INFLUENCE OVER WATER QUALITY DUE TO NUTRIENT LOADING IN THE ROYAL RANGE OF THE ANDES

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1. INTRODUCTION

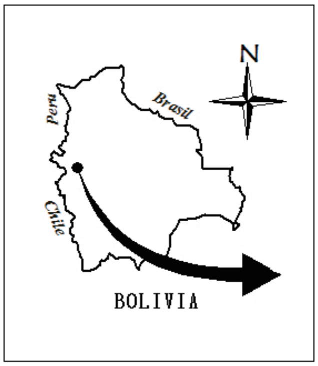
Many researches have focused on the study of water quality in rivers worldwide. Water quality in a river basin is influenced by various factors related to the hydrochemical processes. In general, chemical water composition is determined by the presence of inorganic ions, organic dissolved substances and dissolved gases. The presence of nitrogen, phosphorus and major ions have big influence over water quality especially in the streams of a river basin.

Nutrient loading and chemical water composition have been widely studied (Meybeck, 1987). However, regional studies in remote areas are very rare. Studies in water chemistry in Andes are mainly concentrated in the Apure River in Venezuela (Saunders and Lewis, 1989), Amazon River in Brazil (Mortatti and Probst, 2003), Andean Altiplano in Chile, Patagonian rivers in Argentina and Andean Amazon rivers in Peru (Saunders, et al., 2006) while few studies were done in Condoriri River basin. In the present study, field measurements were conducted in this basin on major ions composition, total nitrogen, total phosphorus, total organic carbon and physicochemical parameters. Thus, the water quality in the river basin is an important parameter that needs to be assessed. Knowledge of this study can provide information on the nutrient loading and the chemical weathering in a high altitude river in the Andes.

2. MATERIALS AND METHODS

Condoriri River basin is located 36 kilometers north - west from La Paz city, Bolivia between 4400 m and 5300 m over sea level in the Royal Range of the Andes. Condoriri, Tuni and Huayna Potosi cover a total basin area of 90.39 km^2. The river flows downhill towards Tuni Lake and provides drinking water to La Paz and El Alto, the two major cities in Bolivia.

The field work was conducted to analyze water quality in the streams and the lakes of the Condoriri River basin. 20 sampling points were taken through the whole basin in a dry season (July, 2012). The study area is showed in Fig. 1.



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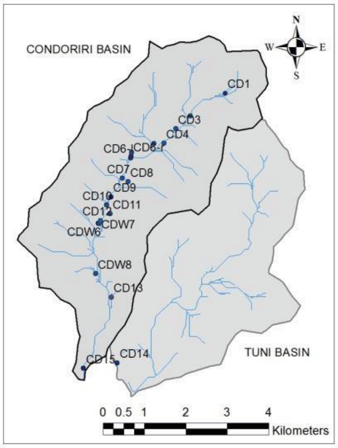

Figure 1: *Condoriri River basin, location of field measurement area*

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The sampling sites were carefully chosen in order to maximize the representation of the river system. The measurements began from the highest point near the glacier to the end of the river basin near the Tuni Lake. The field work was conducted to analyze water quality in the streams and the lakes of the Condoriri River basin in a dry season (July, 2012). The measurements began from the highest point near the glacier to the end of the river basin near to the Tuni Lake. Water samples were taken from each monitoring point in the stream to analyze total nitrogen, total phosphorus, total organic carbon (TOC) and major ions. The chemical composition, the location of monitoring points and the physicochemical parameters are listed in Table 1.

Table 1: *Chemical composition of surface water within the Condoriri River basin*

Description	Sample ID	Latitude S	Longitude W	Elevation (m)	pH	T (◦C)	DO (mg/l)	TDS (mg/l)	TOC (mg/l)	SiO_2 (mg/l)	TN (mg/l)
Right below glacier	CD1	16°10'57.8"	68°13'32.4"	4847	8.3	0.20	7.74	158.00	0.39	2.72	
Upstream of lake	CD2*	16°11'12.7"	68°13'59.4"	4706	7.9	7.20	7.25	148.00	0.43	4.25	0.35
Down area of lake	CD3	16°11'26.8"	68°14'10.6"	4690	8.2	9.20	7.05	129.00	0.73	4.74	
Runoff of subsurface water	CD4	16°11'3.0"	68°14'22.8"	4678	8.1	7.60	6.89	106.00	0.67	5.07	
Northeast side of lake	CD5i	16°11'42.7"	68°14'26.5"	4661	8.4	9.40	7.21	95.00	0.76	3.47	
Outflow from lake	CD5o	16°11'44.8"	68°14'49.6"	4662	8.2	9.40	7.00	90.00	0.79	3.62	
Spring water of right side	CD6*	16°11'47.3"	68°14'50.2"	4661	7.9	5.90	5.72	128.00	0.44	5.07	2.10
Spring water of left side	CD6l	16°11'49.3"	68°14'50.1"	4656	8.1	6.00	6.39	120.00	0.40	4.57	
Middle between the lakes	CD7*	16°12'15.3"	68°15'1.9"	4579	8.1	7.70	6.87	128.00	0.50	4.57	2.10
Stream from the left side	CD8	16°12'8.2"	68°14'52.4"	4634	8.3	1.30	7.86	142.00	0.85	4.74	
Inflow to the lagoon	CD9	16°12'19.8"	68°15'5.6"	4559	8.1	7.40	7.04	117.00	0.50	4.74	
Middle of the lagoon	CD10	16°12'26.6"	68°15'9.7"	4563	7.7	8.50	7.29	88.00	0.75	4.09	
Outflow from the lagoon	CD11*	16°12'33.0"	68°15'6.5"	4541	7.8	6.30	7.47	126.00	0.68	4.90	1.40
Hydrometric station	CD12*	16°12'38.6"	68°15'14.5"	4512	8.0	4.90	7.26	132.00	0.62	4.25	0.70
Stream right side from the wetland	CDW6	16°12'40.9"	68°15'16.4"	4499	7.7	5.10	6.14	73.00	0.56	4.57	1.40
Stream left side from the wetland	CDW7	16°12'41.3"	68°15'15.6"	4497	7.7	5.40	7.40	127.00	0.68	4.41	2.10
End of the wetland	CDW8	16°13'20.5"	68°15'18.3"	4485	7.8	5.00	6.26	119.00	0.92	3.47	2.10
Weir	CD13	16°13'39.4"	68°15'5.6"	4474	7.8	5.00	6.99	122.00	1.00	3.32	
Inflow to Tuni lake	CD14	16°14'28.5"	68°15'2.1"	4468	7.6	2.70	7.25	121.00	0.91	3.94	
The most downstream	CD15	16°14'35.0"	68°15'27.4"	4438	7.9	3.60	6.91	123.00	1.76	2.72	

Table 1: (continued)

Sample ID	F^- (mg/l)	Cl^- (mg/l)	NO_2^- (mg/l)	NO_3^- (mg/l)	PO_4^{3-} (mg/l)	SO_4^{2-} (mg/l)	Na^+ (mg/l)	K^+ (mg/l)	Ca^{2+} (mg/l)	Mg^{2+} (mg/l)	NH_4^+ (mg/l)
CD1	0.12	0.34	<0.01	0.11	<0.01	89.07	1.21	0.57	47.55	4.27	0.03
CD2*	0.12	0.20	<0.01	0.14	<0.01	51.92	2.39	0.65	35.30	3.83	0.06
CD3	0.03	0.11	<0.01	0.01	<0.01	8.31	0.45	0.24	3.48	<0.01	0.04
CD4	0.02	0.12	<0.01	0.04	<0.01	2.14	0.85	0.24	9.63	<0.01	0.06
CD5i	0.08	0.18	<0.01	<0.01	<0.01	20.43	1.39	0.42	17.72	1.71	0.07
CD5o	0.07	0.15	<0.01	<0.01	<0.01	17.66	1.43	0.44	18.23	1.87	0.04
CD6*	0.08	0.16	<0.01	0.17	<0.01	24.84	1.72	0.48	22.30	2.99	0.02
CD6l	0.13	0.50	<0.01	0.15	<0.01	50.43	1.93	0.59	26.06	3.32	0.03
CD7*	0.07	0.14	<0.01	0.11	<0.01	22.32	1.91	0.51	25.43	3.37	0.06
CD8	0.13	0.35	<0.01	0.17	<0.01	36.81	1.69	0.28	36.93	5.82	0.04
CD9	0.03	0.05	<0.01	0.13	<0.01	8.16	0.53	0.23	3.91	<0.01	0.07
CD10	0.02	0.04	<0.01	0.07	<0.01	4.94	0.45	0.21	2.66	<0.01	0.05
CD11*	0.02	0.04	<0.01	0.08	<0.01	6.19	0.55	0.24	4.16	<0.01	0.04
CD12*	0.07	0.14	<0.01	0.09	<0.01	18.55	1.44	0.40	17.87	2.03	0.03
CDW6	0.14	6.20	<0.01	0.50	<0.01	9.77	2.24	0.36	16.87	4.78	0.05
CDW7	0.68	0.08	<0.01	0.09	<0.01	8.50	1.17	0.34	14.04	1.38	0.07
CDW8	0.03	0.25	<0.01	0.08	<0.01	5.72	1.39	0.41	15.83	1.85	0.03
CD13	0.02	1.14	<0.01	0.08	<0.01	51.29	2.83	0.67	34.23	5.34	0.07
CD14	0.18	0.69	<0.01	0.08	<0.01	52.42	2.72	0.65	34.27	5.27	0.04
CD15	0.20	14.09	<0.01	<0.01	<0.01	48.66	4.14	0.77	30.36	8.40	0.02

Total dissolved solids (TDS) were estimated and parameters in situ like dissolved oxygen (DO), Temp and pH were measured using a water quality analyzer. For ions analysis and TOC water samples were filtered in situ on collection through membrane filters of 0.45 µm pore size. A 50 ml aliquot was stored in a plastic bottle. For total nitrogen and total phosphorus 500 ml of water samples were collected from 8 monitoring points and stored in a plastic bottle.

Ions were determined by ion chromatography using a DX-120 Dionex analyzer and total organic carbon was determined by 680 °C combustion catalytic oxidation method, which was developed by Shimadzu. A TOC-L analyzer was used for the analysis of water samples at Tohoku University. Total nitrogen was determined by method EPA 351.1 and total phosphorus was determined by method EPA 365.2 for the analysis of water samples. This procedure was made in the Institute of Sanitary and Environmental Engineering (Major San Andres University).

Historical discharge data of Condoriri River basin was obtained from the daily measurement of water level (Fig. 2) and the rating curve (Fig. 3) development by Glacier Retreat Impact Assessment and National Policy Development (GRANDE) and French Institut de Recherche pour le Développement (IRD). Daily discharge data (Fig. 4) was considered for this study in order to calculate the transport of nutrients and ions. The transport was calculated for dry season as the product of discharge and concentration. Discharge for July was 0.117 m^3/s.

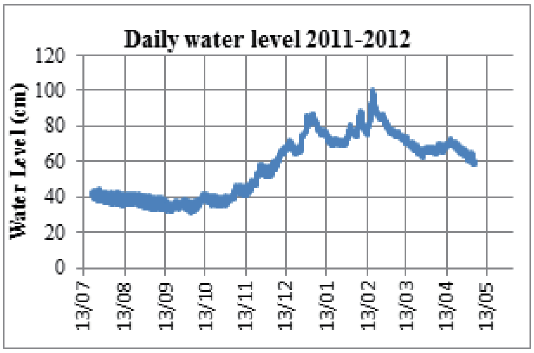

Figure 2: *Daily water level Condoriri*

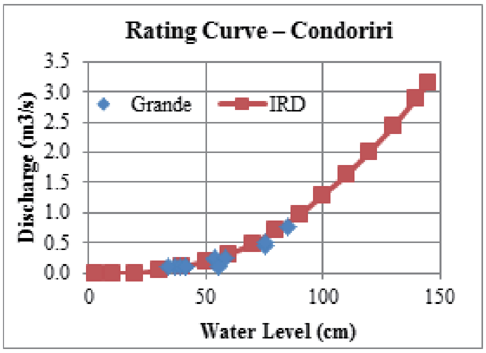

Figure 3: *Rating curve for Condoriri River basin*

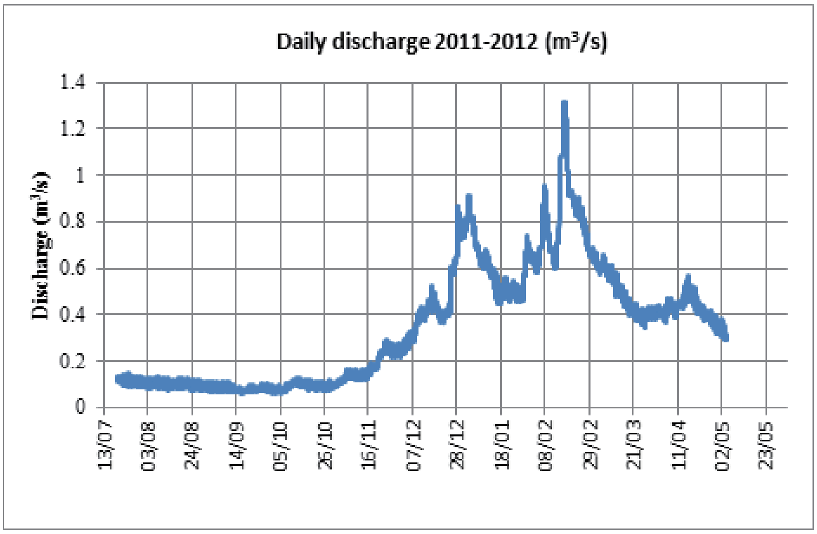

Figure 4: *Daily discharge for Condoriri River basin*

3. RESULTS AND DISCUSSIONS

Nutrients

Total Nitrogen had values ranging from 0.35 to 2.10 mg/l with a mean value of 1.53 mg/l higher compared with the average value of 0.20 ml/g from Chontabamba River in Peru and 0.01 mg/l in the Patagonia stream in Argentina. The values of total phosphorus were below limit detection.

Physicochemical parameters

All the water samples were slightly alkaline with pH values from 7.6 to 8.4 and with a mean value of 8.0. The average value of pH was a little high compared with most of the Andean rivers except of those rivers located in extremely arid areas like in upstream of Atacama-Chile with a pH average value of 8.2. The average value of pH was high compared with Amazon upstream rivers with a pH average value of 6.7.

The water temperatures ranged from 0.2 to 9.4 °C with a mean value of 5.89 °C. Dissolved oxygen varied from 5.72 to 7.86 mg/l with a mean value of 7.00 mg/l. The average value of dissolved oxygen was lower compared with Andean rivers but higher compared with the streams of Cordillera Blanca in Peru with a dissolved oxygen average value of 5.08 mg/l. The total dissolved solids varied from 73 to 158 mg/l with a mean value of 119.6 mg/l which was similar compared with most of the Andean rivers. Total Dissolved Solids average value of Condoriri basin was higher compared with 34.2 mg/l in the Orinoco River.

Major ion chemistry

Calcium had values ranging from 2.66 to 47.55 mg/l with a mean value of 20.84 mg/l, which is higher than 6.4 mg/l in Chillan River in Chile and 2.59 mg/l in rivers in the Amazon basin. Magnesium had values ranging from 0.01 to 8.4 mg/l with a mean value of 2.81 mg/l similar to the Andean rivers, a little higher compared with 1.2 mg/l in Cumbaza River in Peru and lower than 3.15 mg/l in Cordillera Blanca in Peru. Potassium had values ranging from 0.21 to 0.77 mg/l with a mean value of 0.44 mg/l lower compared with Andean and Amazon rivers. Sodium had values ranging from 0.45 to 4.14 mg/l with a mean value of 1.62 mg/l slightly lower compared with other Andean rivers.

Sulfate had values ranging from 2.14 to 89.07 mg/l with a mean value of 26.91 mg/l higher compared with Andean rivers but lower compared with 375 mg/l from rivers in extremely arid areas. Sulfate had higher values compared with Amazon upstream rivers. Ammonia had values ranging from 0.02 to 0.07 mg/l with a mean value of 0.05 mg/l slightly higher compared with other Andean and Amazon rivers except with the Bermejo River in Bolivia. Chlorine ion had values ranging from 0.04 to 14.09 mg/l with a mean value of 1.25 mg/l slightly lower compared with Andean rivers. However there was a big difference compared with Lauca River (Bolivia), San Pedro River (Chile), those rivers were located in extremely arid areas. Chlorine ion had not big difference compared with Amazon upstream rivers. Silica had values ranging from 2.72 to 5.07 mg/l with a mean value of 4.16 mg/l is lower compared with the rivers in extremely arid areas.

A Pearson correlation was done (Table 2) and high positive correlations were obtained between F^{-}-NH_4^{+}, Cl^{-}-NO_3^{-}, Cl^{-}-Mg^{2+}, NO_3^{-}-Mg^{2+}, SO_4^{2-}-K^{+}, SO_4^{2-}-Ca^{2+}, Na^{+}-K^{+}, Na^{+}-Ca^{2+}, Na^{+}- Mg^{2+}, K^{+}-Ca^{2} and Ca^{2+}-Mg^{2+} indicating the predominance of weathering process. The concentration of cations and ions ranked in the order of $Ca^{2+}>Mg^{2+}>Na^{+}>K^{+}>NH_4^{+}$ and $SO_4^{2-} > Cl^{-} > F^{-} > NO_3^{-}$ respectively.

Table 2: *Pearson correlation between parameters*

Parameters	Elevation	pH	T	DO	EC	TDS	TOC	F^{-}	Cl^{-}	NO_3^{-}	SO_4^{2-}	Na^{+}	K^{+}	Ca^{2+}	Mg^{2+}	NH_4^{+}	SiO_2
Elevation	**1**																
pH	0.360	**1**															
T	0.677	0.488	**1**														
DO	-0.088	-0.023	0.250	**1**													
EC	0.428	0.092	0.391	0.482	**1**												
TDS	0.546	0.425	0.471	0.492	**0.902**	**1**											
TOC	**-0.769**	-0.439	-0.564	0.083	0.117	-0.157	**1**										
F^{-}	-0.251	-0.403	-0.195	0.311	0.054	0.010	0.078	**1**									
Cl^{-}	-0.293	-0.398	-0.324	-0.413	**-0.844**	**-0.923**	-0.117	-0.030	**1**								
NO_3^{-}	-0.121	-0.334	-0.245	-0.489	**-0.831**	**-0.867**	-0.285	-0.039	**0.979**	**1**							
SO_4^{2-}	**0.891**	0.383	0.605	0.096	0.455	0.554	**-0.726**	-0.170	-0.218	-0.086	**1**						
Na^{+}	0.477	0.231	0.276	-0.392	-0.204	-0.171	-0.601	-0.128	0.449	0.539	0.662	**1**					
K^{+}	**0.771**	0.475	0.552	-0.151	0.394	0.452	-0.574	-0.182	-0.189	-0.074	**0.904**	**0.785**	**1**				
Ca^{2+}	**0.733**	0.455	0.522	-0.144	0.285	0.363	-0.635	-0.106	-0.076	0.039	**0.899**	**0.853**	**0.987**	**1**			
Mg^{2+}	0.355	0.190	0.186	-0.506	-0.429	-0.380	-0.590	-0.137	0.614	0.699	0.496	**0.970**	0.632	**0.718**	**1**		
NH_4^{+}	-0.066	-0.249	0.311	0.494	0.089	-0.017	-0.122	**0.710**	0.144	0.111	0.138	0.229	0.123	0.210	0.185	**1**	
SiO_2	0.372	0.160	0.321	-0.048	-0.319	-0.056	-0.664	0.004	0.093	0.216	0.077	-0.091	-0.163	-0.124	0.015	-0.081	**1**
TN	-0.327	-0.021	-0.082	-0.446	-0.194	-0.237	0.335	0.260	-0.077	-0.087	-0.583	-0.296	-0.313	-0.341	-0.187	-0.031	0.069

Values in bold are different from 0 with a significance level alpha=0.05

Table 3: *Ions ratio.*

Ions ratio	
SO_4^{2-}/SiO_2 (*)	4.6
SO_4^{2-}/Cl^- (*)	41.0
SO_4^{2-}/F^- (*)	81.0
SO_4^{2-}/NO_3^- (*)	188.1
Ca^{2+}/Mg^{2+} (*)	4.7
Ca^{2+}/Na^+ (*)	7.4
Ca^{2+}/K^+ (*)	44.4
Ca^{2+}/NH_4^+ (*)	235.9
Na^+/Cl^-(*)	11.7
$Ca^{2+}+Mg^{2+}/Na^++K^+$ (**)	3.7
(*) = molar ratio; (**)= equivalent ratio	

Sources of major ions

TDS values depended more on the concentration of Ca^{2+}, Mg^{2+} and SO_4^{2-} since these ions were more abundant compared with the rest. If halite dissolution is responsible for the presence of sodium the Na^+/Cl^- molar ratio = 1, if this ratio > 1 the presence of sodium indicates silicate weathering (Meybeck, 1987). The possible source of Na^+ and K^+ concentrations in natural waters are atmospheric precipitation, dissolution of rock salt (halite) and weathering of Na-bearing silicate minerals. If halite dissolution is responsible for the sodium, the Na^+/Cl^- molar ratio is approximately one, whereas a ratio of $Na^+/Cl^- > 1$ is interpreted as Na^+ and K^+ released from silicate weathering or Na-K bearing salts. The Na^+/Cl^- molar ratio was 11.7 suggesting the origin of Na^+ and K^+ from silicate weathering processes. The $(Ca^{2+}+Mg^{2+})/(Na^++K^+)$ ratio was used to evaluate the relative contribution of rocks. If in the area there is a predominance of carbonates weathering the ratio >1, in evaporates areas this ratio <1. In our case the $(Ca^{2+}+Mg^{2+})/(Na^++K^+)$ ratio was 3.7>1 indicating carbonate weathering as primary contributor for the major ions. The plot of $(Ca^{2+} + Mg^{2+})$ versus SO_4^{2-} and $(Na^+ + K^+)$ versus SO_4^{2-} showed the weathering of carbonates (Figure 5 and 6). The plot of $(Ca^{2+} + Mg^{2+})$ versus $(SO_4^{2-}+Cl^-)$ and the plot of $(Na^+ + K^+)$ versus $(SO_4^{2-}+Cl^-)$ also showed the common source of these ions and the presence of $MgSO_4$, $CaSO_4$, Na_2SO_4, K_2SO_4, $MgCl_2$, $CaCl_2$, NaCl and KCl. These ions could be considered derivatives from chlorides and sulfate mineral (Figure 7 and 8). The plot of $(Ca^{2+} + Mg^{2+})$ versus $(SO_4^{2-}+F^-)$ and the plot of $(Na^+ + K^+)$ versus $(SO_4^{2-}+F^-)$ could suggest the presence of MgF_2, CaF_2, NaF and KF (Figure 9 and 10).

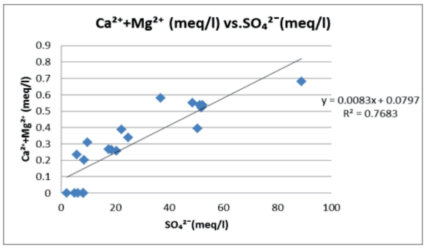

Figure 5: *$(Ca^{2+} + Mg^{2+})$ versus SO_4^{2-}*

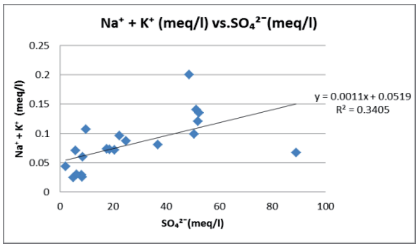

Figure 6: *$(Na^+ + K^+)$ versus SO_4^{2-}*

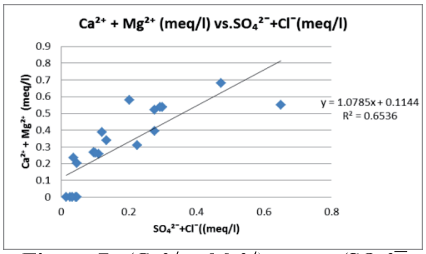

Figure 7: *$(Ca^{2+} + Mg^{2+})$ versus $(SO_4^{2-}+Cl^-)$*

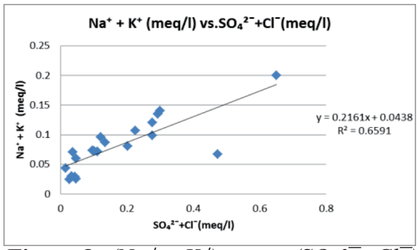

Figure 8: *$(Na^+ + K^+)$ versus $(SO_4^{2-}+Cl^-)$*

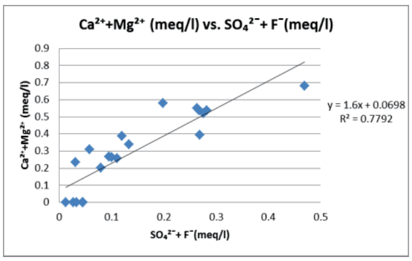

Figure 9: *$(Ca^{2+} + Mg^{2+})$ versus $(SO_4^{2-}+F^-)$*

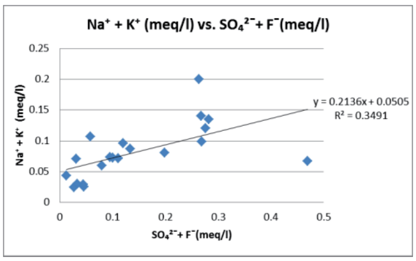

Figure 10: *$(Na^+ + K^+)$ versus $(SO_4^{2-}+F^-)$*

Transport of nutrients and ions

Nutrient loading is calculated by equation 1 like the product of the discharge (Q = 0.117m^3/s = 10.1*10^6 l/day) and the nutrient concentration C (kg/l), and the same analysis is also applicable to ions transport (Correll et al., 1999). For this purpose, data at hydrometric station (point CD12*) were considered. Results are showed in **Table 4**.

$$Transport\ rates\ \left(\frac{kg}{day}\right) = Q\ \left(\frac{l}{day}\right) * C(\frac{kg}{l}) \qquad (1)$$

Table 4: *Nutrient loading and ions transport*

Nutrient	NO_3^-	SO_4^{2-}	Na^+	K^+	Ca^{2+}	Mg^{2+}	SiO_2	TOC	TN
Concentration (kg/l)	0.09*10^{-6}	18.55*10^{-6}	1.44*10^{-6}	0.4*10^{-6}	17.87*10^{-6}	2.03*10^{-6}	4.25*10^{-6}	0.62*10^{-6}	0.7*10^{-6}
Transport rates (kg/day)	0.9	187.5	14.6	4.0	180.6	20.5	43.0	6.3	7.1

Nutrients are represented by total nitrogen (7.1 kg/day) and the transport of mayor ions are mostly composed by SO_4^{2-} (187.5 kg/day) and Ca^{2+} (180.6 kg/day). The transport of SiO_2 is also important (43.0 kg/day) and total organic carbon (6.3 kg/day). It is clear that most of the composition of total nitrogen is due to the contribution of organic nitrogen because the concentration of nitrate is rather low. The nutrient loading and the transport of ions depend on local or regional condition such as lithology, climate, topography, discharge, etc. However, according to the results chemical weathering remains the main resource of dissolved substances and the presence of organic matter contributes with organic nitrogen and carbon. Through the whole basin were observed different species of macrophytes (*Isoetes lechleri, Elodea potamogeton, Lilaeopsis macloviana, Myriophyllum quitense)* and attached algae, most of them have influence over the concentration of nutrients in this river basin.

4. CONCLUSIONS

The assessed parameters show that the transport of nutrients is represented by total nitrogen (6.3 kg/day). The presence of macrophytes and attached algae in the streams contributes with organic nitrogen and carbon. The transport of mayor ions are mostly composed by SO_4^{2-} (187.5 kg/day) and Ca^{2+} (180.6 kg/day). Major ion concentrations have big variations through the whole basin and the ion composition has a strong influence in total dissolved solutes (TDS) values. Despite nutrient loading and the transport of ions depend of many factors chemical weathering remains the main resource of dissolved substances. According to the results, Na^+ released from silicate weathering with Na^+/Cl^- molar ratio = 11.7 > 1 and $(Ca^{2+}+Mg^{2+})/(Na^++K^+)$ ratio = 3.7 > 2.2 represents carbonate rocks as the main sources of dissolved loads.

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