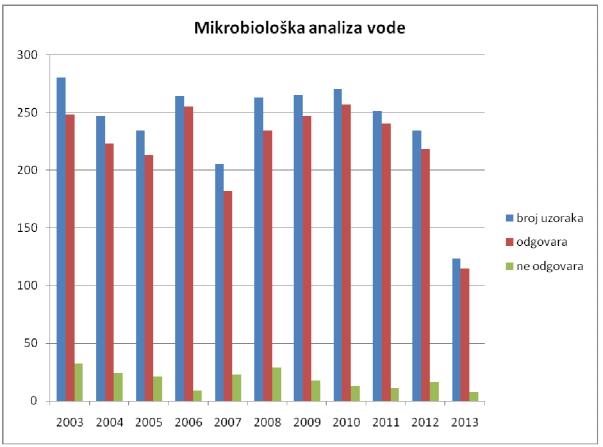


Chart No. 2: Graphic microbiological analysis of water in the pilot area in Nikšić for the period of 2003-2013. (No of samples, correspond not correspond).

With reference to these microbiological parameters, in the last period it was recorded the occurrence of a bacteria Escherichia coli and total coliforms (their maximum registered value is 1/100 ml).

This occurs during the rainy season because the sources Gornji Vidrovan and Donji Vidrovan are capped karst springs very sensitive to changes in the hydrological regime.

4 Conclusion

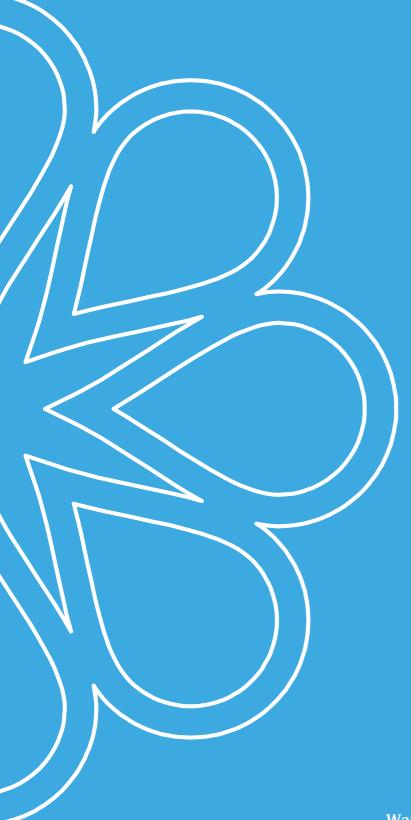
Based on the current analysis, it can be concluded that water used for water supply in the pilot area in Niksic has a good quality. Deviations of quality parameters (turbidity and mild microbiological contamination) from maximum allowable concentration occur only during heavy precipitation. The only treatment that is applied is the chlorination at springs.



5 References

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Water quality analysis and trends on pilot areas in Niksic – Nikšić 2015

Let's grow up together



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WP4.3 Report: Water Quality analysis and trends on Corfu test area in Greece

Civil Engineering Department University of Thessaly, Greece

Volos, 2015

Lead Author/s	Assoc. Prof. Vasilis Kanakoudis
Lead Authors Coordinator	Assoc. Prof. Vasilis Kanakoudis
Contributor/s	Dr. S. Tsitsifli, A. Papadopoulou, I. Argyriadou, A. Rouva, I. Hitiri
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1 Introduction

In this report water quality trends and data analysis is provided for the Island of Corfu which is a pilot area within the project DRINKADRIA.

In Greece, following the Water Framework Directive (WFD 2000/60/EC) implementation monitoring stations have been identified to monitor surface waters, groundwater, transitional and coastal water systems. There are surface water and groundwater bodies identified in the River Basin District of Corfu – Paxi (Tables 1&2; Figures 1&2).

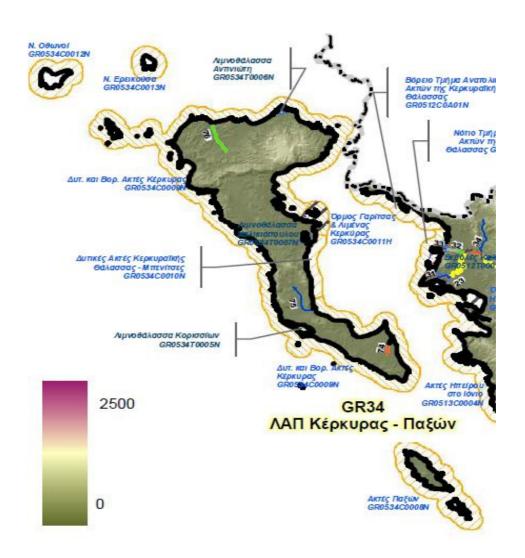


Figure 1: Identification of Surface Water Bodies in the River Basin District of Corfu – Paxi (GR34) [1]



			Bodies		Water	Coastal Water Bodies			
Name		Potami	Number	•	3	Number (t	6		
Code		GR0534R000101074N		Min		Heavily M		1	
Name		Messagis	Surface	Average	2.34		Min	20.48	
Code		GR0534R000301075N		Max	4.16	Surface	Average	101.16	
Name		Fonissa		Total	7.01	(Km²)	Max	406.14	
Code		GR0534R000501076N		1	•		Total	606.95	
	Min	2.16				L			
Length	Average	5.52							
(Km)	Max	7.54							
. ,	Total	16.57	-						
	Κωδικός ΥΥΣ	Ονομασία Υγ	GR05000 20 R050002		2050 003 ¹⁰		GR050A		
	GR0500010 GR0500020	Σύστημα ασβεστολίθων Ν.Κέρκυρας Σύστημα Τριαδικών λατυποπαγών Ν.				GR34	Ş		
	GR0500030 GR0500040	Σύστημα κοκκωδών υδροφοριών Ν. Κέ Σύστημα Ν.Παξών	ερκυρας			ΛΑΠ	<u>د</u>		
	GR0500050	Σύστημα Ν.Οθωνών			Κέρκυ	ρας - Πα	EUN		
	GR050A060 GR050A070	Σύστημα Μουργκάνας Σύστημα Φιλιατών-Ηγουμενίτσας			Repro	pus - nu			
	GR0500080	Σύστημα μέσου ρου Καλαμά							
	GR0500090 GR0500100	Σύστημα Σουλίου-Παραμυθιάς Σύστημα Τύμφης							
	GR0500100 GR0500110	Σύστημα Κληματιάς			G	R050040			
	GR0500120 GR0500130	Σύστημα Κασιδιάρη Σύστημα Κορώνης							
	GR0500130 GR0500140	Σύστημα Χερσονήσου Πρέβεζας				4			
	GR0500151 GR0500152	Σύστημα Λούρου Σύστημα Λούρου							
	GRUSUU152	zoodiju noopod		I					

Table 1: Surface Water Bodies in the River Basin District of Corfu – Paxi [1]

Figure 2: Identification of Groundwater Bodies in the River Basin District of Corfu – Paxi (GR34) [1]



Groundwater Bodies								
Name		Limestone	Ternary	Granular	Paxi island	Othones		
		system –	breccia	aquifers	system	island		
		Corfu island	system –	system –		system		
			Corfu island	Corfu island				
Code		GR0500010 GR0500020 GR0500030 GR0500040 GR050				GR0500050		
	Min	10,614,240						
Surface (m ²)	Max	290,184,931						
	Total	553,828,908						

Table 2: Groundwater Bodies in the River Basin District of Corfu – Paxi [1]

2 Pilot area and tested water quality parameters

In Corfu, the water bodies identified are: 3 rivers, namely Messagis (7.5Km), Fonissa (7Km) and Potami (2.1Km); 3 transitional water bodies (lagoons); 6 coastal water bodies, one of them heavily modified; and 3 groundwater bodies (Tables 1&2) [1].

According to the WFD 2000/60/EC a monitoring stations' network already established monitors water quality in the water systems. In Corfu the monitoring stations are shown in Figure 3 and Table 3 [2].



Figure 3. Water quality monitoring stations in Corfu (green: groundwater; red: rivers; blue: coastal; grey: transitional) [2]



Table 3: Monitoring stations in Corfu [2]

Station	Station Code	Water	Water System Code	Type of Water
Name		System		System
Korission	GR000500020005N500	Korission	GR000500020005N	Transitional
		laggon		
Kerkyraiki	GR000500010009N500	West coast of	GR000500010009N	Coastal
		Kerkyraiki		
		sea		
FK5	GR05020502	Perithia-	GR0502	Groundwater
		St.Martinos		
		system		
FK6	GR05010501	Lakones-	GR0501	Groundwater
		Krini system		
KF56	GR05010554	Lakones-	GR0501	Groundwater
		Krini system		
KF58	GR05010555	Lakones-	GR0501	Groundwater
		Krini system		
KΓ71	GR05010556	Lakones-	GR0501	Groundwater
		Krini system		
KF133	GR05010557	Lakones-	GR0501	Groundwater
		Krini system		
KF135	GR05010558	Lakones-	GR0501	Groundwater
		Krini system		
SK3	GR05010559	Lakones-	GR0501	Groundwater
		Krini system		
SK7	GR05040503	Gouvia-	GR0504	Groundwater
		Chrysiida		
		system		
FK136	GR05030504	St Mathaios	GR0503	Groundwater
		system		
MESAGGI	GR0005000400280100N500	Messaggis	GR0005000400280100N	River
		River		
FONISSA	GR0005000400270100N500	Fonissa River	GR0005000400270100N	River

The surface water bodies are classified according the classification system set by the WFD 2000/60/EC [1]. Groundwater bodies are monitored measuring the following parameters: pH, conductivity, chlorides, sulfates, nitrates and ammonium.



3 Analysis results and water quality trends

3.1 Surface water bodies

Point pollution sources

The following point pollution sources are identified in the Water Sub-Basin District of Corfu-Paxi [1]: wastewater; industry (20% of the total industrial activity of the Water District of Epirus: 82% of the industrial activities are oil mills); livestock farming; fish farms; unmonitored waste disposal sites; landfill sites; and mining activities.

The total number of industrial units identified is 121. The pressure of the point pollution sources to the surface water bodies is assessed as high (H), medium (M) and low or none (L) (Table 4) [1].

Code	Name			Sewage treatment plants			Livestock farming	Fish farms		Waste disposal sites
GR0534R0001 01074N	Potami		R	L	Н	L	L	L	L	М
GR0534R0001 01075N	Messagis		R	L	Н	L	L	L	L	L
GR0534R0001 01076N	Fonissa		R	L	Н	L	L	L	L	М
GR0534C0000 9N		& coast	С	М	L	L	L	М	L	L

Table 4: Pressure assessment to surface water bodies [1]

According to the RBMP [1], the diffuse pollution sources are not considered as a significant pressure given that the estimated concentrations of organic carbon, nitrogen and phosphorus do not exceed the allowable values.

Quality assessment

The "good status" of surface water and groundwater bodies is examined in the River Basin Management Plan of Epirus (GR05) [1] which includes the island of Corfu. The 3 rivers identified (Table 1 & Figure 1) are classified as IsL1, meaning that the rivers belong to the bio geographical region of Ionion Sea, with small runoff, low altitude and steep slope (>1.2‰) (Figure 4). The lagoons are classified as TW2 systems with salinity from 5 to 30 PSU and micro tide (Figure 4). All coastal systems in Greece are classified as C1 (Figure 4) [3].



The heavily modified coastal system is the bay of Garitsa and the port of Corfu. Its surface is 20.48Km², classified as C1 and its code is GR0534C0011H (Figure 5). This system is used for navigation purposes. The chemical status of the surface water bodies is unknown [1].

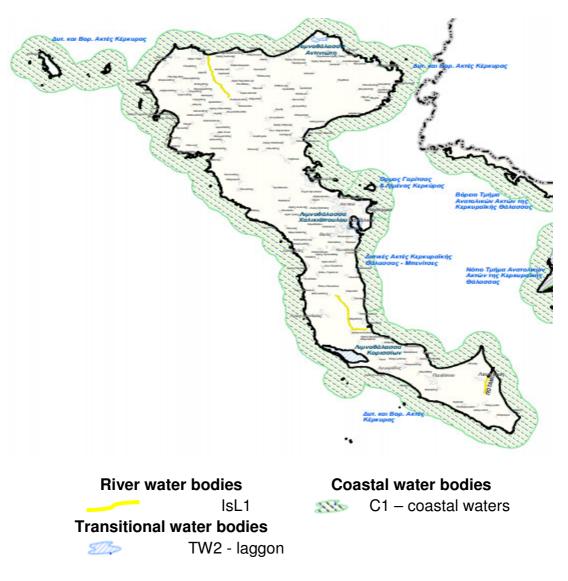


Figure 4. Characterisation of the surface water bodies in Corfu [3]





Figure 5. The Garitsa – Port of Corfu bay [4]

3.2 Groundwater bodies

There are 3 groundwater bodies identified in Corfu: the limestone system (GR0500010); the ternary breccia system (GR0500020) and the granular aquifers system (GR0500030). According to the Ministerial Decision 1811/Official Gazette (FEK)3322/ β /30.12.2011 (implementing the paragraph 2 of the article 3 of the Joint Ministerial Decision 39626/2208/E130/2009) the Maximum Allowable Concentration (MAC) of a list of water parameters is provided (Table 5). The following parameters are monitored in the 3 groundwater bodies in Corfu: pH, conductivity, chlorides, sulfates, nitrates and ammonium.

Parameter	Maximum Allowable Concentration (MAC)
Nitrates (NO3)	50 mg/l
Total pesticides	0,5µg/l
Active substances in pesticides	0,1 μg/l
Arsenic (As)	10 µg/l
Cadmium (Cd)	5 μg/l
Lead (Pb)	25 μg/l
Mercury (Hg)	1 µg/l
Ammonium	0,5 mg/l
Conductivity	2500 μS/cm
Chlorides (Cl-)	250 mg/l
Sulfates	250 mg/l
Total synthetic substances	10 µg/l
(trichloroethylene & tetrachlorethylene)	
рН	6,5-9,5
Nitrites	0,5 mg/l
Nickel (Ni)	20 µg/l
Chromium (Cr)	50 µg/l
Aluminum (Al)	200 µg/l

Table 5: Maximum Allowable Concentration of water parameters [5]



Limestone system (GR0500010)

According to the RBMP [5], the Institute of Geology and Mineral Exploration has performed random samplings and chemical analyses in 50 points in 2004-2008 while the Municipal Water and Sewage Enterprise of Corfu in 10 points (1996-2008) (Figure 6). There is no pollution trend diagnosed for this system due to anthropogenic factors. Some point and diffusion pollution sources are noted beyond the local agricultural activities. Two are the main threats for the water quality due to natural pollution: the seawater intrusion and the salination of the water and the high values of sulfates because of the ternary breccia [5].

The mean values of pH, conductivity, CI-, SO4, NO3 and NH4 concentrations in various sampling points are provided in Figures 7-12 [5].



Figure 6. Points of monitoring of chemical status of the groundwater body GR0500010 [5]



According to the RBMP [5] many values of conductivity, chlorides and sulfates exceed the threshold of 75% of the Maximum Allowable Concentrations as they have been defined in the legislation. Specifically the maximum conductivity value registered is 8726 µS/cm, the maximum Cl- value is 2642,4 mg/l and the maximum SO4 value is 1465 mg/l. It is generally concluded from the RBMP [1;5] that these values indicate high values due to the natural background. The increased values of the chlorides (Cl-) are connected to the exploitation of the aguifer but they are also due to natural causes. The increased values of sulfates are due to the natural geological background met in the central part of the water basin district. Increased values of nitrates are met in two boreholes and they are due to anthropogenic activities. Since the values in nearby boreholes are not increased, a point pollution source is the cause. This system is used to pump water for human consumption and it is therefore included in the protected areas register (Figure 14) [6]. There are no available measurements of trace elements in this system. It is therefore concluded that the quality - chemical status of this system is good and it is marked in green (Figure 13) [1;5]. Some increased values are due to salination of the system Lakones-Krini and to the geology of the area [5].

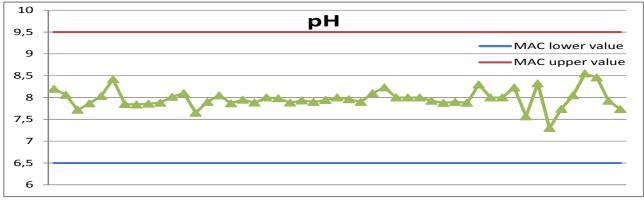
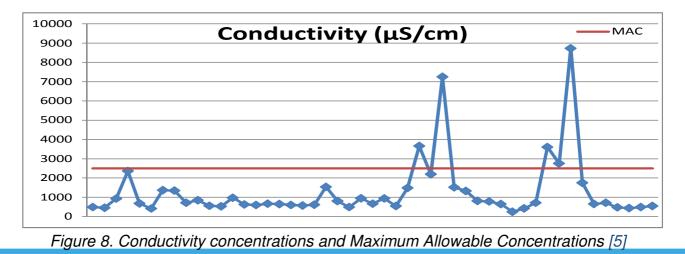


Figure 7. pH concentrations and Maximum Allowable Concentrations (lower and upper limits) [5]





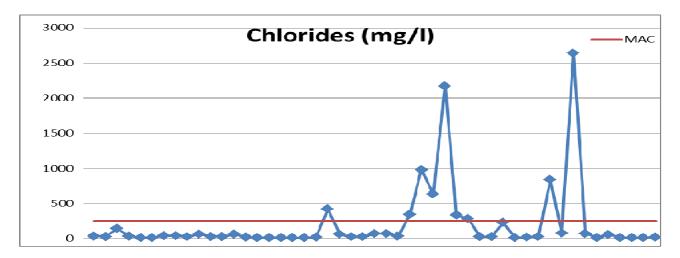


Figure 9. Chlorides concentrations and Maximum Allowable Concentrations [5]

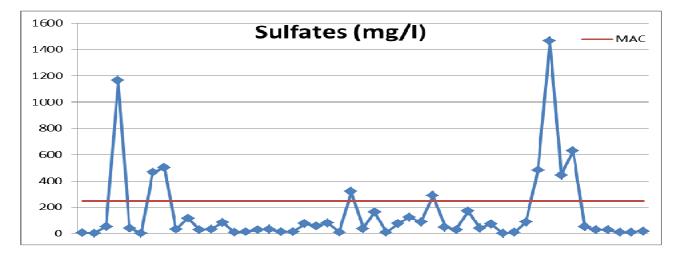


Figure 10. Sulfates concentrations and Maximum Allowable Concentrations [5]

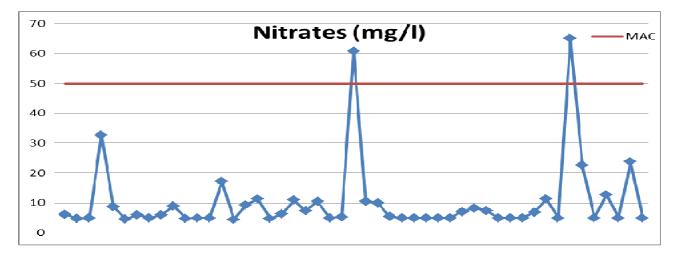


Figure 11. Nitrates concentrations and Maximum Allowable Concentrations [5]



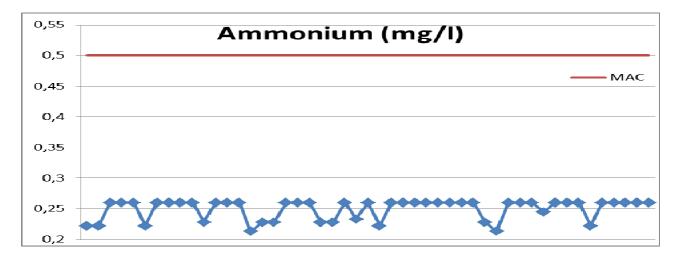


Figure 12. Ammonium concentrations and Maximum Allowable Concentrations [5]

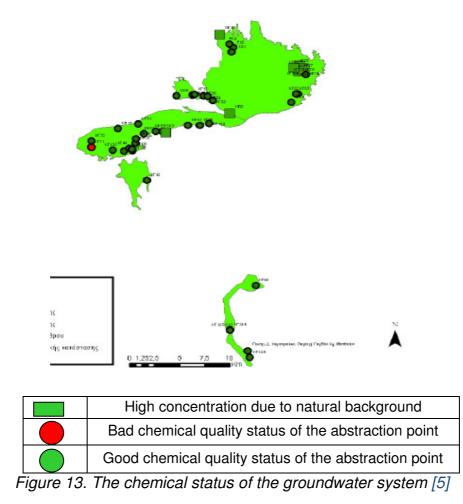






Figure 14. Protected areas for drinking water [6]

Ternary breccia system (GR0500020)

According to the RBMP [5], the Institute of Geology and Mineral Exploration has performed random samplings and chemical analyses in 59 points in 2004-2008 while several Municipal Water and Sewage Enterprises in the island in 2 points (Figure 15). There is no pollution trend diagnosed for this system due to anthropogenic factors. Some point and diffusion pollution sources are noted because of the local agricultural activities and the increased urbanization [5]. Increased values of sulfates and conductivity are due to the natural geological background. Increased values of sulfates and conductivity are due to the presence of gypsum in the terniary breccia of the Ionian zone [5]. The mean values of pH, conductivity, CI-, SO4, NO3 and NH4 concentrations in various sampling points are provided in Figures 16-21.



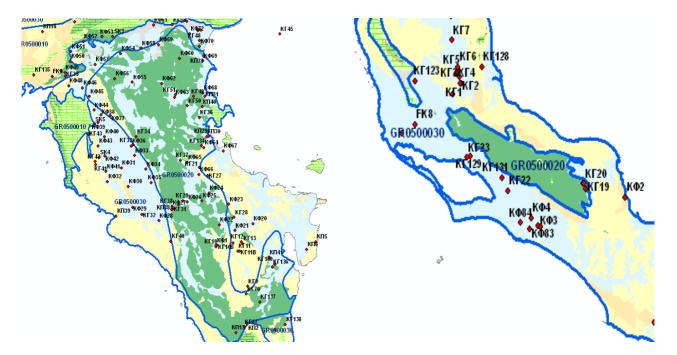


Figure 15. Points of monitoring of chemical status of the groundwater body GR0500020 [5]

According to the River Basin Management Plan (RBMP) [5], the increased presence of sulfates and conductivity is connected to the high values of the natural geological background. The values of the remaining parameters do not exceed the MAC of the threshold of 75% of the MAC. Only in some points there is increased concentration of nitrates and ammonium due to anthropogenic activities. Since the values in nearby boreholes are not increased, a point pollution source is indicated as the cause [5]. A part of the water system is agricultural land while the remaining one is woodland with increased urbanization. The water system is used for abstraction of drinking water. There are no available measurements for trace elements in this system. It is therefore concluded that the quality - chemical status of this system is good and it is marked in green (Figure 22) [1;5]. Some increased values are due to the geology of the area (high values of natural background) and some are due to local factors [5].

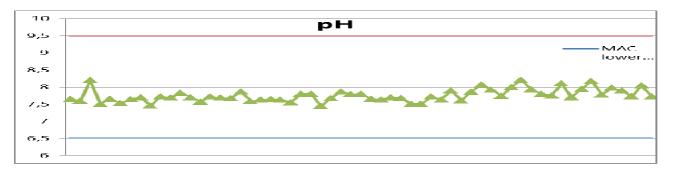


Figure 16. pH concentrations and Maximum Allowable Concentrations (lower and upper limits) [5]



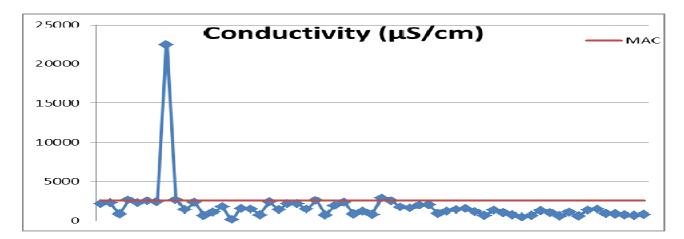


Figure 17. Conductivity concentrations and Maximum Allowable Concentrations [5]

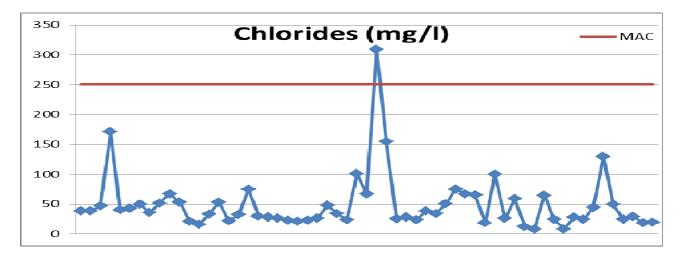


Figure 18. Chlorides concentrations and Maximum Allowable Concentrations [5]

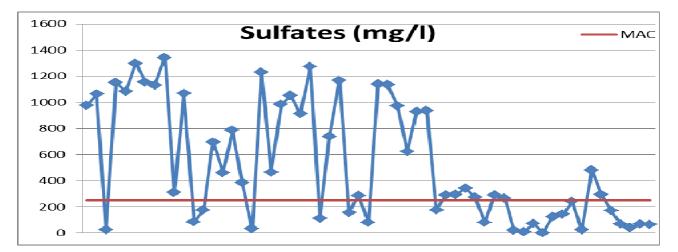


Figure 19. Sulfates concentrations and Maximum Allowable Concentrations [5]



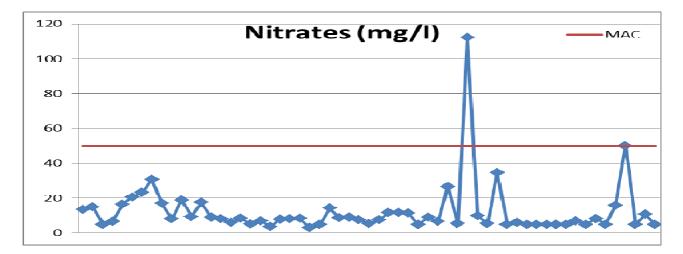


Figure 20. Nitrates concentrations and Maximum Allowable Concentrations [5]

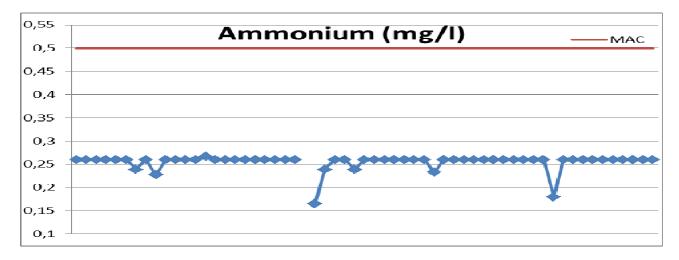


Figure 21. Ammonium concentrations and Maximum Allowable Concentrations [5]



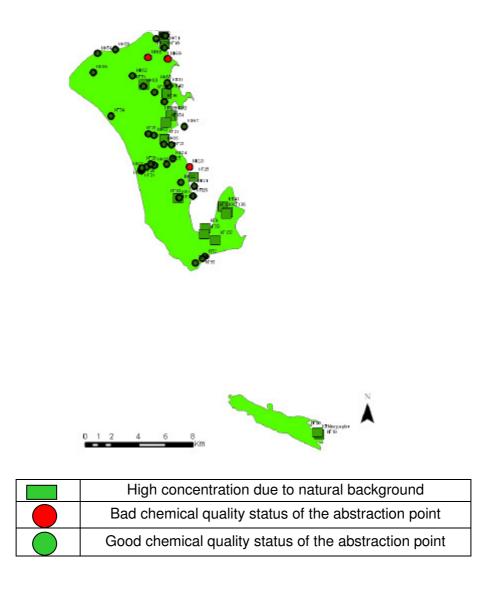


Figure 22. The chemical status of the groundwater system [5]

Granular aquifers system (GR0500030)

According to the RBMP [1;5], the Institute of Geology and Mineral Exploration has performed random samplings and chemical analyses in 188 points in 2004-2008 (Figure 23). The mean values of pH, conductivity, Cl-, SO4, NO3 and NH4 concentrations in various sampling points are provided in Figures 24-29 [5].



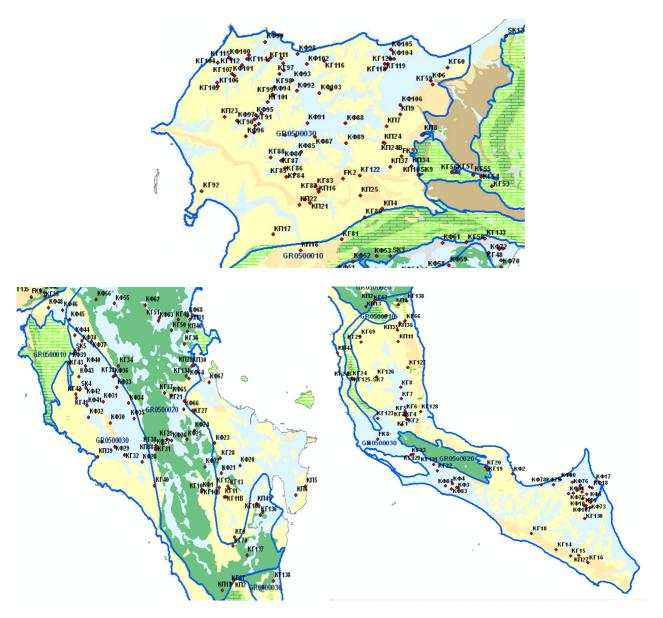


Figure 23. Points of monitoring of chemical status of the groundwater body GR0500030 [5]

According to the RBMP [1;5] the mean concentration values exceed the threshold of 75% of the Maximum Allowable Concentrations in some points. Specifically the maximum conductivity value registered is 2670 μ S/cm, the maximum CI- value is 1900 mg/l and the maximum SO4 value is 1320 mg/l. The increased presence of sulfates is connected to the increased value of the natural background due to the geological status of the area [5]. In some points there is an increased concentration of nitrates and ammonium due to human activities. A big part of the water system is agricultural land. The point and diffusion pollution pressures include the agricultural activities, the presence of oil mills etc. This system is used to pump water for human consumption. There are no available measurements for trace elements in this system.



It is generally concluded [5] that there is no other charge in the groundwater system but the locally increased concentrations of sulfates. The local increased concentrations of nitrates, chlorides and conductivity are due to human activities and exploitation. The number of points where the increased concentrations are registered does not exceed 13% of the total sampling points. The quality - chemical status of this system is good (Figure 30) [1;5]. Some increased concentrations are of local importance and others due to the natural background.

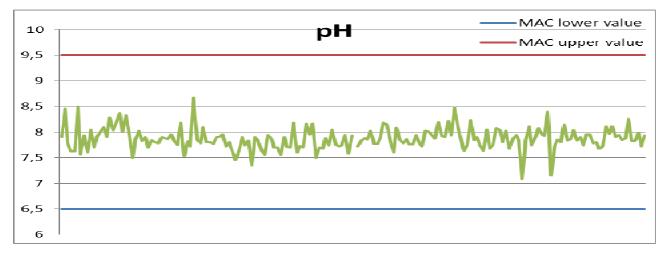


Figure 24. pH concentrations and Maximum Allowable Concentrations (lower and upper limits) [5]

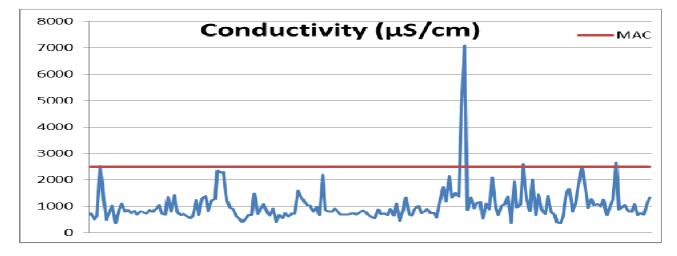


Figure 25. Conductivity concentrations and Maximum Allowable Concentrations [5]



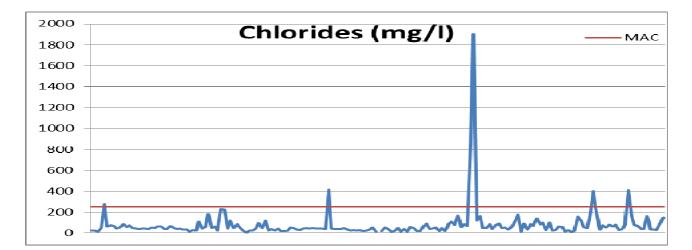


Figure 26. Chlorides concentrations and Maximum Allowable Concentrations [5]

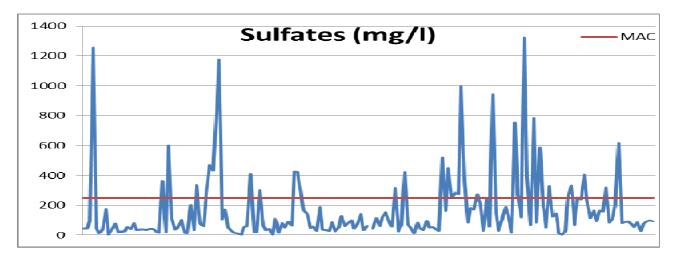


Figure 27. Sulfates concentrations and Maximum Allowable Concentrations [5]

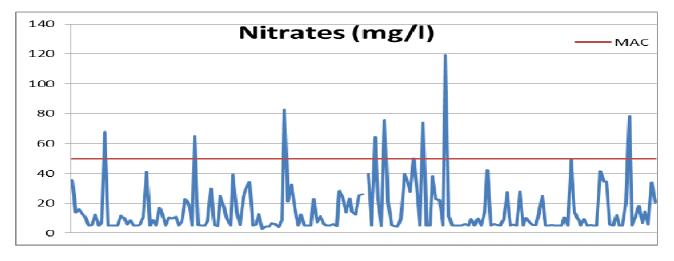


Figure 28. Nitrates concentrations and Maximum Allowable Concentrations [5]



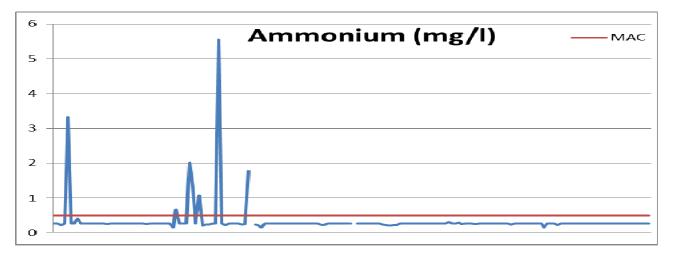
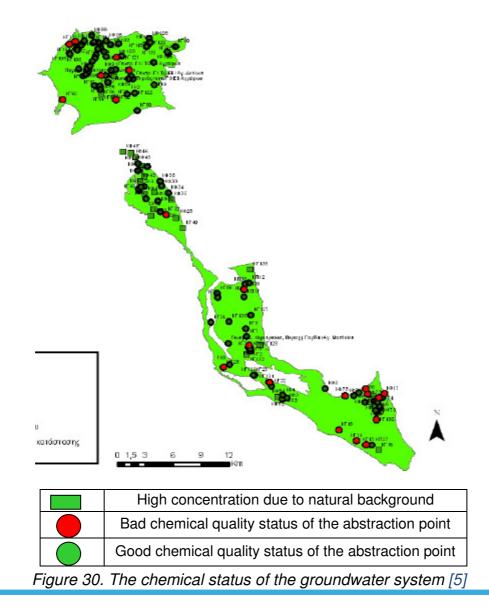


Figure 29. Ammonium concentrations and Maximum Allowable Concentrations [5]





The final assessment of the chemical condition of the groundwater bodies in the island of Corfu is shown in Figure 31 [7]. It is generally assessed as good [7].

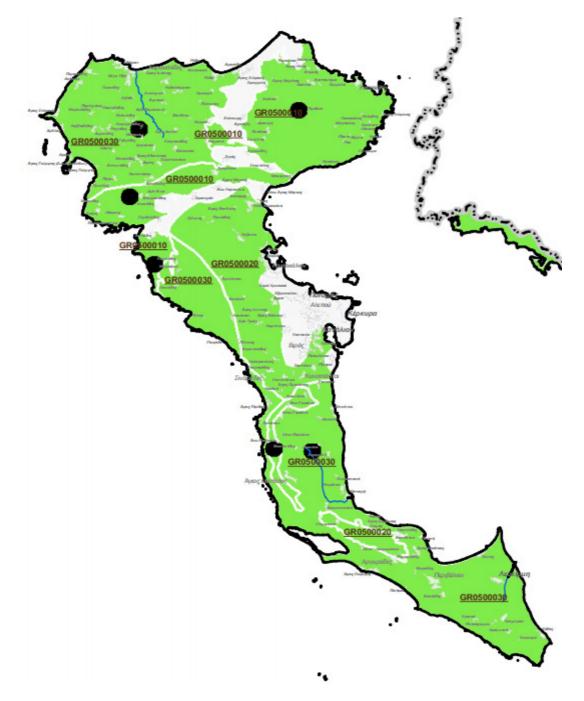


Figure 31. The chemical condition of the groundwater bodies in the island of Corfu [7]



4 Conclusions

The quality of surface and groundwater systems in the island of Corfu is presented in this report. The data and the assessment are based on the River Basin Management Plan of the Water District of Epirus (GR05) and specifically the water basin of Corfu-Paxi (GR34) [1;3;5;6;7]. It is generally concluded that the water quality of the surface water systems of Corfu is good. There are no heavy pressures identified. The three groundwater systems identified in the island of Corfu are assessed to be in a good chemical quality status [1;5] (Table 6). There are high concentrations of sulphates due to the increased values because of the natural geological background. Locally some increased values of nitrates and ammonium are due to the diffuse and point pollution sources of human activities. Locally in the coastal areas there are some increased values of chlorides due to the sea intrusion because of the exploitation and of natural causes.

Code	Name	Type of aquifer	Quality problems	Pollution trend	Chemical status of groundwater system
	Limestone system	Karstic	Locally increased values of nitrates due to agricultural activities	Local	Good
GR500020	Ternary breccia system	Karstic	Natural charge of sulphates due to gypsum - Locally increased values of nitrates due to agricultural activities		Good
GR500030	Granular aquifers	Granular	Locally increased values of nitrates due to agricultural activities- Natural charge of sulphates due to gypsum		Good



5 References

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