PRELIMINARY STUDY ON THE GEOCHEMISTRY OF STREAM SEDIMENTS FROM GRINTIESUL MARE BROOK, EASTERN CARPATHIANS, ROMANIA

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Abstract: The Grintiesul Mare Brook located in the East Carpathian Mountains in the vicinity of closed Uranium mine exploration is the subject of this study. There are plans to open a new uranium mining facility in the Tulgheș-Grințieș area, where geological surveys have proven that the area holds the largest uranium deposit in the country. Geochemical analysis of the stream sediments samples collected from Grintiesul Mare Brook, and the water quality analysis (physical parameters) were made to establish the pollution level and the potential pollution sources. The elemental analysis shows normal values for U and Th, with values under the pollution limit. For the rest of the elements, V, Cr, Cu, Zn, As, Sr, Mo, Rb, Pb, Co, Nb, Zr, except Ni, higher values have been detected comparing to those published for the Upper Continental Crust. The water quality parameters analyzed by using a multiparameter probe have an increasing trend from upstream to downstream for Salinity, Conductivity and TDS, probably due to the influence of the human factor. The XRD analysis of the stream sediments identified the following minerals: quartz as a predominant mineral, followed by illite-muscovite, albite and clinochlore. The XRF and XRD analyses were carried out at Geolog International, Geochemistry Department, Milan, Italy.

Key words: Grinties Brook, major elements, trace elements, stream sediments, XRF, XRD, water quality parameters

1. INTRODUCTION

Romania is one of the few European states (alongside the Czech Republic, France, Germany, Ukraine) and one of the few in the world with uranium deposits, mainly used in the energy sector. The geological survey of the area started in 1963, when the first gamma anomalies and ore deposits were found. After a short prospecting period, the perimeter began to be excavated. During 1994-1997, the mining activity involved an experimental face cut, later followed by proper mining procedures, single geological block only, and single gallery (between the second semester of 1997 and the first semester of 2001). Later, in 2005, the National Uranium Company proposed a project aiming to reopen the mining operations for the existing uranium deposits found in Tulgheș and Grințieș area. The area currently holds several mining galleries, in different conservation stages (Tofan et al, 2016). The main objective of this study is to determine the geochemistry of stream sediments from Grintiesul Mare Brook.

2. GEOLOGICAL FRAMEWORK

The perimeter of the study area lies in the Central Group of the Eastern Carpathians (Fig. 1), in Bistricioara Mountains (Bistriței Mts.), Preluca Ursului-Pietrele Roșii subunit, between Harghita and Neamț counties. Hovering at approximately equal distance (20 km) from Durău and Borsec mountain spas, the perimeter is crossed by the Prisecani, Bradu, Primatar and Grințieș streams, left side tributaries of Bistricioara river.

The studied area is located in the Crystalline-Mesozoic Zone of the Eastern Carpathians, in the Tulghes terrane (Fig. 2). The geological formations from this area were formed during Precambrian to Upper Cretaceous. Most of the geological formations are composed of metamorphic rocks. The Tulgheş metamorphic unit is a low-grade sequence lithostratigraphically subdivided into 5 formations (from bottom to top): a blastodetrital, quartzitic formation; a mainly graphitic with metalydites and associated manganese carbonate ore bodies formation; a rhyolitic meta-sedimentary formation with associated base metal ore bodies; a blastodetrital formation with phyllites; a mainly graphitic formation with greenschists and limestones (Balintoni and Balica, 2013).
The flysch area is represented by the marly limestone series known in the literature as the “Layers of Sinaia” (Fig. 2).

3. MATERIAL AND METHODS

Twelve alluvial sediment samples were collected during November 2017 from the bed of the Grintiesul Mare brook located in the North East part of Romania. About 2 kg of sediments were collected manually

from the main stream using a metal bucket. The samples were dried in the electrical oven at 50° C and

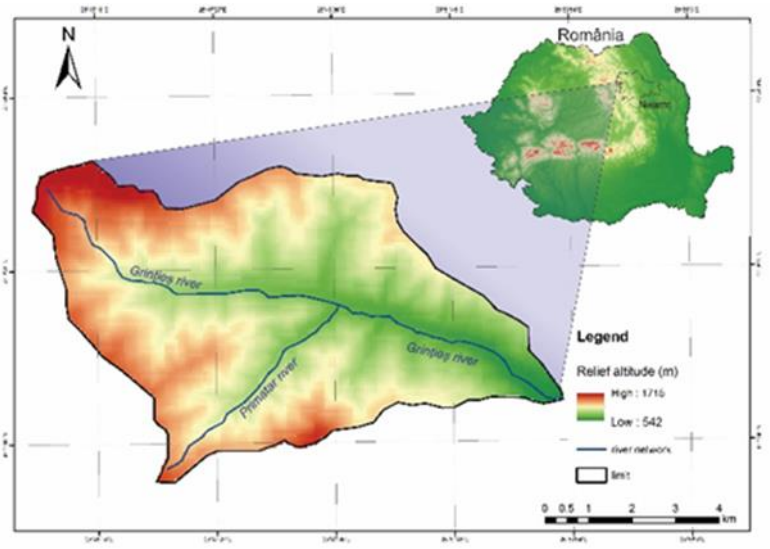

Fig. 1. Localization of Grintiesul Mare Brook.

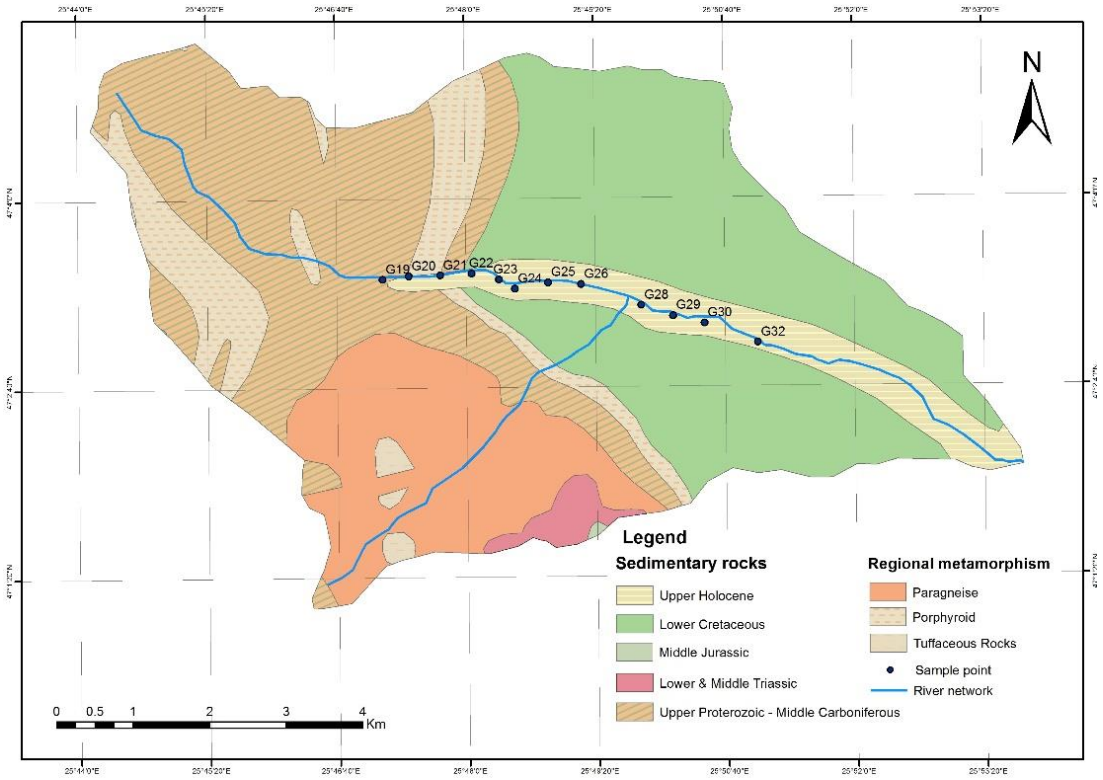

Fig. 2. Geological map of the study area (after Geological Map of Romania, scale 1:200000, Toplita sheet, modified from Alexandrescu et al., 1968).

sieved at 0.063 mm. The XRD analyses were carried out at Geolog International, Geochemistry Department, Milan, Italy.The elemental composition was determined by using Energy dispersive X-ray fluorescence spectrometer (XRF) Benchtop, and the calibration method is based on more than 20 certified standards from USGS, NIST and NGS to provide the most accurate results. XRD measurements were performed by X-Ray Diffraction benchtop instrument - Equinox 100, equipped with a Cobalt tube (Co Kα radiation $\lambda = 1.78896$ Å), and a Curved Position Sensitive X-ray Detector scanning simultaneously from 5 to 120° 2θ. Water quality parameters were measured for each sampling point using the multiparameter probe SmarTROLL in order to determine the following parameters: conductivity, pH, oxydation reduction potential (ORP), dissolved oxygen (DO), water level/pressure, salinity, total dissolved solids (TDS), resistivity, density, air and water temperature, and barometric pressure.

4. RESULTS

4.1 Mineralogy

The X-ray diffractograms (XRD) for the sediment samples collected from Grintiesul Mare brook revealed the presence of quartz, illite-muscovite, albite, clinochlore, as shown in Fig. 3. These minerals were determined semi-quantitatively as well (Fig. 4).

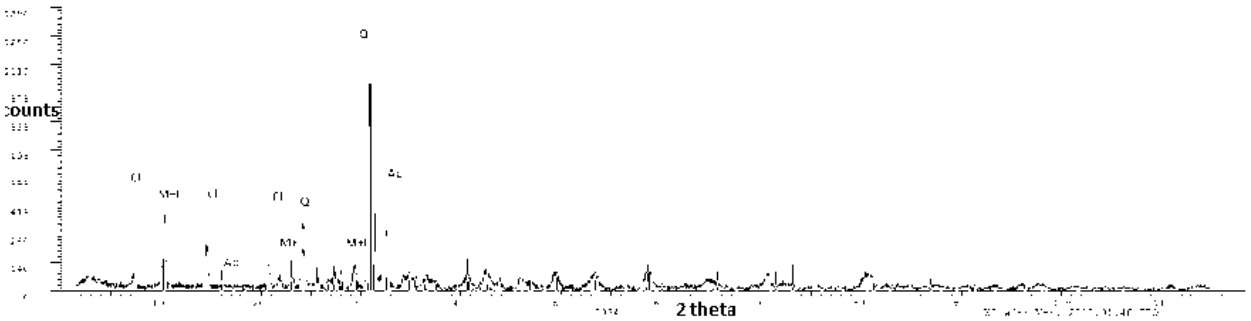

Fig. 3. The diffractogram of the G024 sample: Q=Quartz, M+I=Muscovite + Illite, Cl=Clinochlore, Ab=Albite

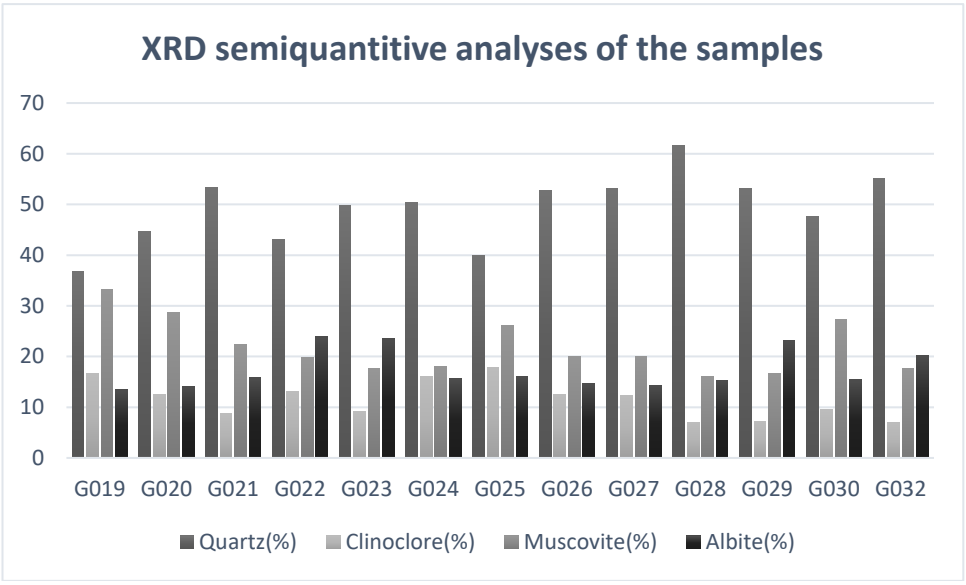

Fig. 4. XRD semiquantitative analyses of stream sediments from Grințieșu Mare Brook

4.2 Major oxides:

The bulk geochemistry of the major elements of twelve samples of the Grintiesul Mare alluvial sediment is presented in Table 1. The stream sediments have a content of SiO_2 with an average concentration of 56.14%. They have relative low contents of CaO (average 1.21 %), MgO (average 1.73%), K_2O (average 3.45 %), MnO (average 0.10%), TiO_2 (average 1.21%) and P_2O_5 (average 0.23%). MgO follows the trend of Al_2O_3 indicating that MgO and Al_2O_3 are associated with micaceous clay minerals (Akarish and El-Gohary, 2011). This is further confirmed by their correlation with Al_2O_3 (i.e. Al_2O_3 has positive strong correlation with MgO, r=0.67 and TiO_2, r=0.17, Fig. 5), showing that Al_2O_3 and MgO are associated and most likely from the same source. Furthermore, Al_2O_3 has positive correlation with Fe_2O_3 (r=0.41), CaO (r=0.56) and P_2O_5 (r=0.77). However, Al_2O_3 has a very good correlation with K_2O (r=0.85) which depicts the same origin, (Fig. 5). This suggests that most of the oxides result from aluminosilicate minerals like the plagioclase feldspars and mica group minerals (Jin et al., 2006).

4.3 Trace elements

The trace elements analyzed from the alluvial sediments are presented in Table 1. Their descriptive statistical summary is presented in Table 2 in comparison to published Upper Crust Concentrations (Rudnick and Gao, 2003) and Crucea river sediment analysis (Petrescu et al., 2010).

Table 1. XRF analyses of major and trace elements

Major oxides in %												
	G19	**G20**	**G21**	**G22**	**G23**	**G24**	**G25**	**G26**	**G28**	**G29**	**G30**	**G32**
SiO_2	53.06	57.71	54.95	56.72	55.59	58.27	55.98	58.27	57.09	56.08	59.55	57.48
Al_2O_3	18.82	17.69	20.13	19.91	19.41	16.84	17.62	16.66	18.80	17.53	17.17	15.61
Fe_2O_3	5.97	5.62	6.72	6.55	6.28	6.51	6.48	5.61	6.15	5.50	5.36	5.53
CaO	0.61	0.61	0.86	0.59	0.60	2.72	1.30	1.58	1.08	1.27	1.34	2.02
MgO	1.89	1.55	2.53	2.41	1.94	1.37	1.73	1.33	1.84	1.27	1.31	1.67
K_2O	3.76	3.17	4.07	3.91	3.76	2.98	3.16	2.98	4.04	3.54	3.22	2.84
MnO	0.11	0.10	0.11	0.11	0.10	0.10	0.11	0.10	0.08	0.08	0.08	0.09
TiO_2	1.22	1.32	0.96	1.10	1.18	1.25	1.81	1.15	0.97	1.05	1.12	1.37
P_2O_5	0.22	0.24	0.17	0.18	0.20	0.23	0.26	0.24	0.17	0.23	0.26	0.33
Trace elements in ppm												
S	410	300	510	435	430	280	450	290	500	850	123	125
Cl	NQ	NQ	34.4	NQ	NQ	20.5	NQ	NQ	NQ	NQ	27	10.6
As	15.2	13.4	13.9	13.4	13.7	14.5	15.9	13.4	13.4	11.2	12.8	12.9
Ba	728.8	611	877.1	805	762.3	586.5	677.7	600.3	749.5	807.4	672.2	861.6
Co	34.6	36.1	36.9	36.6	38.1	40.6	37.7	36.3	38.6	36.9	36	35.1
Cr	123.4	127.7	123.5	121.7	112.9	124.1	120.9	126.1	125	121.8	121.6	122.7
Cs	29.4	37.3	11.5	33.9	31.8	36.7	61.6	27.4	18.2	21.2	25.4	47.6
Cu	38.8	34.3	31.4	36.8	34.9	36.7	39.1	35	38.5	39.2	35.3	43.9
Ga	25.6	21.4	25.7	26.2	25.4	19.2	23.1	20.2	25.2	21.2	19.5	18.7
Gd	5.7	5.4	6	6.2	5.8	5.7	5.9	5.4	5.7	5	4.9	5.1
Mo	1.6	2.1	2.1	2.6	2.1	4.6	3.2	2	2.8	0.5	1.5	1.3
Nb	20.4	22.1	18.5	20.7	19.7	22.4	27.6	16.2	19.4	15.5	18.9	24.7
Nd	22.6	16	23.5	26.6	15.6	31.2	22	25.2	37.6	24.1	33.2	25.3
Ni	40.2	38.7	36.6	40.3	38.4	47.5	43.8	41.5	40.2	41.9	38.9	43.1
Pb	24.6	25.2	24.6	25.4	25.8	23.4	24.5	21.7	28.3	21.1	23.8	22.1
Rb	144.3	119.4	159.2	151.3	144.1	120.5	119.9	107.4	153.3	104.8	113.2	98.8
Sr	125.8	120.8	112	113.4	117.7	148.6	129.8	119.5	137.5	107.9	124.6	132.4
Th	18	17.4	17	17.7	18.3	16.4	18.7	14.9	14	11.7	13.5	12.4
U	4.7	4.7	3.9	5.2	5.1	3.4	4.4	3.5	4.7	3.8	4.6	5.3
V	117.5	108	112.7	116.8	122.5	112.8	120.2	106.8	115.7	114.5	98	94.8
Zn	114.8	110.4	125.5	121.5	114.2	120.8	113.7	105	130.8	113.8	106.4	108.7
Zr	463.5	356.4	289.2	326.9	350.2	336	726.5	294.2	262.5	218.7	290.9	564.4

Table 2. Statistical Summary of Trace Elements concentrations in comparison to published Upper Crust Concentrations - UCC (Rudnick and Gao, 2003) and Crucea river sediments analyses (Petrescu et al., 2010).

This study						**Crucea region**					**UCC**
Element (ppm)	**Min**	**Max**	**Median value**	**Mean value**	**Std Dev.**	**Min**	**Max**	**Median value**	**Mean value**	**Std Dev.**	
V	94.8	122.5	112.8	110.65	8.91	105.23	123.29	117.39	115.29	5.70	97.00
Cr	109.2	127.7	122.7	121.58	5.10	81.82	110.68	88.88	90.74	6.34	92.00
Ni	36.6	47.5	40.2	40.84	2.79	35.78	125.09	46.03	50.41	19.92	47.00
Cu	31.4	43.9	36.7	36.82	3.12	39.83	70.86	54.64	55.12	9.29	28.00
Zn	96.6	130.8	113.8	114.01	9.13	124.63	161.68	142.00	141.18	10.48	67.00
Sr	100.0	148.6	120.8	122.30	12.97	100.26	120.17	106.57	108.96	7.36	320.00
U	3.4	5.3	4.6	4.36	0.68	17.20	5023.96	63.46	236.81	291.09	2.70
Th	11.7	18.7	16.4	15.55	2.53	18.70	6643.92	47.78	309.89	391.16	10.55
Pb	18.0	28.3	24.5	23.73	2.56	37.16	371.57	183.54	192.16	97.16	17.00
Co	30.9	40.6	36.6	36.49	2.29	15.03	21.54	18.34	18.41	1.87	17.30

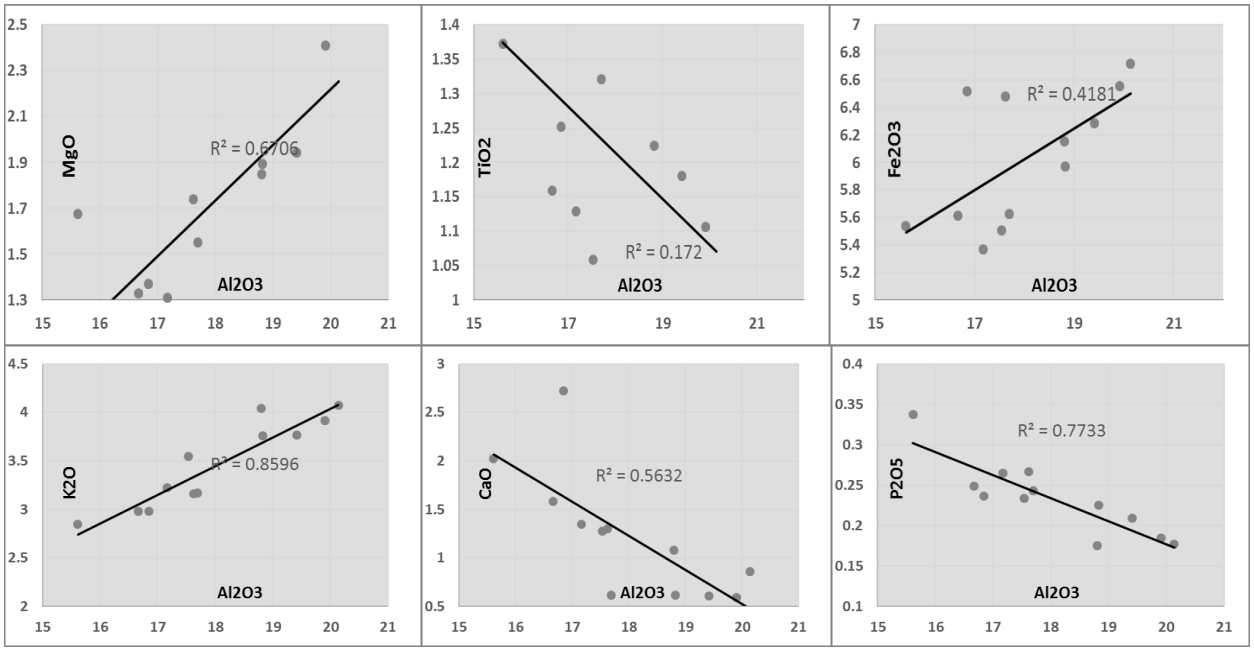

Fig. 5. Relationships among major oxides (%) from Grintiesul Mare stream sediments samples.

V/Cr ratio has been used as a paleo – oxygenation indicator (Dill et al., 1988, Garver et al., 1996 and Ghandour et al., 2003), so that the V/Cr > 2 is thought to represent anoxic depositional condition, and the V/Cr <2 represents deposition under relatively oxidizing conditions. In this study, the V/Cr ratio ranges from 0.7 to 1.08 with an average of 0.91, suggesting a deposition under relatively oxidizing conditions.

The Mn belt is situated at the bottom of Tulghes Group and the sulphide belt at the top of it. The Ba mineralization is present in the whole Tulghes Group together with both Mn and sulphide belts. The Mn belt also contains other Ba minerals, including celsian, hyalophane, barite and cymrite as accessory minerals (Hirtopanu et al, 2012). This indicates a genetic link between the Ba and Mn mineralizations, suggesting to have formed by the same submarine hydrothermal processes on the Cambrian sea floor. In the analyzed samples, Ba follows the same trend as MnO, this may suggest they have the same provenance.

Vanadium concentrations (94–122 ppm) are relatively higher than the levels commonly recorded in sediments (about 20 ppm) and given that V is concentrated in mafic rocks, they suggest some mafic input into the depositional system (McCann, 1991).

4.4 Water quality parameters

For each sampling point the main quality parameters have been measured using a multiparameter probe. The results are presented in Table 3. The investigations have been made during the first part of November 2017. The Conductivity increases from upstream to downstream, from 95 to 234 µS/cm and follows the same trend (increase from upstream to downstream) as Salinity and TDS. The pH is between 7.85 and 8.3 (average 8.11) with no significant variations in the sampling points. Dissolved oxygen is almost constant with values between 9 and 10 mg/l.

5. CONCLUSIONS

The XRF analyses conclude that for the radioactive elements such as U and Th, the values are in normal limits. For the rest of the elements, V, Cr, Cu, Zn, As, Sr, Mo, Rb, Pb, Co, Nb, Zr, except Ni, higher values have been measured comparing to published UCC but may be comparable with the elemental concentration reported in Crucea Brook sediments (except U and Th with high values in Crucea river sediments). Using XRD the following minerals have been identified: quartz as a predominant mineral, illite-muscovite, albite and clinochlore. The XRF elemental analysis (major elements) confirms as well the presence of the above mentioned minerals in the analyzed samples from the stream sediments. Some ratios such as V/Cr may be used as a paleo – oxygenation indicator. In this study this ratio has an average value of 0.91, suggesting deposition under relatively oxidizing conditions. High values of V may suggest some mafic input into the depositional system. The water quality parameters such as

Conductivity, Salinity and TDS increase from upstream to downstream. This behavior is due to natural processes in the upstream sector, while in downstream it is enhanced by anthropogenic activities.

Table 3. Water quality parameters measured in the sampling points.

Sample ID	Temperature °C	Conductivity (µS/cm)	Salinity (PSU)	TDS (ppt)	pH	ORP (mV)	DO (mg/l)
G019	8.09	95.29	0.065	0.091	8.06	75.33	10.02
G020	8.56	99.09	0.067	0.093	8.02	65.8	9.91
G021	8.73	102.8	0.069	0.096	8.05	63.53	9.93
G022	8.8	104.02	0.07	0.09	8.13	66.88	9.98
G023	9.51	111.24	0.074	0.102	8.07	65.92	9.94
G024	9.71	111.53	0.073	0.102	8.17	64.86	9.74
G025	10.11	148.17	0.097	0.134	7.85	68.11	8.99
G026	10.01	154.31	0.102	0.14	8.12	64.85	9.67
G028	10.17	187.35	0.124	0.169	8.3	63.57	9.66
G029	10.23	203.56	0.134	0.184	8.2	66.15	9.49
G030	10.22	220.53	0.146	0.199	8.11	65.74	9.27
G032	10.25	234.18	0.155	0.211	8.27	63.00	9.59

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