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Relationship between geological domain and physicochemical parameters in lotic system

Relação entre domínios geológicos e parâmetros físico-químicos em sistemas lóticos

Sandra Martins Ramos[1], Ana Paula de Melo e Silva Vaz[2], Donizeti Antonio Giusti[1] and Ernani Francisco da Rosa Filho[1]

[1]Universidade Federal do Paraná, Curitiba, PR, Brasil
[2]Centro Universitário Cesumar, Maringá, PR, Brasil
E-mails: sandraramos_bio@yahoo.com.br (SMR), anapaulamsvaz@gmail.com (APMSV), donizeti@ufpr.br (DAG), rosafilhoernani@gmail.com (EFRF)

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ABSTRACT

In natural conditions, the characteristics of surface water and river sediments are determined by geological formation. These can be changed due to human activities and interfere with maintenance of aquatic biota. Thus, identifying patterns of surface water and sediments in different geological areas can help to detect possible changes in orientation and contribute to decision-making within the maintenance and conservation of aquatic environments. The objective of this research was to identify changes in physical and chemical characteristics of surface water and geochemistry of sediments inserted catchments in three geological areas in Paraná: metasedimentary carbonate domain (MSCD), terrigenous-carbonate sedimentary domain (TCSD) and basic magmatic domain (MBD). The electrical conductivity, alkalinity, hardness, concentration of Ca and Mg in water were higher in MSCD. The concentration of SiO_2 is more representative of the MBD and CO_2 in the TCSD. In PCA, with the results of physico-chemical parameters of water, the first axis explained 99.43% of the variance between the sampling stations. In geochemical analysis of sediment and only Fe_2O_3 CaO showed statistically significant difference (ANOVA = $p<0.05$). The results suggest that the studied catchments are in good condition and reflect the natural conditions for each geological domain, demonstrating the need for adequacy of law inherent in assessing the quality of surface water. This work can be used as a reference for future studies and monitoring programs of the assessed catchments.

Kewords: Water resources; River sediment; Environmental geology; Geochemistry; Surface water.

RESUMO

Em condições naturais, as características das águas superficiais e dos sedimentos fluviais são determinadas pela formação geológica. Estas podem ser alteradas devido a atividades antrópicas e interferir na manutenção da biota aquática. Assim, identificar padrões das águas superficiais e dos sedimentos em domínios geológicos distintos, pode auxiliar na detecção de possíveis alterações e contribuir na orientação para a tomada de decisões no âmbito da manutenção e conservação dos ambientes aquáticos. O objetivo desta pesquisa foi identificar mudanças nas características físicas e químicas da água superficial e na geoquímica de sedimentos em microbacias inseridas em três domínios geológicos no Paraná: domínio metassedimentar carbonático (DMSC), domínio sedimentar terrígeno-carbonático (DSTC) e domínio magmático básico (DMB). Os parâmetros condutividade elétrica, alcalinidade, dureza, concentração de Ca e de Mg na água foram mais elevados no DMSC. A concentração de SiO_2 foi mais representativa no DMB e de CO_2 no DSTC. Na Análise de Componentes Principais, com os resultados dos parâmetros físico-químicos da água, o primeiro eixo explicou 99,43% da variância entre as estações de amostragem. Na análise geoquímica do sedimento apenas Fe_2O_3 e CaO apresentaram diferença estatística significante (ANOVA= $p<0,05$). Os resultados sugerem que as microbacias encontram-se em bom estado de conservação e refletem as condições naturais para cada domínio geológico, demonstrando a necessidade de adequação da legislação inerente a avaliação da qualidade de águas superficiais. Este trabalho pode ser utilizado como referência para estudos futuros e em programas de monitoramento das microbacias avaliadas.

Palavras-chave: Recursos hídricos; Sedimento fluvial; Geologia ambiental; Geoquímica; Águas superficiais.

INTRODUCTION

Lotic aquatic environments are composed of natural hierarchical systems, determined by the geology, geomorphology and climate, in large spatial scale that act in maintaining the heterogeneity of watersheds in smaller scale (MELLES; JONES; SCHMIDT, 2012; LLOYD et al., 2014).

The watersheds are ecosystem units of the landscape that integrate the natural cycles of energy, nutrients and water. The areas of riparian vegetation play a key role in maintaining the hydrological natural processes (NOBREGA et al. 2015). Studies show that human activities change the natural characteristics of aquatic environments in different spatial scales (TU, 2013; MCCLUNEY et al., 2014), interfering with the quality of drainage sediment and the structure of aquatic communities (BURDON; MCINTOSH; HARDING, 2013).

In natural conditions, the physicochemical characteristics of surface water and river sediment are determined by geological formation, which moves with drainage sediments. For Mortatti et al. (2012) the origin of chemical species is related to the geochemical fractions own sediment. However, studies aimed at evaluating the correlation between geology and patterns of physical and chemical parameters of surface water and sediment geochemical signatures are still incipient in Brazil.

The scarcity of studies on this topic is reflected in the national legislation on established standards for physicochemical parameters of surface water. The legislation is general and does not consider the geological heterogeneity, geomorphology and climate occurring in the country, as already pointed out by other studies (RODRIGUES et al., 2015).

Andrade et al. (2009) evaluated geochemical signatures in surface waters of Itacolumi State Park (MG) station to the absence of consideration of geological factors in drafting legislation of water quality. In the state of Paraná geochemical surveys to surface water, soils and river sediments started from 1995 (LICHT; BITTENCOURT, 2014).

In 2001 was published the Geochemical Atlas of Paraná, which is presented data on multielement geochemical survey in the state (LICHT, 2001) where it is possible to identify geochemical signatures derived from geological background or human activities. However, as presented recommendation of that Atlas, the use of geochemical data will depend on further investigations depending on the purpose of the research.

Thus, research on watershed scale showing results in the range of physicochemical parameters of surface water and river sediments in different geological areas are of great importance to assist in identifying the source of chemical compounds present in aquatic environments.

Moreover, the dissemination of scientific data inherent in the conditions of environmental quality watersheds contribute information to environmental agencies and may be useful in decision making on allocation of resources and efforts for the maintenance and conservation of water resources.

In this context, the objective of this research was to identify changes in physical and chemical characteristics of surface water and drainage sediment in watersheds, located in three distinct geological areas in Parana - Brazil.

We hope that the results presented here can be used as reference for future research and monitoring of the environmental quality of the assessed watersheds.

MATERIALS AND METHODS

Study area

The study area is located in southern Brazil, in the state of Parana where, according to Köppen classification, the climate is Cfb - humid temperate climate, mesothermal. The hottest month average temperature is 22 °C and the coldest month below 18 °C. Does not present dry season, summer is mild and frosts are severe and frequent. The sample design was delimited from the watersheds selection distributed in three different geological areas in the state of Paraná, spanning three geomorphological compartmentalization (first, second and third plateau) as illustrated in Figure 1.

For the study were prioritized watersheds that do not have large agricultural areas, urban or industrial, in order to minimize possible changes in physical and chemical characteristics of water and sediment caused by human activities. Sampling was carried out from 25/10 to 02/11/2014. Assessed geological domains were: Metasedimentary Carbonate Domain (MSCD), Terrigenous-carbonate sedimentary domain (TCSD) and Basic magmatic domain (MBD).The nomenclature and geographical location of the sampling stations in each geological domain is presented in Table 1.

Table 1. Identification and location of sampling stations in each of the evaluated geological domains.

Sampling stations	Rivers	City	Geographic coordinates	
MSCD1	Bacaetava	Colombo	S25°13'53"	W49°13'53"
MSCD2	Capivari	Colombo	S25°14'35"	W49°09'09"
MSCD3	Conceição	Campo Magro	S25°18'34"	W49°28'06"
MSCD4	Tributary of Conceição River	Campo Magro	S25°18'35"	W49°28'08"
MSCD5	Javacaí	Campo Magro	S25°19'57"	W49°31'40"
TCSD1	Guaraúna	Palmeira	S25°27'09"	W50°11'05"
TCSD2	Imbituvinha	Irati	S25°27'30"	W50°34'00"
TCSD3	Arroio Cerro Azul	Prudentópolis	S25°17'00"	W0°58'30"
TCSD4	Despraiado	Prudentópolis	S25°16'11"	W51°05'54"
TCSD5	Barra Grande	Prudentópolis	S25°04'56"	W51°10'37"
MBD1	Furnas	Guarapuava	S25°15'03"	W51°31'05"
MBD2	Marrequinha	Guarapuava	S25°11'24"	W51°21'45"
MBD3	Marrecas	Guarapuava	S25°11'04"	W51°21'15"
MBD4	São Francisco	Guarapuava	S25°03'57"	W51°17'54"
MBD5	Das Pedras River	Guarapuava	S25°21'24"	W1°21'37"

Metasedimentary Carbonate Domain (MSCD); Terrigenous-carbonate sedimentary domain (TCSD); and Basic magmatic domain (MBD).

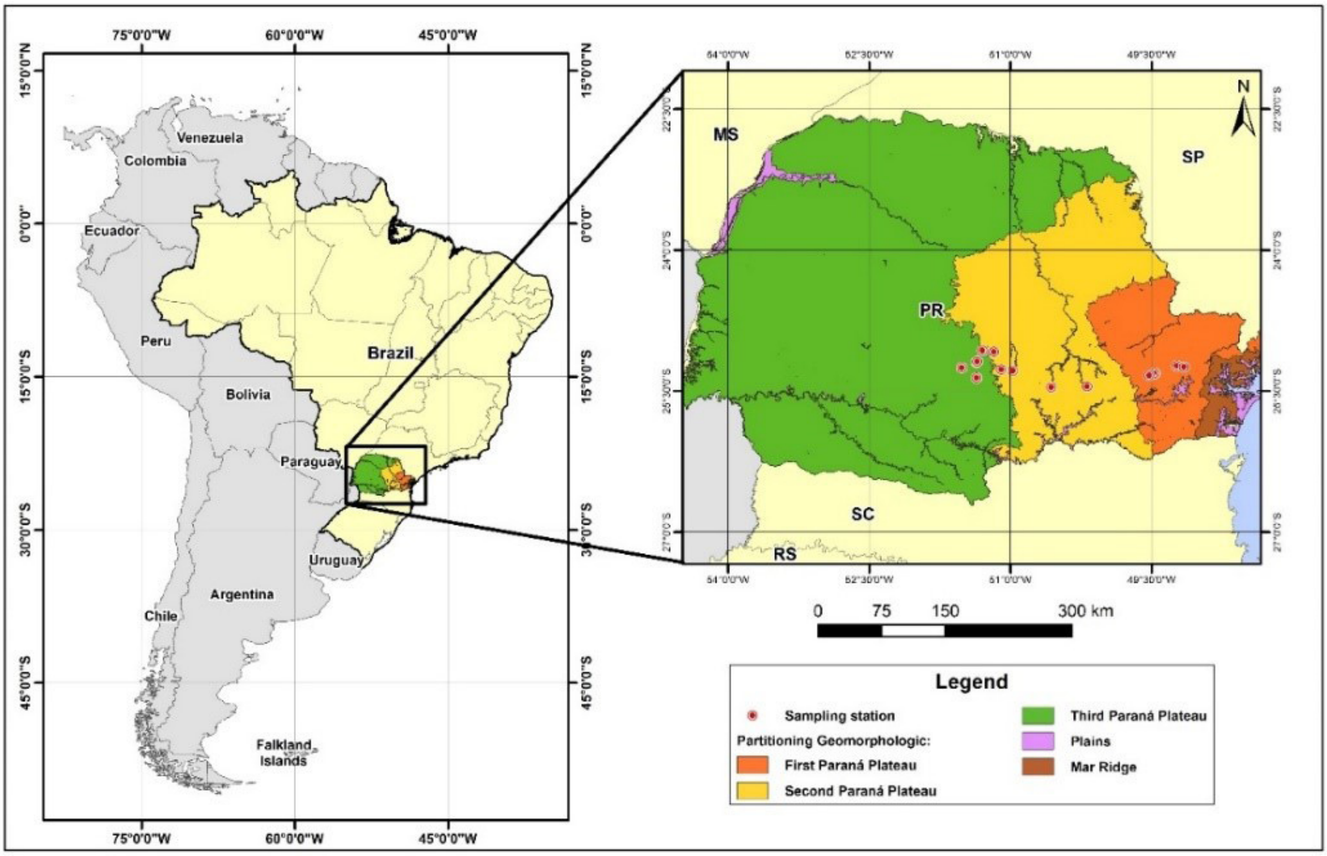

Figure 1. Location map of the study area. Adapted from MINEROPAR (2005).

Characterization of local geology

The metasedimentary carbonate domain (MSCD) is the geological context of the Group Açungui occurrences of carbonate rocks of Capiru formation. These geological formations are located sampling sites of rivers Bacaetava (MSCD1), Capivari (MCSD2) Javacaí (MSCD5), Conceição (MSCD3) and Tributary of Conceição (MSCD4).

The carbonate rocks of Capiru formation are interspersed with phyllites and quartzites (rivers Javacaí and Capivari) and sometimes crossed by diabase dikes of basic magmatism of Paraná (Conceição River). To Fiori (1993), Capiru formation Precambrian age encompasses all metasediments Acungui Group, including a track with reddish phyllites, with interbedded quartzites not very frequent; one with marble and / or metalimestones and their intercalation of phyllites and quartzites; and another track with switching banks or layers of quartzite, phyllites and marbles, with thicknesses in the range of hundreds of meters (ROSA FILHO; GUARDA, 2008). Phyllites and marbles are generally banded or rhythmic and more homogeneous quartzite.

The areas sampled in terrigenous-carbonate sedimentary domain (TCSD) are part of the second plateau of Paraná, where there are the Paleozoic formations of the Paraná Sedimentary Basin (MINEROPAR, 2005). The areas studied in this field correspond to the Itararé Group and Passa Dois Group (Irati, Teresina and Rio do Rasto formations).

The Itararé Group is the most important glaciation developed in the Permo-Carbonífer (ARAB; PERINOTTO; ASSINE, 2009). This group consists mainly of fine grained sandstones to reddish, whitish and yellowish thick, siltstones, shales and gray rhythmites, varvites, diamictics with stratifications and convolute laminations, parallel, crossed and wavy deposited in glacial environments. For Vesely et al. (2015) sediments of this group correspond to the subglacial sedimentation glacial sea.

The Passa Dois Group of Permo-Triassic age is subdivided into: Irati, Serra Alta, Teresina and Rio do Rasto. In Prudentópolis region, lithologically present rhythmical interbedded siltstones and shales, laminates and thin, changing colors, light gray, dark gray and reddish tones. The Irati Formation documents the evolution of the Paraná watershed: an effective restriction on water circulation and under such conditions. Accumulated up carbonates and evaporates in the northern portion, and bituminous shales in the southern portion of bowl, similar to Irati region. The sedimentary succession, follows the Serra Alta Formation a package of dark gray shales finely rolled, clay decanting product in a marine context of low energy and facies fine silicates at the top of Irati training (Warren et al., 2008).

Dominantly pelitic deposits with sedimentary structures linked to tidal action represent the Teresina Formation, giving rise to a progradational complex "redbeds" including deltaic lobes, lacustrine pelites, aeolic and fluvial deposits of Rasto River formation that is distinguished from the Passa Dois Group due to higher arenitic character of its composition in transition to the desert-like system of training Pirambóia (Warren et al., 2008).

The areas sampled in basic magmatic domain (MBD) are part of the São Bento Group inserted in the Serra Geral Formation of Cretaceous age (Milani et al., 1994) which is represented by a thick sequence of continental basaltic lavas with chemical and textural important variations, resulting from a more bulky volcanic processes continents.

In the areas studied in this field, the predominant rocks are basic effusive of tholeiitic character, generically known as basalts, may or may not occur acidic volcanic rocks consisting of rhyodacites, rhyolites and andesites. The magmatism has thickness of up to 2,000 m represented by basic nature spills. (Reis et al., 2014).

In addition to this main pattern, you can find: compact basalt with thick drusen and siliceous fillers, such as agate and rock crystal; and compact basalt with thin druse of calcite and heulandita; diabases interstitials, diabase-porfiritos or augite-porfiritos and tholeiites.

Land use

For the classification of types of land use and calculation of the size of the areas was used ArcGIS software 10.3 and GeoEye Satellite images with a spatial resolution of five meters. The Maximum Likelihood method was applied consisting of a supervised, punctual classification, based on the radiometric value of the pixel, which has to be determined through samples, object information to be classified (Correia et al., 2007).

Surface water samples

In each domain were selected five watersheds, totaling 15 sampling stations which were held collections of surface water sample, drainage sediment. Samples of surface water were collected directly into watercourses identified, preserved in ice and transported to the Hydrogeological Research Laboratory of the Federal University of Paraná which were carried out the following analysis method recommended by APHA (2012). The parameters analyzed were: color, turbidity, total hardness ($CaCO_3$), total solids dissolved (TDS), total nitrogen (N), nitrate (NO_3), calcium (Ca), magnesium (Mg), sodium (Na), potassium (K), chloride (Cl) and iron (Fe). With METTLER TOLEDO mark equipment at the time of collection were measured the following parameters: pH (MP120 pH meter), electrical conductivity (MC126 Conductivity Meter), dissolved oxygen (MO128 Dissolved Oxygen Meter), air temperature and water temperature.

Drainage sediment samples

To determine the geochemical characteristics of the drainage sediment samples were obtained manually with plastic shovel aid in its central portion bed of the watercourses, corresponding to the first five centimeters deep, and the samples, which consist of several aliquots taken a stretch of about 10 m along the rivers. Sediment samples were taken to the Minerals and Rocks Analysis Laboratory of the Federal University of Paraná, which were prepared for application of the technique of fluorescence X-rays (XRF). In preparing, the samples passed through the drying process in oven at 100 °C for 24 hours. Subsequently it was quartered to obtain required amount for crushing procedure. After milling were separated approximately 30 g of each sample, which remained in a greenhouse for 24 hours to humidity elimination. Following separated 7 g of sediment and added to 1 g of paraffin in order to improve compaction. To obtain the samples tablets were pressed and then subjected to geochemical analysis.

Statistical methods

Statistical analysis of data was performed in the Past software v 3.07. The result of physicochemical parameters of water were subjected to Principal Component Analysis (PCA) in order to identify the variation between the geological domains studied. The principal component analysis is a statistical method, multivariate of transforming a set of original variables in another set of the same size variables called principal components (LATTIN et al., 2011). This analysis is widely known and used for processing data on quality of surface water (YIDANA; OPHORI; BANOENG-YAKUBO, 2008; JIANG-QI et al., 2013; TORRES; LEMOS; MAGALHÃES JUNIOR, 2016).

To assess differences in the values of the physicochemical parameters of samples of surface water and geochemistry of sediment samples and drainage between the geological domains assessed, was used one-way ANOVA test at 95% significance level.

The analysis of variance (ANOVA) tests the hypothesis that the mean of two or more populations are equal and can be used to compare quality water between sampling station (LLOYD et al., 2014; BU et al., 2014).

Cluster analysis (*Ward's method*) was applied to test the similarity between the sampled sites. For hydrogeochemical classification of surface water samples was used Diagrammes software v. 6.48.

RESULTS AND DISCUSSION

The result of the type of land use survey showed that, overall, the watersheds studied have low degree of human disturbance. As can be seen from Figure 2 the percentage of

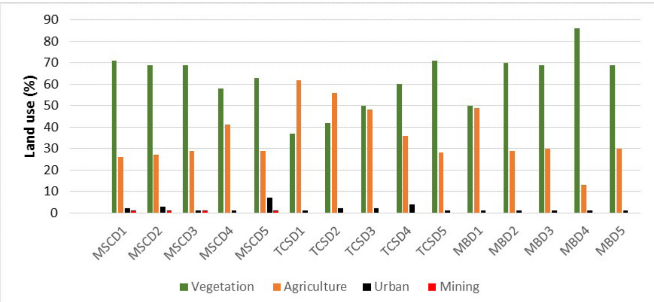

Figure 2. Percentage of each type of land use identified in the watershed study. Metasedimentary carbonate domain (MSCD), Terrigenous-carbonate sedimentary domain (TCSD) and Basic magmatic domain (MBD).

area with vegetation is predominant (between 37% to 86%). The area occupied by agriculture ranged from 13% (MBD4) to 62% (TCSD1) and the watershed more urbanized area (7%) was recorded in the field metasedimentary carbonate (MSCD1). Areas occupied by mining activity were found only in MSCD and did not exceed 1% of the area of the watershed.

We analyzed 20 physical and chemical parameters of surface water. The results are shown in Table 2 with the maximum concentrations permitted by Brazilian law. The water and air temperatures do not presented significant difference between the assessed stations. The water temperature varied between 21.2 °C and 23.8 °C, while the air temperature varied between 23.6 ° and 25.6 °. These values are normal for the season that the samples were taken (spring).

The amounts recorded for the parameters color and turbidity of the water had to be lower than the maximum allowed by law. According to CONAMA resolution 357/2005 (BRASIL, 2005) the value to the true color in Class 2 waters, shall not exceed 75 mg P/L^{-1} and turbidity maximum value allowed is 100 UNT.

The pH presented in the general basic, ranging from 7.58 to 8.09 in the field metasedimentary carbonate domain (MSCD), from 6.56 to 6.88 in the terrigenous- carbonate sedimentary domain (TCSD) and from 7.11 to 7.46 in basic magmatic domain (MBD). These values are within the standard set by CONAMA Resolution 357/2005 for Class 2 water (6 to 9) (BRASIL, 2005).

The higher values for pH were recorded in MSCD1 (river Bacaetava) and MSCD2 located in Capivari (7.81 and 8.09 respectively). Fritzsons et al. (2009) says that to evaluate the characteristics of surface waters of these rivers, warn that the high values of pH may be related to the limestone mining activities in these watersheds and highlight the existence of pumping water from the pits deposits, the river bed Bacaetava. But in this case, as seen in the survey of land use in the watersheds are limestone-mining activity downstream of the stations (MSCD1 and MSCD2) and shows that the results are related to geological domain.

The pH in the terrigenous-sedimentary domain (TCSD) had intermediate values that reflect the mineralogical characteristics of rich sedimentary formations in clay minerals, bituminous shales and limestone lenses. Similar values for pH were recorded by Batista and Gastmans (2015) in Paleozoic formations in the watershed of Alto Jacaré, São Paulo – Brazil.

In the MBD the pH ranged from 7.11 to 7.46 demonstrating a basic character and standard for surface water to leach basaltic rocks. At this station the pH values suggests that the mineralogical composition of basalts these watersheds is similar between them.

The electrical conductivity and the concentration of total dissolved solids was higher metasedimentary carbonate domain and showed high correlation. Batista and Gastmans (2015) also recorded similar results for these parameters in a study conducted in the central portion of the State of São Paulo where there are basaltic rocks of the Serra Geral Formation and derivative clastic sediments of Botucatu and Pirambóia.

The concentration of calcium (Ca) and magnesium (Mg) was higher in the stations sampled in MSCD and showed a statistically significant difference between the assessed geological domains ($p<0.01$) as shown in Figure 3. This result is due to the fact that the provision of Ca and Mg ions is greater in carbonate rocks, giving a higher electrical conductivity, in contrast with terrigenous domains whose silica dioxide (SiO_2) concentration is increased and consequently the electric conductivity is smaller.

In general, the concentration of SiO_2 in water was higher in MBD (on average 17.70 mg.L^{-1}), with the exception of MSCD4 station that among the stations sampled in the field metasedimentary carbonate, showed the highest concentration of this compound (17.10 mg.L^{-1}). This result is due to the fact that this watercourse has its source in phyllites and quartzites. Similar values for silica were found by Silva et al. (2011) analyzed Itaqui

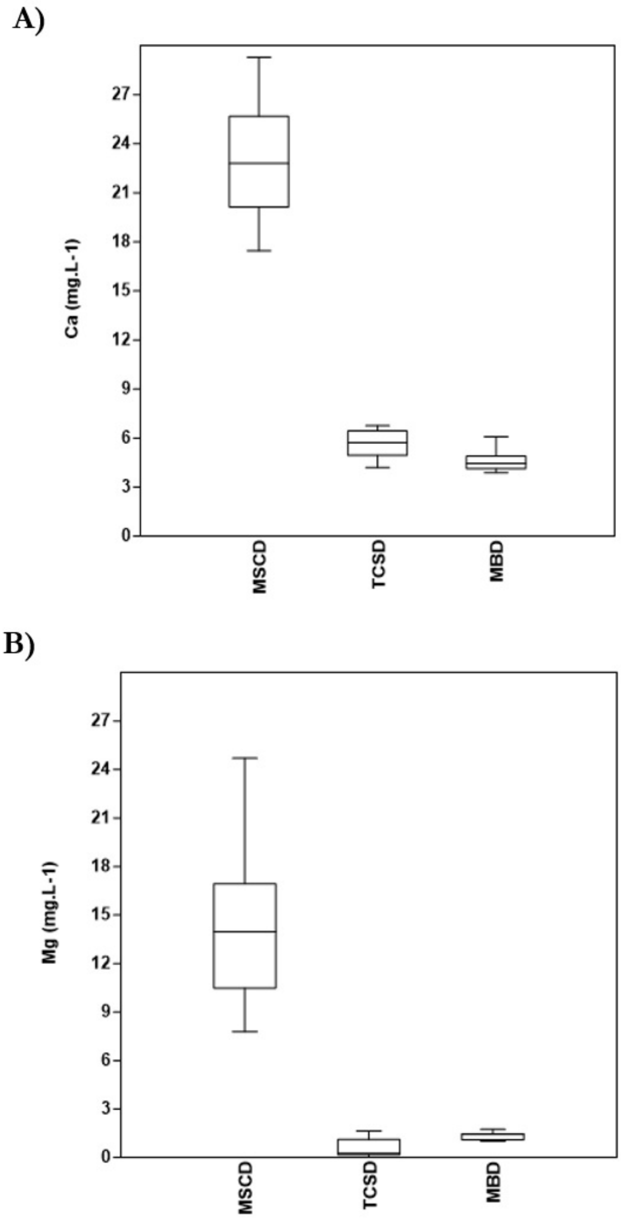

Figure 3. Graphs of the concentration of Ca graphs (A) and Mg (B) in mg.L^{-1} recorded in Metasedimentary carbonate domain (MSCD), Terrigenous-carbonate sedimentary domain (TCSD) and Basic magmatic domain (MBD). The box is the quartile 25-75%, the median is shown with a horizontal line in the box, and the maximum and minimum values are represented in the short horizontal lines.

Table 2. Analytical results of samples of surface water and allowed maximums value (AMV) by Resolution CONAMA 357/2005 (BRASIL, 2005) for waters of Classe 2.

Station	MSCD1	MSCD2	MSCD3	MSCD4	MSCD5	TCSD1	TCSD2	TCSD3	TCSD4	TCSD5	MBD1	MBD2	MBD3	MBD4	MBD5	AMV
Condutivity (µS)	283.00	181.07	133.03	209.00	149.00	52.00	71.00	52.00	48.00	53.00	37.00	48.00	46.00	41.00	56.00	**-**
pH	8.09	7.81	7.69	7.67	7.58	6.56	6.85	6.88	6.65	7.38	7.11	7.38	7.46	7.34	7.25	**6 - 9**
Alkalinity	138.6	83.60	60.60	96.70	69.10	13.70	17.40	16.40	15.90	20.40	12.30	19.29	16.90	15.20	17.50	**-**
Bicarbonate ($mg.L^{-1}$)	169.09	101.99	73.93	117.97	84.30	16.71	21.23	20.01	19.40	24.89	15.01	23.42	20.62	18.54	21.35	**-**
Hardness	172.16	112.66	85.34	131.77	80.88	16.43	20.69	14.85	12.18	17.62	14.16	19.31	18.02	15.35	17.92	**-**
Acidity $CaCo_3$	0.00	3.91	2.44	4.00	3.12	8.70	10.75	8.89	11.34	6.94	5.05	4.59	5.77	5.67	4.30	**-**
Organic carbon ($mg.L^{-1}$)	0.00	3.44	2.15	3.52	2.75	7.65	9.46	7.83	9.98	6.11	4.47	4.04	5.07	4.99	3.78	**-**
Total nitrogen ($mg.L^{-1}$)	0.59	0.38	0.10	0.11	0.21	0.57	0.68	0.40	0.23	0.21	0.15	0.25	0.17	0.14	0.63	**1.0**
Nitrate ($mg.L^{-1}$)	1.68	1.15	0.31	0.44	0.80	2.52	2.61	1.02	0.49	0.44	0.66	0.57	0.66	0.49	0.12	**10**
Total dissolved solids ($mg.L^{-1}$)	184.00	118.00	86.00	136.00	97.00	33.00	46.00	34.00	31.00	35.00	24.00	31.00	30.00	26.00	36.00	**500**
Silica dioxide ($mg.L^{-1}$)	7.02	5.61	9.46	17.01	8.97	11.27	12.88	12.97	13.40	13.43	10.52	16.88	30.16	16.49	14.44	**-**
Chloride ($mg.L^{-1}$)	2.31	0.72	0.77	0.82	1.18	2.32	3.77	1.08	0.93	1.03	1.19	1.24	1.19	1.08	1.50	**250**
Calcium ($mg.L^{-1}$)	29.28	22.8	17.46	25.68	20.13	6.44	5.71	4.21	4.94	6.76	4.13	6.08	4.46	3.89	4.90	**-**
Magnesium ($mg.L^{-1}$)	24.7	13.98	10.48	16.94	7.78	0.17	1.65	1.12	0.02	0.27	1.00	1.09	1.75	1.43	1.46	**-**
Potassium ($mg.L^{-1}$)	1.45	2.11	2.38	2.68	2.79	2.12	2.54	2.75	2.33	1.39	0.88	0.97	0.98	0.88	2.42	**-**
Iron ($mg.L^{-1}$)	0.18	0.36	1.06	0.99	1.70	0.49	0.52	0.46	0.54	0.26	0.72	0.56	0.44	0.55	2.42	**5**
Dissolved oxygen ($mg.L^{-1}$)	7.30	6.80	7.10	6.70	6.30	7.20	6.40	6.80	4.20	5.60	6.40	5.80	7.60	5.60	7.60	**>0.5**
Color (uH)	1.30	2.50	10.10	6.70	8.70	2.00	3.60	3.00	2.80	1.00	3.90	2.70	2.10	2.70	2.70	**75**
Turbidity (UT)	4.00	9.00	47.00	28.00	37.00	7.00	21.00	14.00	10.00	4.00	14.00	13.00	9.00	11.00	12.00	**100**
Water temperature (°C)	22.40	23.30	21.90	22.10	22.30	21.80	23.40	22.80	21.70	22.90	23.20	22.70	21.40	23.80	21.20	**-**
Air temperature (°C)	24.90	25.10	24.30	24.50	24.70	24.20	25.30	25.20	24.60	24.80	25.60	24.50	23.60	25.40	23.90	**-**

Metasedimentary carbonate domain (MSCD); Terrigenous-carbonate sedimentary domain (TCSD) and Basic magmatic domain (MBD); - Brazilian law does not appear maximum allowed value.

river water, in the region of Bateias where the geology is similar to that found in MSCD4 station. The highest concentration of SiO_2 MBD whether the presence of iron and magnesium oxides and feldspathic silicates.

The alkalinity, hardness, and bicarbonate (HCO_3) were also higher in MSCD and statistically different ($p<0.01$), which shows a direct relationship with the dissolution of calcite ($CaCO_3$) and dolomite [$(CaMg(CO_3)_2$] present in rocks of this area.

Regarding the concentration of CO_2 in the water TCSD showed higher values than the others (Figure 4) and showed a statistically significant difference ($p<0.01$). This is probably the bituminous shales leaching process present in the watersheds of this geological domain.

The concentration of potassium (K) was low in all the sampled stations (average 1.91 $mg.L^{-1)}$, with the highest values recorded in MSCD due to intercalation of argillaceous metasedimentary rocks with limestones that release potassium some clay minerals. Characteristic similarly occurs in the TCSD where the presence of potassium is due to leaching of clay minerals. Found statistically significant differences ($p<0.05$) for the potassium concentration of the geological domains evaluated, and the lowest concentrations were recorded in the MBD that had an average concentration of 1.22 $mg.L^{-1}$. The Brazilian law does not appear maximum allowed value for potassium concentration in surface waters. However, the concentration of this element, recorded in this study can be considered normal. Surface water potassium concentration typically range from 1 to 3 $mg.L^{-1}$ (PARRON; MUNIZ; PEREIRA, 2011).

The concentration of iron (Fe) was not very significant in the sampled stations, even in the MBD where it expected a higher content of this element due to the presence of basalt, except in the MBD5 (Das Pedras River) where the value was significantly higher than the others. In MSCD5 station presented amount of Fe above average for the area sedimentary carbonate. This is due to the likely occurrence of diabase dike in the headwaters of the river Javacaí (RAMOS et al., 2015). According Manasses et al. (2011) lower Fe concentrations in the water can be attributed to the fact that only part of this compound is solubilized, the rest remains in the clay minerals.

The presence of nitrate (NO_3), total nitrogen (TN) and chloride (Cl^-) was also low in all sampling stations shown that no indications of changes in water quality due to anthropogenic activities, otherwise the results would be higher, if it happens its related to increase of organic matter. The values for these parameters are below the maximum values established. For surface water the national law provides that the maximum concentration should be 10 mg L^{-1} for NO_3, 1 mg L^{-1} and for total nitrogen 250 mg L^{-1} (BRASIL, 2005).

The concentration of Dissolved Oxygen (DO) was within the standards stipulated for Class 2 waters in most stations. According to Resolution CONAMA 357 (BRASIL, 2005) the minimum value for DO, aimed at protecting the aquatic fauna is 5 $mg.L^{-1}$. Except of TCSD4 station presented DO was 4.2 $mg.L^{-1}$. The value for this parameter ranged from 5.6 to 7.6 $mg.L^{-1}$.

In Principal Component Analysis (PCA) performed with the results of physicochemical parameters of water, the first axis explained 99.43% of the variance between sampling stations (Figure 5). Analysis of variance with eingevalues obtained in the first axis of the PCA indicated statistically significant differences between the evaluated geological domains ($p<0.05$).

In geochemical analysis of pellet drainage were identified seven compounds (SiO_2, Al_2O_3, Fe_2O_3, K_2O, MgO, TiO_2, CaO). The SiO_2 compound was more representative in sediment samples

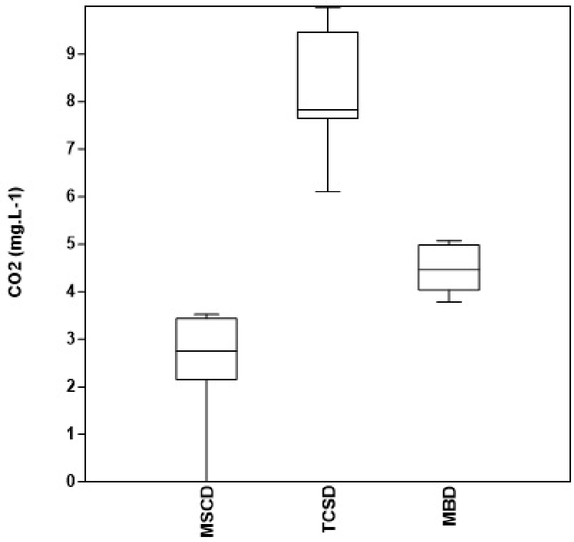

Figure 4. Graphs of CO_2 concentration ($mg.L^{-1}$) in water recorded in Metasedimentary carbonate domain (MSCD), Terrigenous-carbonate sedimentary domain (TCSD) and Basic magmatic domain (MBD). The box is the quartile 25-75%, the median is shown with a horizontal line in the box, and the maximum and minimum values are represented in the short horizontal lines.

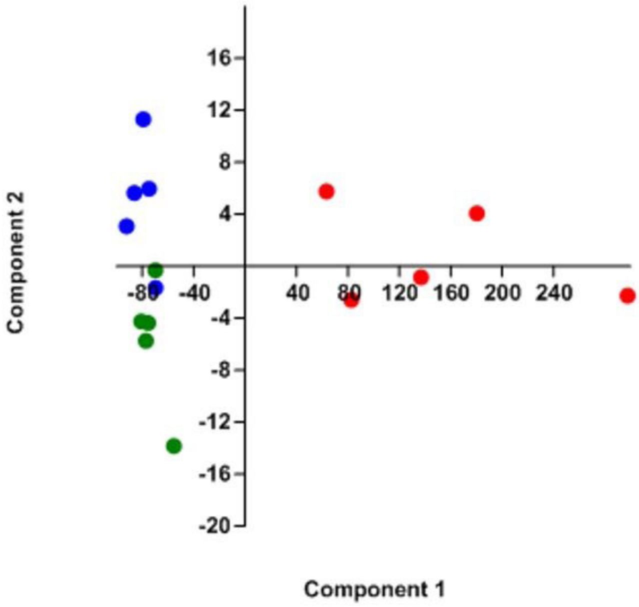

Figure 5. Principal Component Analysis carried out with the analytical results of the surface water samples. The blue dots refer to the areas sampled in the MBD; red dots MSCD and green dots TCSD.

collected in TCSD and MSCD and showed statistically significant difference ($p<0.05$) when compared with MBD that had the lowest concentrations (Figure 6A). This result corroborates the study Licht and Bittencourt (2014) that station to a lower concentration of SiO_2 in basaltic rocks of the Serra Geral formation.

The quantity of K_2O is more representative in TCSD due to the presence of clay minerals, while the MgO and CaO compounds showed a higher concentration in the related MSCD

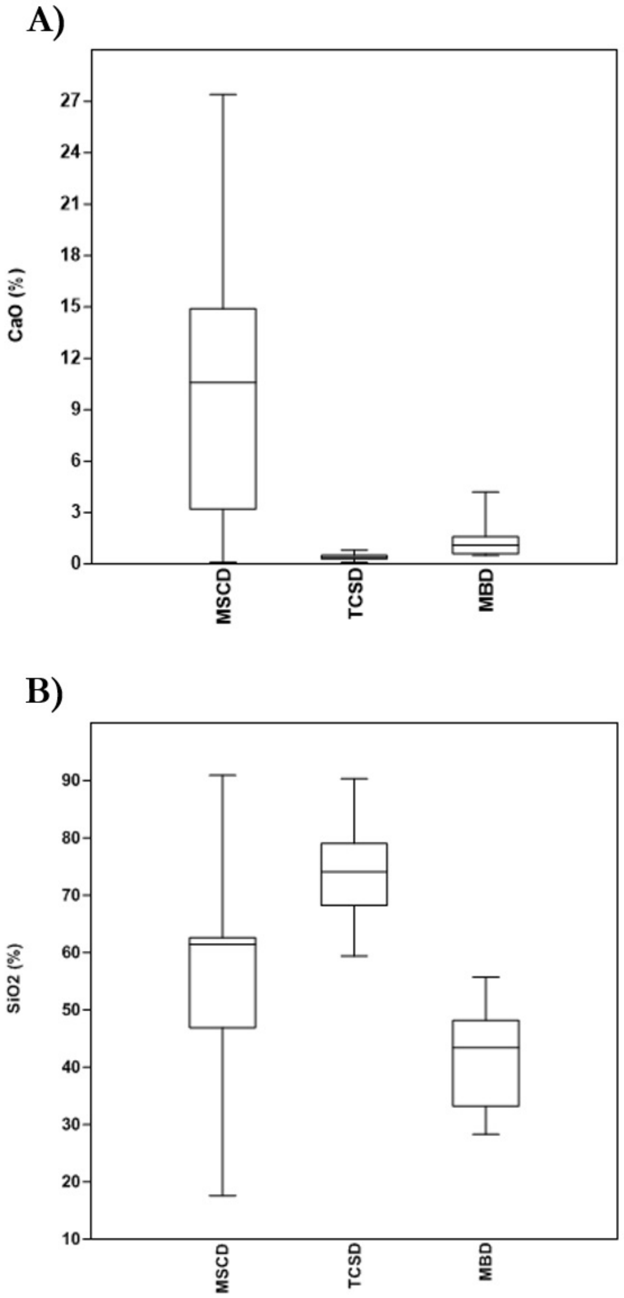

Figure 6. Concentration (%) of SiO_2 (A) and of CaO (B) in the river sediment recorded in Metasedimentary carbonate domain (MSCD), Terrigenous-carbonate sedimentary domain (TCSD) and Basic magmatic domain (MBD). The box is the quartile 25-75%, the median is shown with a horizontal line in the box, and the maximum and minimum values are represented in the short horizontal lines.

dissolution of carbonates. However only CaO showed a significant statistical difference between the domains (Figure 6B).

With respect to Al_2O_3 compound, the concentrations found in sediment samples can be considered normal for these geological domains (Figure 7). It is expected that the concentration of this compound in river sediment, under natural conditions, range from 5% to 15% in most geological domains, except metassediments carbonate (LICHT, 2001). This study found positive anomalies in the concentration of this compound in two sampling points in basic magmatic domain (MBD2 = 19.4%; MBD5 = 30.55) which can be explained by the presence of intermediate magmatic rocks where there is leaching of mineral feldspar. In the case of terrigenous-carbonate sedimentary area, the positive anomaly was in TCSD2 (18.3%) which is due to high clay minerals present in shales and siltstones that make up the rock formations of this area.

The Fe_2O_3 and TiO_2 compounds were more representative in MBD. As can be seen in Figure 8A the average concentration in the sediment Fe_2O_3 of sampled stations in the MBD exceeded 27%, while in other areas not reached 5%. This compound showed significant statistical difference for MBD (ANOVA $p<0.01$). The average concentration of TiO_2 in the river sediment varies between 0.68 (%) in TCSD 2.08 (%) in the MDB (Figure 8B). This results refer to the chemism of basic magmatism of the Parana watershed in Guarapuava region (LICHT; BITTENCOURT, 2014)

The results of the geochemical analysis of river sediment explain the processes hidrogeochemicals adsorption and removal compounds such as Fe_2O_3, TiO_2, SiO_2, Al_2O_3, K_2O, MgO and CaO. Also it shows that the assessed watershed not suffer significant anthropogenic changes, since the sediments reflect the mineralogy of geological areas where they are located.

The applicability of geochemical analysis of river sediment to identify the source of chemical compounds is evidenced by other studies. Soares et al. (2004) studied the sediment geochemistry in Salso Creek, located in Porto Alegre (Rio Grande do Sul) and identified enrichment of Cu, Ni and Zn and the results given to domestic sewage discharge. On the other hand, the presence of high concentrations of fluoride in watersheds located in the region of Cerro Azul and Adrianópolis (Paraná) was identified as

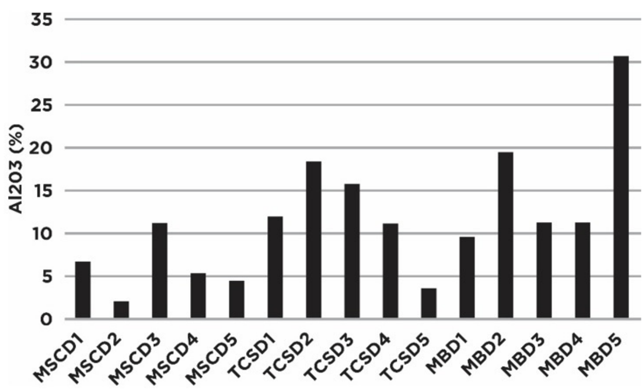

Figure 7. Concentration (%) Aluminum oxide (Al_2O_3), recorded in the fluvial sediment samples. Metasedimentary carbonate domain (MSCD), Terrigenous-carbonate sedimentary domain (TCSD) and Basic magmatic domain (MBD).

a product of the mineralogical composition of the rocks in the region (ANDREAZZI; FIGUEIREDO; LICHT, 2006).

The result of cluster analysis showed similar behavior to that obtained in the principal component analysis, performed only with the physicochemical water variables, demonstrated surface water and drainage sediment are different geological domains studied. The cluster analysis with the results of physicochemical parameters of water and sediment geochemistry generated dendrogram with two large groups, one formed by the sampling stations of MSCD and the other with the sampled stations in TCSD and MBD (Figure 9).

The hydrogeochemical assessment classified the surface waters as calcium or magnesium bicarbonates, as shown in the piper diagram (Figure 10). This result demonstrates a direct relationship with the mineralogical occurrence (calcite, dolomite and plagioclase) present in the rocks of the studied geological domains. With the

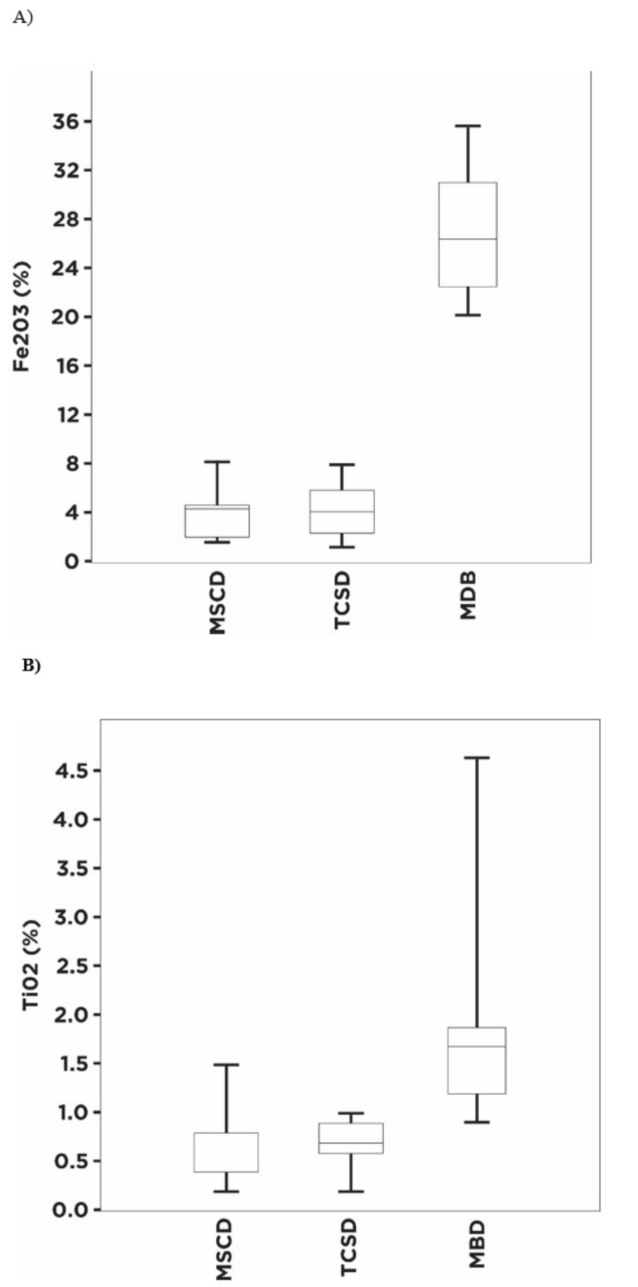

Figure 8. Concentration (%) of Fe_2O_3 (A) and of TiO_2 (B) in the river sediment recorded in Metasedimentary carbonate domain (MSCD), Terrigenous-carbonate sedimentary domain (TCSD) and Basic magmatic domain (MBD). The box is the quartile 25-75%, the median is shown with a horizontal line in the box, and the maximum and minimum values are represented in the short horizontal lines.

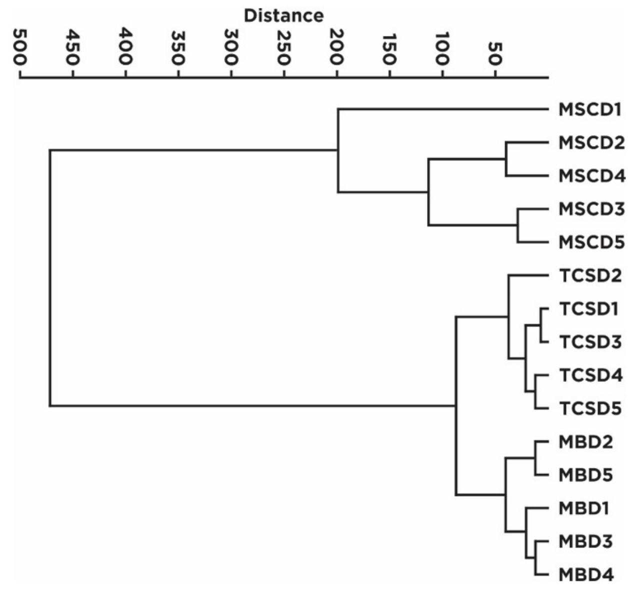

Figure 9. Dendrogram obtained in the cluster analysis with analytical results of samples of surface water and drainage sediment. Metasedimentary carbonate domain (MSCD), Terrigenous-carbonate sedimentary domain (TCSD) and Basic magmatic domain (MBD).

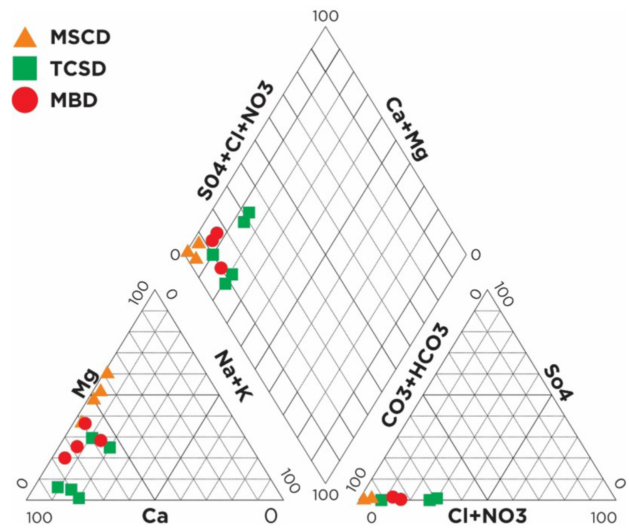

Figure 10. Piper diagram obtained from hydrogeochemistry evaluation with analytical results of surface water samples. The red dots refer to the stations sampled domain metasedimentary carbonate (MSCD); the green stations terrigenous-carbonate sedimentary domain (TCSD) and the blue dots, magmatic basic domain (MBD).

exception of two stations located in Metasedimentary Carbonate Domain (MSCD) that classified as mixed bicarbonate, reflecting a concentration of carbonate minerals and clay minerals, because probably the intercalated limestones and phyllites.

The predominance of calcium and magnesium cations, and bicarbonate anion recorded in this study, was also found by Silva et al. (2011) in the waters of the basin of the Itaqui river, located near the stations sampled. The authors attributed this finding to the presence of carbonate rocks at Capiru formation, which also occur in the stations sampled in MSCD.

The stations analyzed in the Basic Magmatic Domain (MBD) have geology similar to found in the sub-basin of the Rio Jacare-Pepira - SP, that is, basaltic rocks of the Serra Geral Formation, where the waters were also classified as bicarbonate, calcic-magnesium (BATISTA; GASTMANS, 2015). For the authors of this classification is due to dissolution of present minerals in basalts and sandstones, as plagioclase and pyroxene.

CONCLUSION

The results obtained during the study suggest that the evaluated watersheds are in general in good condition, showing no evidence that large impacts arising from human activities. This is important information because the study was to identify whether the physical and chemical parameters of water and drainage sediment are reflecting the natural characteristics, and can be used as reference standards for similar geological areas.

The physicochemical characteristics of samples of surface water and geochemistry of river sediment samples reflect natural conditions for each geological domain assessed. There was a predominance of Ca, Mg in MSCD, due to the geology is dominantly composed of dolomitic limestone. In TCSD the predominant compounds were CO_2 and Al_2O_3, while the MBD stood out the Fe_2O_3 and TiO_2 compounds that are related to composition of basalts which occur in the sampled area.

The significant variation of some parameters of the geological domains, demonstrates the need for adequacy of law inherent in assessing the quality of surface water. There is a gap in the understanding of the relationship between rock and surface water can lead to erroneous interpretations, and therefore, must be completed with the development of research and wide dissemination of the issue to cover several areas aimed at monitoring, conservation and recovery of water resources in the country.

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Authors contributions

Sandra Martins Ramos: Participated in the field work (collecting samples of water, sediment and macroinvertebrate), identification of benthic macroinvertebrates, sediment preparation for geochemical analysis, data analysis, interpretation and discussion of results.

Ana Paula de Melo e Silva Vaz: Participated the interpretation and discussion of results. Assisted in the text correction.

Donizeti Antonio Giusti: Participated in the field work, geological mapping, interpretation results, discussion of results and text correction.

Ernani Francisco da Rosa Filho: Work orientation, interpretation and discussion of results.