D.T2.2.2. Partner-specific pilot action documentation - CROATIA (Golubinka)

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1. Introduction

Partner-specific pilot action documentation is an "on-going" report to demonstrate the actual status of implementation of the pilot activities. This report will provide the technical information of the specific activities performed on the pilots (models specifically developed, measurements instruments and so on). Therefore, each pilot has to deliver a report on the actual status implementation of the pilot activities specifically referring to the specific activities and planned costs.

The Croatian Geological Survey is conducting hydrogeological research in the Zadar hinterland in the area managed by the Zadar water supply. Zadar water supply covers the area of two individual catchments and uses several local water intakes: catchment area of the Zrmanja river with Velebit springs Čavlinovac, Dorinovac and Sekulića vrelo and Bokanjac-Poličnik catchment area with Wells B-4 and B-5, Jezerce, Boljkovac and Golubinka spring. The source Golubinka is in the Bokanjac – Poličnik system, a complex set of mutually interrelated Dinaric karst catchments and sub-catchments. It is a highly vulnerable and limited groundwater source for the wider Zadar area in northern Dalmatia. During the summer periods and hydrological minimum, the impact of droughts is becoming more intense, and the need for drinking water is increasing due to tourist activities. In some parts of this coastal area, the need for water is growing. Pumping large amounts of water for drinking water supply reduces the amount of fresh water in the ground, which facilitates the penetration of seawater into the aquifer.

In order to define the zone of fresh and salt water mixing in the immediate hinterland of the Golubinka spring, geophysical surveys were carried out by geoelectric tomography on profiles with a length of 950 meters (depth 165 meters) and two transverse profiles 950 meters (depth 170 meters) and 315 meters (affected depth 40 meters). The interpretation of the aquifer in the area to the left of the Golubinka spring will be contributed by aerial images made by an unmanned aerial vehicle equipped with a thermal camera on the basis of which the discharge zones of underground freshwater sources will be located.

In addition to monthly monitoring of all physico-chemical parameters, trace metal concentrations are also observed on the pilot Golubinka. For this purpose, the project has provided funds for the purchase of a laboratory instrument polarograph that works on the principle of electrochemistry.

2. Specific activities performed on the pilot site

Description of the key activities that are implemented on the pilot site Golubinka during the project implementation

- hydrogeological mapping
- dataloggers: loggers were set up on the springs during last year. In situ measurements (water level, turbidity, EC) were performed. Sampling places: springs - Golubinka, Boljkovac, Oko, Bokanjac (well), Jezerce and possibly some smaller springs in the wider area (eg. Ljubača).
- hydrochemical and stabile isotope monitoring and interpretations (sampling and measurements - in situ and laboratory)
- aerial mapping of the discharge zone with drones – thermal and RGB cameras - capturing of different hydrological and temperature conditions
- geophysical research
    - geoelectrical tomography – deep interpretation (profile 1360 m long with a depth of up to 250 m)

2.1. In situ sampling (faildwork)

Hydrogeological measurements are conducted every month on the pilot area of the Golubinka. In situ sampling - measured temperature, pH, conductivity, oxygen content at springs Golubinka, Bokanjac B-4, Oko, Jezerce, Boljkovac and Vruljica are performed. They represent monthly observations of groundwater. Hydrochemical and isotope monitoring and interpretations: sampling and measurements during the whole period.

Figure 1 Hydrogeological measurements

Table 1 Activities in the project MUHA –In situ sampling – measured temperature, pH, conductivity, oxygen content

For example:

Month – May, 2021

Location		Bokanjac zdenac B4	Jezerce	Boljkovac	Golubinka	Oko	Vruljica
Date		21.05.2021.	21.05.2021.	21.05.2021	21.05.2021	21.058.2021.	21.05.2021.
T	˚C	14,60	15,7	15,4	15,2	14,8	15,5
pH	-	6,88	6,81	6,99	6,80	6,79	6,79
U	mV	-2,30	2,30	-4,70	2,80	3,20	3,20
EC	µS/cm	773	990	1306	1509	2240	2240
O_2	%	53,81	46,5	39,2	69,5	40,8	43,5
O_2	mg/l	5,54	4,62	4	7,15	4,39	4,39

Month – June, 2021

Location		Bokanjac zdenac B4	Jezerce	Boljkovac	Golubinka	Oko	Vruljica
Date		30.06.2021.	30.06.2021.	30.06.2021.	30.06.2021.	30.06.2021.	30.06.2021.
T	˚C	16,30	16	15,9	16,2	-	15,7
pH	-	7,05	6,68	7,00	6,89	-	7,00
U	mV	-10,90	-1,80	-7,30	-0,80	-	-7,40
EC	µS/cm	669	1012	1337	5730	-	2750
O_2	%	75,2	46,9	43,5	66,9	-	4,7
O_2	mg/l	7,37	4,58	4,35	6,54	-	47,3

2.2. Hydrochemical and stabile isotope research

The chemical composition of water is measured. The main cations and anions are measured using an ion chromatograph. Ion chromatography is a very useful technique for qualitative and quantitative determination of the ionic species in solution. It is often used in water analysis and quality control. Among other data, there are measurements of cation concentrations such as: calcium (Ca^{2+}), sodium (Na^{+}), magnesium (Mg^{2+}) and potassium (K^{+}), and anions such as nitrate (NO^{3-}), fluorine (F^{-}), bromide (Br^{-}), sulfate (SO_4^{2-}) and chloride (Cl^{-}). Monthly sampling for hydrochemical research is shown in the table 2.

Table 2 Monthly sampling for hydrochemical research

Month – May, 2021

Location		Bokanjac zdenac B4	Jezerce	Bokanjac	Golubinka	Oko	Vruljica
Datum		21.05.2021.	21.05.2021.	21.05.2021	21.05.2021	21.05.2021.	21.05.2021.
Ca^{2+}	mg/l	149,31	181,91	156,96	148,20	159,34	159,34
Mg^{2+}	mg/l	4,99	9,76	19,78	21,37	7,63	27,93
Na^{+}	mg/l	11,42	19,27	80,77	123,44	7,63	239,13
K^{+}	mg/l	1,02	1,28	3,11	5,03	0,79	7,73
Cl^{-}	mg/l	19,90	38,50	162,82	221,95	28,07	418,35
SO_4^{2-}	mg/l	15,66	82,94	62,91	57,80	16,88	59,52
NO^{3-}	mg/l	3,36	4,63	8,52	6,20	6,85	12,41
F^{-}	mg/l	0,10	0,25	0,24	0,16	0,14	0,15
Br^{-}	mg/l	-	-	-	0,82	1,58	-

One of the parameters to be determined is TOC (total organic carbon), the sum of parameters that measure the content of the organic matter in water. Total organic carbon (TOC) analyzers generally differ according to the type of oxidation method used. The basic settings of the instrument are quite similar: a liquid sample is taken out and the sample is converted to an acid to remove inorganic carbon. The organic carbon components are then

oxidized from carbon dioxide (CO_2) and measured using an infrared detector. The value of the carbon concentration (mg/L) is obtained.

The overview of the budget for hydrogeological research is given in the table 3.

Table 3 Information of the budge regarding hydrogeological research

Research and data processing (for third period)	25th to 27th January 2021 1st to 5th March 2021 12th to 14th April 2021 20th to 22th May 2021
Budget (Travel to Pilot Site)	January – 834,9 € March – 7360,6 € April – 814,07 € May - 825,15 €

2.2.1. Automatic groundwater loggers

The automatic groundwater loggers (Figure 2) were installed at several monitoring locations with the purpose of establishing a long time series of high-resolution measurements.

Figure 2 Automatic groundwater loggers - Automatic groundwater loggers CTD-DIVER 100m (9 pieces), Barometric pressure loggers (4) and Logger programming unit (1)

The overview of the budget for automatic groundwater loggers is given in Table 4.

Table 4. Information of the budge related to automatic groundwater loggers

Information of the budge related to automatic groundwater loggers

Budget of the automatic groundwater loggers	19076.79 €

2.3. Geophysical research

As part of the hydrogeological research works in the area of the Golubinka spring which are carried out within the MUHA project, co-financed by the European Union through the Interreg ADRION program, geophysical surveys were performed by geoelectric tomography. Field research was done in the pilot area of the catchment area of the Golubinka spring. A total of three geoelectric tomography profiles were recorded, with a maximum depth of over 180 m. The aim of these studies was to evaluate the composition and condition of rocks in the underground according to the distribution of electrical resistance values. From the 1st to 5th March, Croatian Geological Survey performed geophysical research. Company Terra compacta d.o.o helped with carrying out geophysical research (Figure 3).

Geophysical research (geoelectric tomography method) was carried out on three profile measurements on the pilot area Golubinka. The aim of the research is to define the contact of fresh and salt water mixing (seawater intrusions).

2.3.1. Geoelectric tomography method

Geoelectric methods (Figure 3) are based on measuring surface effects and anomalies obtained during underground currents. The resistance measurement method is the most commonly used geoelectric method.

The data obtained by measuring the resistance are used to forecast the lithological structure of the terrain, to determine fault or crack zones and the character of cracks and fillings in cracks, as well as to determine the difference in the conductivity of deposits.

The parameters of geophysical measurements were selected with a method of geoelectric tomography according to the theoretical settings of the method and field tests, in order to obtain the final result, which will be in accordance with the required depth and satisfactory resolution.

A total of three profiles of geoelectric tomography (Figure 4, Figure 5 and Figure 6), with a total length of 2215 m, were recorded at the research location. The lengths and depths are shown in Table 5.

Table 5 Measured values of geoelectric tomography method

Measured values of geoelectric tomography method

	Length	Depth
First profile:	950 m	165 m
Second profile:	950 m	170 m
Third profile:	315 m	40 m

Figure 3 Geophysical research (geoelectric tomography method)

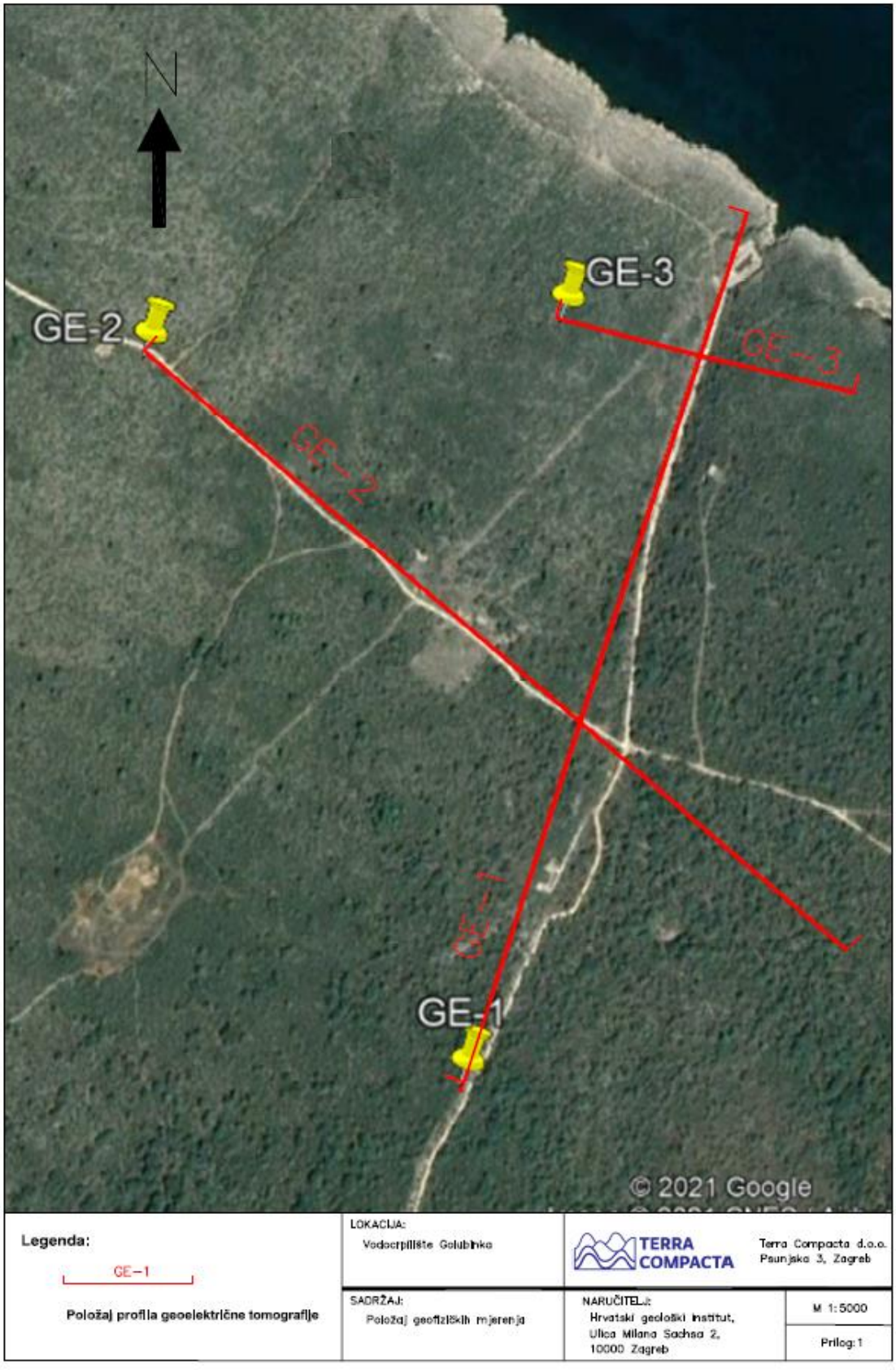

Figure 4 Review of performed geophysical research

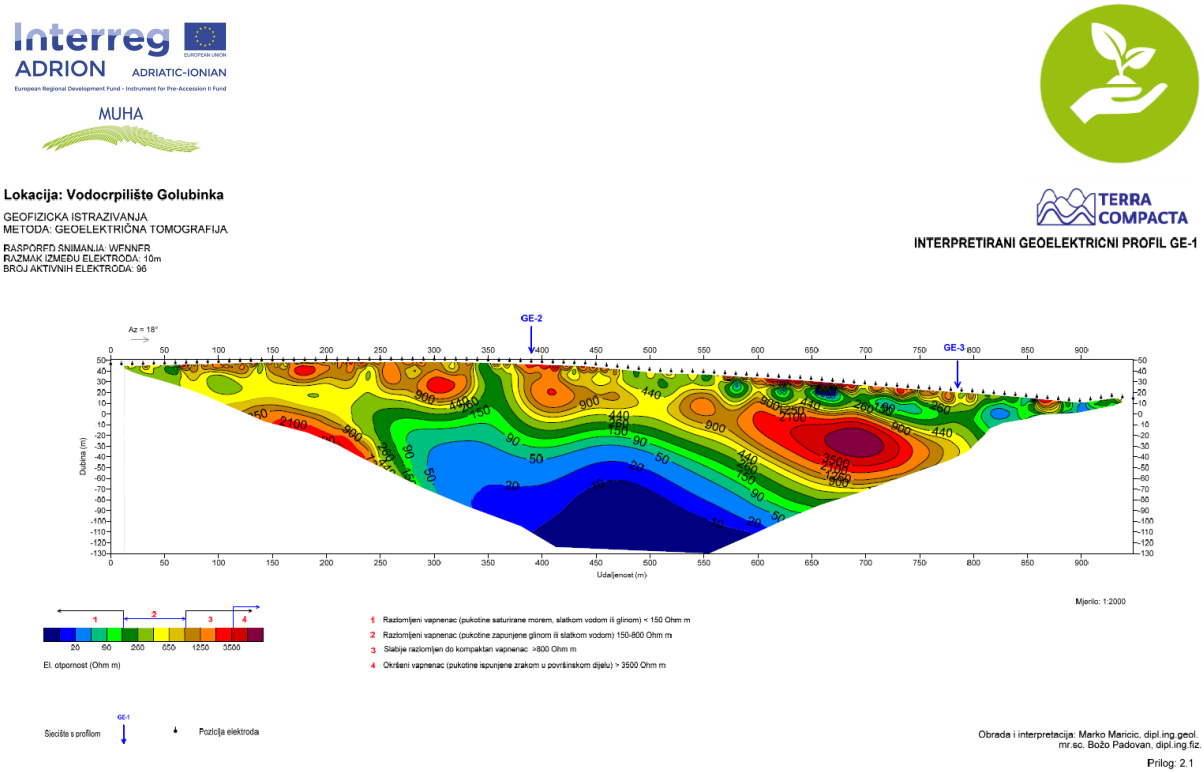

Figure 5 Interpreted geoelectric profile GE-1

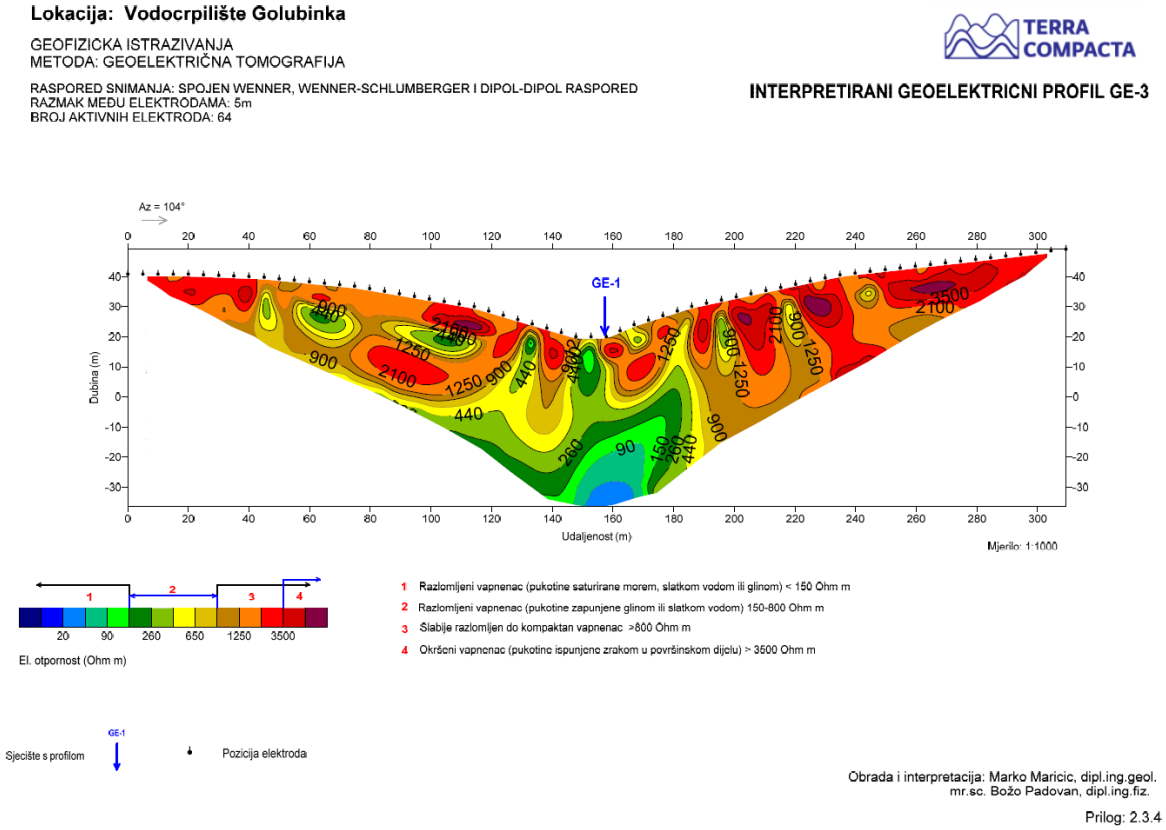

Figure 6 Interpreted geoelectric profile GE-3

The overview of the budget for geophysical research is given in the table 6.

Table 6 Information of the budge regarding geophysical research

Information of the budge regarding geophysical research

Research and data processing	From 1st to 5th March 2021
Budget (Travel to Pilot Site)	March –7360,6 €
Budget of the geophysical research (company Terra compacta d.o.o.)	5836,44 €

2.4. Laboratory research

Croatian Geological Survey acquired an instrument for voltammetric (Figure 7) determination of trace metals in water samples used in the pilot action Golubinka, near Zadar, Croatia.

Figure 7 Voltammetric instrument for determination the trace of metals

2.4.1. Polarograph for automatic detection of trace metals

The instrument is used to determine the concentration of metals in natural waters by chemical reactions that occur between an electrical conductor or a metal electrode and an ionic conductor or electrolytes during which an electrolyte is transferred between the electrode and the electrolyte.

The instrument consists of the following equipment: unit for automatic sampling of samples (50 places), computer program viva, two-channel peristaltic pump, set of electrodes for measuring arsenic and mercury in traces and set of electrodes (dripping mercury electrode) for determination of Cu, Cd, Zn, Co, Pb, Mn, Fe, Ni.

Obtained values of the metal traces are showed in table 7.

Table 7. Obtained metal concentration results

For example – June, 2020

Location	Bokanjac zdenac B4	Jezerce	Bokanjac	Golubinka	Oko	Vruljica
Datum	17.06.2020	17.06.2020	17.06.2020	17.06.2020	17.06.2020	17.06.2020
Method name	Ni,Co					
First value ng/L	332,3125	611,1644	812,8981	852,3355	Invalid	1,1029
Second value ng/L	360,3145	Invalid	45,59	788,7849	319,0933	202,4298
Method name	Cu, Zn,Cd, Pb					
ng/L	Invalid	Invalid	Invalid	Invalid	Invalid	66,4299
ng/L	Invalid	Invalid	Invalid	285,3876	1,8049	6,2436

The overview of the budget for voltammetric instrument is given in the table 7.

Table 2 Information of the budge related to voltammetric instrument

Budget of the voltammetric instrument (amortization value for RP02)	5470.82 €
Budget of the voltammetric instrument (amortization value for RP03)	5507.31€
Budget of the voltammetric instrument (amortization value for RP04)	Will be added
Budget of the voltammetric instrument (amortization value for RP05)	Will be added

2.4.2. Education for the use of voltammetric instrument for water sample analyses

The instrument was successfully installed in the hydrochemical laboratory. On the 20th May 2020 the first education was conducted (Figure 8).

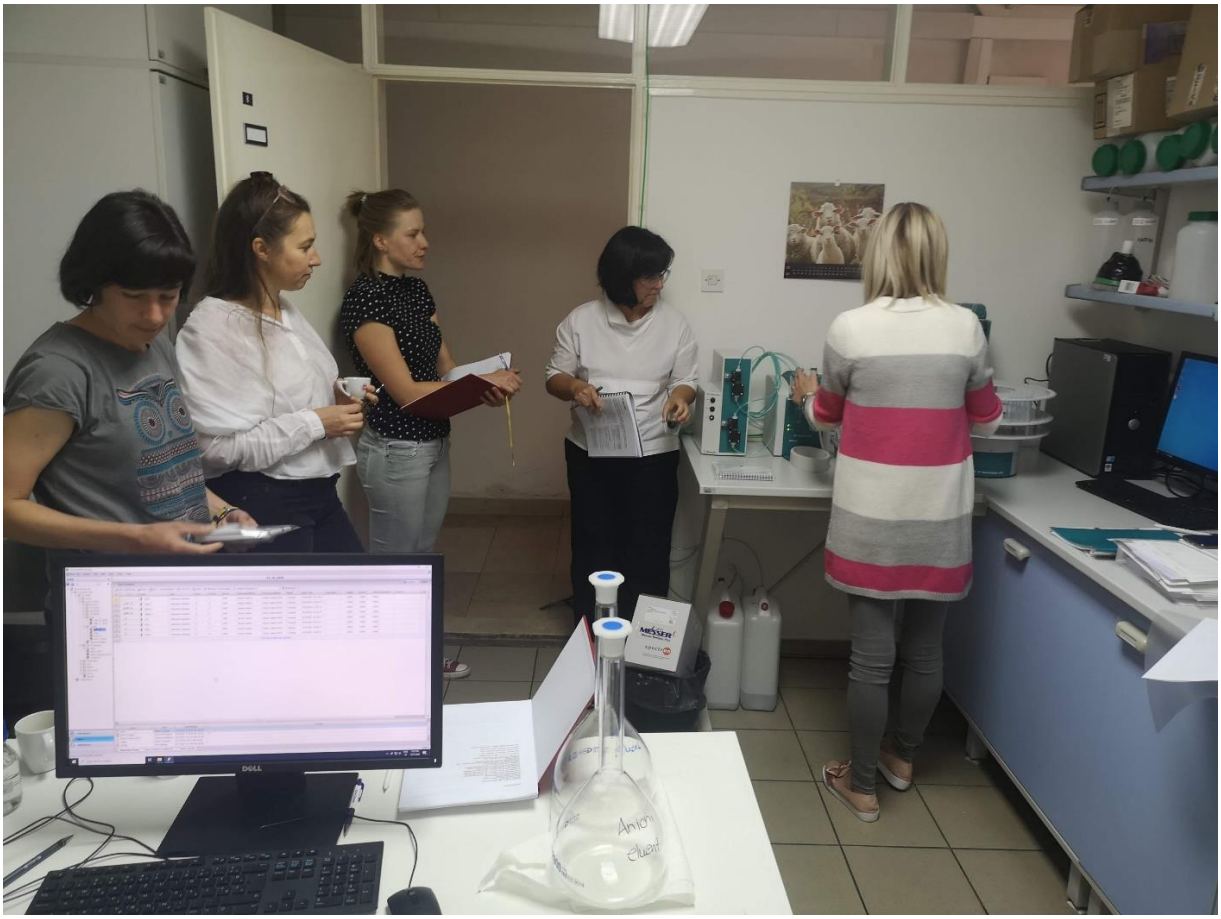

Figure 8 Education for using polarograph instrument

The overview of the budget for education for using polarograph instrument is given in the table 8.

Table 3 Information of the budge related to education for using polarograph instrument

Budget of the education for using polarograph instrument	2477.20 €

3. Anticipated effects of applied measures

There are several hazard impacts observed during the field research campaign of the Golubinka spring:

Drought – salinization of the spring and limited extraction quantities at some springs;

Floods – causing turbidity on springs (usually connected with the bacteria increase) – main parts of the catchment area with possible flooding;

Accidental Pollution – different causes and possible impacts, relatively limited; Earthquakes – no available data or no impact recorded.